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Photochemical synthesis of triazolo[3,4-*b*]-1,3(4*H*)-benzothiazines: a detailed mechanistic study on photocyclization/photodesulfurisation of triazole-3-thiones

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Abstract—Irradiation of 4-(2-halobenzyl)-5-substituted-1,2,4-triazole-3-thiones under base mediated (CH_3CN/2 M NaOH) condition afforded triazolo[3,4-*b*]-1,3(4*H*)-benzothiazines and desulfurized triazoles. Benzophenone sensitized photolysis of triazole-3-thiones gave desulfurized triazoles exclusively. The mechanism of the photocyclization/photodesulfurization and the involvement of singlet and triplet energy levels are discussed.

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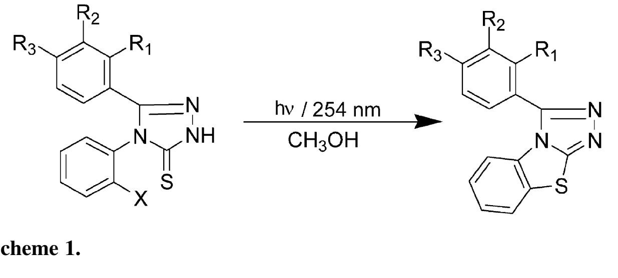
1. Introduction

The photochemistry of thiocarbonyl compounds has received much attention from both synthetic and mechanistic points of views. Earlier workers from our laboratories reported[1] the synthesis of condensed benzothiazoles from thioamides, such as the synthesis of *s*-triazolo[3,4-*b*]-benzothiazoles (Scheme 1) from 4-(*o*-halophenyl)-5-substituted 1,2,4-triazole-3-thiones by photolysis. Recently, we reported the synthesis of isoquinoline-fused benzoxazole and benzoxazine systems, under base mediated photolytic conditions.[2]



Scheme 1.

In continuation of our interest in the synthesis of biologically active nitrogen and sulfur containing heterocycles, and the importance of triazole fused benzothiazine ring systems,[3–6] we focused our work on the synthesis of condensed benzothiazines. In a preliminary communication, we reported the synthesis of triazolo[3,4-*b*]-1,3(4*H*) benzothiazines and desulfurization of 1,2,4-triazole-3-thiones.[7] In this paper, we discuss the synthesis and mechanistic aspects on the formation of triazolo benzothiazines and desulfurization of triazole-3-thiones on irradiation under basic and triplet sensitized conditions.

2. Results and discussion

Refluxing a mixture of *o*-halobenzyl isothiocyanate (1 equiv.) and the substituted acid hydrazide (1 equiv.) in ethanol[8] afforded the corresponding thiosemicarbazides which were directly converted into the respective 4-(*o*-halobenzyl)-5-substituted-1,2,4-triazole-3-thiones **1a–g** in good yield (Scheme 2) using 10% K_2CO_3 (Table 1).

The structures of triazole-3-thiones **1a–g** were confirmed by spectral and analytical data. IR spectra of thiones **1a–g** were comparable with those reported in the literature.[9,10] The presence of a strong band in the region of 1300 cm^{-1} corresponds to the thione (–C=S) form and a weak band around 2600 cm^{-1} indicates the thiol (–SH) form. In the ^1H NMR of the triazole-3-thiones, a singlet around δ 13 showed

Table 1. Synthesis of substituted 1,2,4-triazole-3-thiones **1a–g**

Compound	R^1	X
1a	Phenyl	Cl
1b	*p*-Tolyl	Cl
1c	*p*-Anisyl	Cl
1d	*o*-Tolyl	Br
1e	Benzyl	Cl
1f	*o*-Chlorophenyl	Cl
1g	*o*-Chlorophenyl	Br

Keywords: Cyclization; Benzothiazines; Desulfurization; Triazoles.

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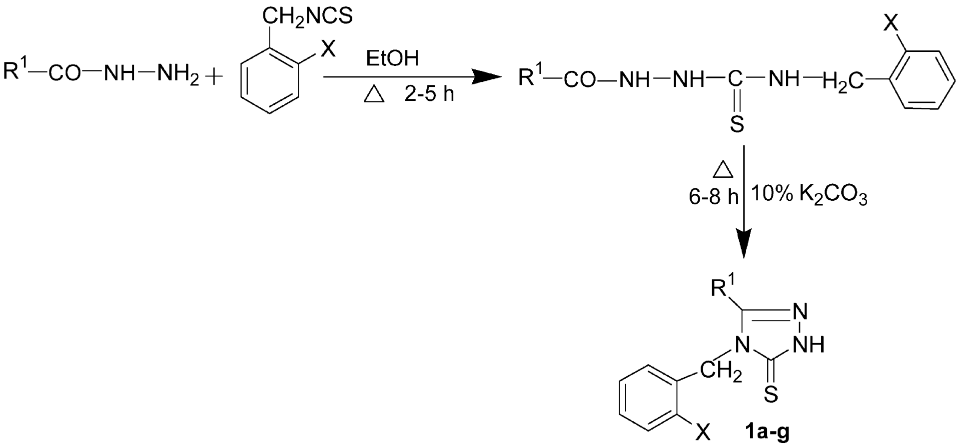


Scheme 2.

the presence of –SH proton. ^{13}C NMR also showed the presence of thiocarbonyl carbon around δ 169. In the ^{13}C NMR, the thiocarbonyl carbon appears upfield compared to the carbonyl carbon signal.[11] The signal at δ 160 for the above compounds could be represented as for the thiol form.

The ^1H NMR spectra of **1a** exhibited a singlet at δ 5.37 for the $-CH_2$ protons, a multiplet between δ 6.96–7.46 for aromatic protons and a singlet at δ 13.88 for the –SH proton. The ^{13}C NMR spectrum of **1a** showed a peak at δ 45.7 for $-CH_2$ carbon, which was confirmed by the DEPT-135 spectrum, which showed $-CH_2$ carbon as an inverted peak. The X-ray crystallography data confirmed the structure of **1b**.[12]

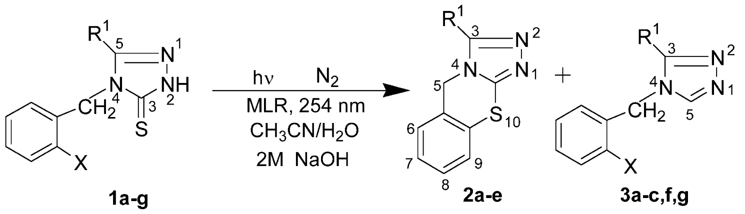
2.1. Irradiation studies

The irradiation experiments were carried out at 254 nm in an Applied Photophysics multilamp reactor (MLR). The various conditions are tabulated in Table 2. An acetonitrile solution (150 mL) of 4-(2-chlorobenzyl)-5-phenyl-1,2,4-triazole-3-thione **1a** (0.3 g, 0.9 mmol) containing 30 mL of aqueous 2 M NaOH (entry 6 in Table 2) was flushed with nitrogen for 1 h and irradiated at 254 nm for 18 h; workup and chromatographic purification furnished the photosubstituted 3-phenyl-1,2,4-triazolo [3,4-*b*]-1,3(4*H*)-benzothiazine **2a** (41%) and photodesulfurized 4-(2-chlorobenzyl)-5-phenyl-1,2,4-triazole **3a** (10%). Similarly, irradiation of triazole-3-thiones **1b–e** (entries 8, 9, 11 and 12 in Table 2) in CH_3CN containing 2 M NaOH in MLR for 11–21 h, furnished the corresponding photosubstituted triazolobenzothiazines **2b–e** and photodesulfurized triazoles **3b**,**c**. In the case of **1d**,**e**, no desulfurized product was observed (Scheme 3).

The photosubstitution reaction described here would involve the intramolecular displacement of the halogen atom present in the *N*-benzyl moiety of the triazole-3-thiones **1a–e** by the thiocarbonyl sulphur of the thioamide. The photodesulfurization would take place in the thiol (–SH) form of the triazole-3-thiones.

In the presence of base such as NaOH, the UV–Vis absorption behaviour of thione **1a** (λ_{max}=262 nm) in CH_3CN changed to λ_{max}=300 nm. The absorption at 300 nm in the UV spectra is believed to be the formation of anionic form of the triazole-3-thione, due to deprotonation by base. Thus, the anionic species is formed in solution, which induces the photosubstitution reaction. When the irradiation of **1a** was carried out in acetonitrile containing weak bases such as aqueous K_2CO_3 (0.5 M) or NaOH (0.5 M) (entries 4, 5 in Table 2), the product **2a** was formed in lower yield compared to using 2 M NaOH conditions (entry 6). A Similar trend was observed in the case of **1b** (entries 7, 8) also. Probably an anionic thiol of the thioamide bond was not efficiently populated in this medium for the substitution reaction.

The irradiation of **1a** in protic solvent (methanol) containing 0.5 M K_2CO_3 or 0.5 M NaOH (entries 2,3) was carried out; the formation of desulfurized product **3a** increased by more than three times compared to the substituted product **2a**. This is due to the proton donor behavior of methanol, which probably inhibits the substitution by blocking the formation of anionic sulphur of **1a** by its protonation, which invariably increases the population of the thiol (–SH) form. In order to study the reaction pathway for the photosubstitution and photodesulfurization of triazole-3-thiones, the photolysis of thione **1a** was carried out under nitrogen as



Scheme 3.

Table 2. Irradiation of triazole-3-thiones **1a-g** under various reaction condition

Entry	Compound	Reaction medium	R_1	Reaction time (h)	X	**2** Yield (%)	**3** Yield (%)
1	**1a**	CH_3OH/Ph_2CO	Ph	62	Cl	-	67
2	**1a**	CH_3OH/0.5 M K_2CO_3	Ph	45	Cl	11	50
3	**1a**	CH_3OH/0.5 M NaOH	Ph	30	Cl	15	48
4	**1a**	CH_3CN/0.5 M K_2CO_3	Ph	20	Cl	30	15
5	**1a**	CH_3CN/0.5 M NaOH	Ph	20	Cl	32	16
6	**1a**	CH_3CN/2 M NaOH	Ph	18	Cl	41	10
7	**1b**	CH_3CN/0.5 M NaOH	*p*-Tolyl	22	Cl	38	11
8	**1b**	CH_3CN/2 M NaOH	*p*-Tolyl	17	Cl	47	8
9	**1c**	CH_3CN/2 M NaOH	*p*-Anisyl	20	Cl	38	15
10	**1d**	CH_3OH/Ph_2CO	*o*-Tolyl	48	Br	-	71
11	**1d**	CH_3CN/2 M NaOH	*o*-Tolyl	11	Br	50	-
12	**1e**	CH_3CN/2 M NaOH	Benzyl	21	Cl	45	-
13	**1f**	CH_3CN/2 M NaOH	*o*-Chlorophenyl	32	Cl	-	47
14	**1g**	CH_3CN/2 M NaOH	*o*-Chlorophenyl	13	Br	-	48

well as oxygen atmosphere. Hence, an acetonitrile solution (50 mL) of **1a** (0.1 g) containing aqueous NaOH (0.5 M, 10 mL), was irradiated in a MLR (254 nm) for 20 h under nitrogen (or oxygen) atmosphere. The photoproducts of the reaction mixture were analysed by HPLC. Under a nitrogen atmosphere, the photosubstitution reaction is faster than the photodesulfurization (entry 1 in Table 3). Whereas, in oxygen atmosphere, which is a triplet quencher, the substitution reaction was not affected, but the desulfurization was reduced considerably (entry 2 in Table 3).

The irradiation of **1a** (0.3 g) in methanol (180 mL) containing benzophenone (1.2 equiv.) a triplet sensitizer, was carried out in a MLR (254 nm) for 62 h (entry 1 in Table 2) to afford exclusively the desulfurized triazole **3a** in 67% yield. In this reaction, no substitution product was formed. A Similar trend was observed in the irradiation of the bromo analogue **1d** (entry 10 in Table 2). Hence, in the base mediated irradiation reactions of triazole thiones, a singlet state is involved for substitution reaction and a triplet state in the photodesulfurization reaction.

The irradiation of 4-(2-chlorobenzyl)-5-(2-chlorophenyl)-1,2,4-triazole-3-thione **1f** in CH_3CN/2 M NaOH conditions (entry 13 in Table 2) for 32 h furnished exclusively the desulfurized triazole **3f**. In this reaction, no photosubstituted product was formed. Similarly, the irradiation of 4-(2-bromobenzyl)-5-(2-chlorophenyl)-1,2,4-triazole-3-thione **1g** in CH_3CN/2 M NaOH conditions (entry 14 in Table 2) also afforded the desulfurized product **3g** exclusively. This is due to the presence of the *o*-chlorine atom as the 5-aryl substituent of triazole thione, which increases the population of the triplet state involved for the desulfurization of triazole thiones by enhancing inter system crossing effect (heavy atom effect).[13]

Table 3. Relative rates of the formation of **2a** and **3a**

Entry	Compound	Reaction medium	Atmosphere	Relative rate	
				2a	**3a**
1	**1a**	CH_3CN/0.5 M NaOH	N_2	2.0	1.0
2	**1a**	CH_3CN/0.5 M NaOH	O_2	2.0	0.25

HPLC-Column used—Bondapak C18; Solvent—CH_3OH/H_20 (8:2); Rate—1 mL/1 min; UV_{max}—254 nm (detector).

Thus, one possible explanation for the formation of the photosubstitution product is that an anionic nucleophile of thiocarbonyl sulphur of triazole-3-thione in basic medium intramolecularly displaces the halogen of the haloarene in the singlet excited state (S_N2Ar^*).[14] Another possibility is that an anionic radical species photoinduced from anionic thiocarbonyl sulphur of the thioamide bond in basic medium intramolecularly substitutes the halogen of the haloarene ($S_N(ET)Ar^*$)[14] (Scheme 4).

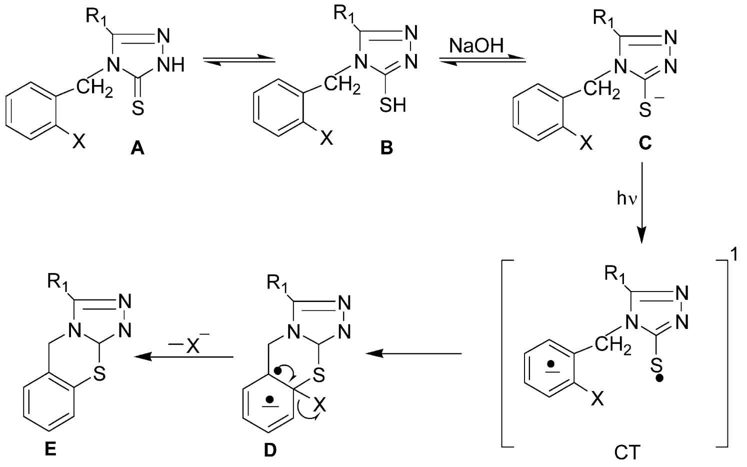
An intramolecular electron transfer mechanism has been proposed for the formation of 2-(pyridinyl)-benzoxazoles.[15] Earlier, we proposed intramolecular electron-transfer mechanism for the formation of benzothiazoles from the photoreaction of *o*-halothioacetamide,[1] and we observed the $Cl_2^{\cdot-}$ (anion radical) at λ_{max} ~345 nm by laser flash and steady state experiments.

The structure of photoproducts **2** and **3** were consistent with the spectral and analytical data. The IR spectra of 3-(*p*-tolyl)-1,2,4-triazolo-(3,4-*b*)-1,3(4*H*)-benzothiazine **2b**, showed bands at 1593 (C=N), 748 (C–S) cm^{-1}. ^1H NMR spectrum of **2b** showed singlets at δ 2.45 and 5.20 for CH_3 and C_4-CH_2 protons, while the ^{13}C NMR showed signals at δ 21.44 (CH_3), 47.61 (CH_2). The mass spectra of **2b** showed the molecular ion M^+ (*m/z* 279) as a base peak. The mass fragment at *m/z* 161 indicates the fragmentation of Ph–CN from the M^+-1 peak. The other compounds follow the same pattern.

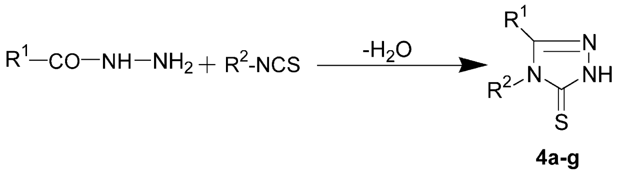
The ^1H NMR spectra of photodesulfurized triazoles **3a–d**,**f**,**g** exhibited a singlet around δ 8 for triazole C_5-CH proton and another singlet around δ 5.2 for the methylene protons. The ^{13}C NMR spectra of triazoles **3** showed a peak around δ 144 for C_5-CH carbon of the triazole ring. The mass spectrum of **3b** showed molecular ion M^+ peak (*m/z* 283). The fragmentation of $Cl^\cdot$ from molecular ion was observed (*m/z* 248).

2.2. Triplet sensitized photolysis of substituted 1,2,4-triazole-3-thiones 1a–d and 4a–g

The substituted 1,2,4-triazole-3-thiones **4a–g** were synthesized (Scheme 5) from the corresponding acid hydrazide (1 equiv.) and isothiocyanate (1 equiv.) in good yield (Table 4). The triazolethiones **4a–e**[16] and **4f**[1] were reported



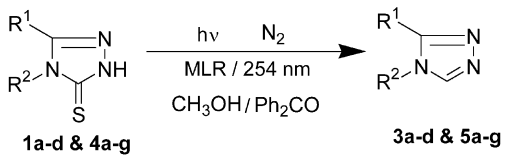
Scheme 4.



Scheme 5.

earlier. The structure of compound **4g** was confirmed by spectral and analytical data, and XRD.[17]

A methanolic solution of triazole-3-thione **4a** (0.3 g, 1 mmol), after flushing with nitrogen for 1 h, was irradiated in multilamp reactor (254 nm). Even after 100 h of irradiation, no reaction was observed. Next, thione **4a** in methanol containing 1.2 equiv. of benzophenone, was flushed with N_2 and irradiated using multilamp reactor for 62 h, to afford the desulfurized 3-phenyl-4-methylphenyl-1,2,4-triazole **5a** in good yield, (Scheme 6). A trace of sulfur was also isolated along with the desulfurized product. Likewise, irradiation of the triazole-3-thiones **4b**–**e** in methanol, also afforded the corresponding desulfurized triazoles **5b**–**e** in good yields (Table 5). The irradiation of **1a**–**d** in the presence of benzophenone yielded the respective desulfurized triazoles **3a**–**d**, instead in an experiment in the absence of benzophenone, thione **1a** did not give any product even after 100 h of irradiation. The photoproducts **5a**–**e** were confirmed by mp and mixture mp and superimposable IR with those obtained under thin film reaction (TFR) condition, which has been reported earlier.[16] Likewise the photoproducts **3a**–**c** were confirmed by mp, mixture mp and superimposable IR with those obtained under base mediated photolytic conditions. The structure of **3d** was confirmed by spectral and analytical data.



Scheme 6.

The desulfurization of 1,2,4-triazole-3-thione by (i) using Raney Ni/EtOH and (ii) using 17% HNO_3, to the corresponding 1,2,4-triazole is known.[18,19] Reaction of **4a** (0.5 g, 1.9 mmol) in the presence of Raney Ni for 23 h, afforded **5a** (47%). Likewise, the treatment of **4b** (2.1 mmol) with 17% HNO_3 (50 mL) under reflux for 5 h, afforded the desulfurized triazole **5b** in 55% yield, compared by mp, mixture mp and superimposable IR.

Benzophenone sensitized irradiation of 4-(2-chlorophenyl)-5-phenyl-1,2,4-triazole-3-thione **4f** in methanol for 50 h afforded the desulfurized 3-phenyl-4-(2-chlorophenyl)-1,2,4-triazole **5f**, instead of the respective triazolobenzothiazole, which was obtained[1] earlier by the irradiation of **4f** in methanol, in the absence of benzophenone using MLR. The structure of photoproduct **5f** was confirmed by spectral and analytical data.

Irradiation of **4g** using MLR (100 h) did not afford any product, but the starting triazole-3-thione in 82% yield. However, the irradiation of **4g** in the presence of benzophenone (1.2 equiv.) in MLR for 65 h, furnished the desulfurized product 3,4-di-(2-chlorophenyl)-1,2,4-triazole **5g** in 60% yield.

The triazole-3-thione **4a** (no *o*-halogen in the 4-aryl ring) and 4-(2-chlorobenzyl)-5-phenyl-1,2,4-triazole-3-thione **1a** in methanol, do not undergo any photochemical reaction in MLR (254 nm) in the absence of benzophenone. Whereas, the photolysis of these thiones in the presence of benzophenone, which is a well-known triplet sensitizer (E_T=69 kcal/mol) produced desulfurized triazole in MLR

Table 4. The various substituted 1,2,4-triazole-3-thiones **4a**–**g**

Compound **4a**–**g**	R^1	R^2
4a	Phenyl	*p*-Tolyl
4b	*p*-Tolyl	*p*-Tolyl
4c	*o*-Tolyl	1-Naphthyl
4d	4-Pyridyl	*p*-Tolyl
4e	Phenyl	Benzyl
4f	Phenyl	*o*-Chlorophenyl
4g	*o*-Chlorophenyl	*o*-Chlorophenyl

Table 5. Photodesulfurization of triazole-3-thiones using multilamp reactors (MLR)

Starting compound	R^1	R^2	Product	Reaction time (h)	Yield (%)
4a	Phenyl	*p*-Tolyl	**5a**	38	42
4b	*p*-Tolyl	*p*-Tolyl	**5b**	40	59
4c	*o*-Tolyl	1-Naphthyl	**5c**	30	70
4d	4-Pyridyl	*p*-Tolyl	**5d**	43	30
4e	Phenyl	Benzyl	**5e**	33	57
4f	Phenyl	2-Chloro phenyl	**5f**	50	52
4g	2-Chloro phenyl	2-Chloro phenyl	**5g**	65	60
1a	Phenyl	2-Chloro benzyl	**3a**	62	67
1b	*p*-Tolyl	2-Chloro benzyl	**3b**	53	60
1c	*o*-Anisyl	2-Chloro benzyl	**3c**	47	48
1d	*o*-Tolyl	2-Bromo benzyl	**3d**	48	71

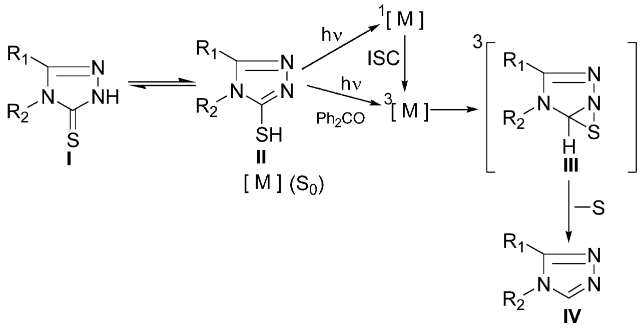
using methanol as a solvent. In this line, photolysis of **1b–d** and **4b–g** also afforded the desulfurized triazole (Table 5), in the presence of benzophenone.

Similarly, photolysis of a methanolic (180 mL) solution of **1a** containing xanthone (1.2 equiv.) (E_T=74 kcal/mol), after flushing with nitrogen, in MLR for 48 h also yielded desulfurized triazole **3a** in 75%yield.

To ensure the absorption of light exclusively by benzophenone, a longer wavelength experiment was carried out. Photolysis of **1a** in methanol (180 mL) containing benzophenone (1.2 equiv.), after flushing with nitrogen, under multilamp reactor with wave length 365 nm for 70 h, also afforded the desulfurized triazole **3a**, but in a slightly lower yield (59%), when compared with the benzophenone experiment (67% yield) at 254 nm. This indicates that some reaction proceeds from the direct excitation of the substrate [M] to S_1, followed by ISC to T_1, which will undergo the reaction in the triplet state. The slightly higher yield (75%) of the product, when xanthone with higher E_T was used, also supports the triplet state reaction for the desulfurization.

From the above observations, we believe that photodesulfurization of triazole-3-thiones using MLR, in presence of benzophenone is a triplet state reaction. This was further evidenced by quenching the triplet state with a triplet quencher. For that, the photolysis of **1a** was carried out in methanol (180 mL) containing benzophenone (1.2 equiv.) after flushing with oxygen for 1 h in MLR (254 nm). After 67 h of irradiation, chromatographic separation afforded 50% of recovered starting triazole-3-thione, in addition to a trace of desulfurized triazole **3a**. The formation of a trace amount of the desulfurized product **3a** could be due to inefficient oxygen supply, since oxygen was not bubbled throughout the reaction. From the above observations, it is concluded that the desulfurization of triazole-3-thiones must be a triplet state reaction.

The irradiation of thione in CH_3CN/NaOH medium giving cyclization product probably takes place in the singlet state by electron transfer mechanism from the thioenolate anion. On the other hand, the formation of desulfurization product could be from the thiol itself in the conventional $S_0 \rightarrow S_1 \rightarrow T_1$ pathway involving the triplet state of the thiol. A reasonable mechanism for the formation of desulfurized triazole from triazole-3-thione is represented in Scheme 7.



Scheme 7.

In this postulated mechanism, the triplet state episulfide **III** is formed initially through the thiol tautomer **II** (the thiol form was confirmed by ^{1}H NMR and IR of thione) by (i) direct population of triplet state, under benzophenone sensitized reaction (ii) population of singlet state followed by triplet state, under base mediated condition. Then the episulfide intermediate loses sulfur to give the triazole **IV**. Photoinduced desulfurization of episulfide, and desulfurization of indoline-2-thione to indole via-episulfide had been reported.[20,21] The episulfide intermediate **III** in the reaction could not be confirmed. However, irradiation in a non-protic solvent such as benzene containing **4a** and benzophenone (1.2 equiv.) using MLR for 27 h, furnished the respective desulfurized product **5a**.

3. Conclusions

The triazole-3-thiones **1a–g** and **4a–g** were synthesized from the corresponding acid hydrazides and isothiocyanates. Irradiation of 4-(2-halobenzyl)-5-substituted-1,2,4-triazole-3-thiones **1a–e** under base mediated condition afforded the respective 1,2,4-triazolo[3,4-*b*]-1,3(4*H*)-benzothiazines **2a–e** and desulfurized triazoles **3a–c** depending on the concentration of the base employed. However, photolysis of **1f**,**g** afforded only the desulfurized triazoles **3f**,**g** even under stronger basic condition (CH_3CN/2 M NaOH). Irradiation of triazole-3-thiones **1a–d** and **4a–g**, using MLR in presence of benzophenone (triplet sensitizer) furnished desulfurized triazoles **3a–d** and **5a–g**, exclusively. A reasonable mechanism for the photocyclization involving singlet state, and for the desulfurization of triazole-3-thiones, in the triplet state via an episulfide intermediate has been proposed.

4. Experimental

4.1. General

All the melting points are uncorrected. UV spectra were recorded with Shimadzu 1601 spectrophotometer. IR spectra were recorded on FTIR-8300 Shimadzu spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with Brucker-DPX 200 (200 MHz) and Jeol-GSX 400 (400 MHz) instruments with TMS as internal standard (chemical shift in δ ppm). The mass spectra were recorded with Jeol-JMS-DX 303 HF and GCMS QP 5000 Shimadzu instruments. Chromatographic separations were done using silica gel (ACME samples). Thin layer chromatography (TLC) was performed using glass plates coated with silica gel (ACME samples) of 0.25 mm thickness. Spots were visualized using iodine vapour. The photochemical reactions were carried out in quartz vessel of different capacity in Applied Photophysics multilamp reactor (254, 365 nm, 12 lamps).

4.1.1. Synthesis of substituted 1,2,4-triazole-3-thiones 1a–g 4-(2-chlorobenzyl)-5-phenyl-1,2,4-triazole-3-thione (1a). A mixture of 2-chlorobenzyl isothiocyanate (1.34 g, 7.4 mmol) and benzoic acid hydrazide (1 g, 7.4 mmol) in ethanol (75 mL) was refluxed on a water bath for 2 h, to afford the corresponding thiosemicarbazide upon cooling. The thiosemicarbazide thus obtained was filtered, then it was refluxed in 10% K_2CO_3 for 6 h, cooled, filtered and the filtrate washed with ether. The aqueous layer was acidified with cold, dil. HCl. The separated solid was filtered and washed with water to furnish thiazine **1a**; recrystallized from ethyl acetate. Yield: 1.69 g (76%), colourless solid, mp 210–212 °C; UV (λ_{max}): 260 nm (CH_3CN); IR (KBr): 3084, 2935, 2598, 1554, 1431, 1353, 1276 cm^{-1}; ^{1}H NMR ($CDCl_3$/DMSO-d_6, 200 MHz): δ 5.37 (s, 2H, CH_2), 6.96–7.46 (m, 9H, ArH), 13.88 (s, 1H, SH). ^{13}C NMR ($CDCl_3$/DMSO-d_6, 50 MHz): δ 45.70, 125.86, 127.30, 127.40, 128.10, 129.00, 129.70, 130.90, 132.04, 132.94, 152.06 (C═N), 169.01 (C═S); ^{13}C NMR-DEPT-135 ($CDCl_3$/DMSO-d_6, 50 MHz) δ 45.60 ($CH_2\downarrow$), 127.30, 128.00, 128.90, 129.60, 130.80 (all CH). MS: *m*/*z* (%)=301 (M^+, 6), 303 (M+2, 2), 266 (100), 233 (2), 206 (2), 125 (26), 103 (14), 89 (12), 77 (8). Anal. calcd for $C_{15}H_{12}N_3SCl$ (301.794): C, 59.69; H, 4.00; N, 13.92. Found: C, 59.80; H, 4.11; N, 14.01.

4.1.2. 4-(2-Chlorobenzyl)-5-(*p*-tolyl)-1,2,4-triazole-3-thione (1b). The thiosemicarbazide obtained by the treatment of 2-chlorobenzyl isothiocyanate (1.22 g, 6.6 mmol) and *p*-toluic hydrazide (1 g, 6.6 mmol), when refluxed in 10% K_2CO_3 for 7 h, afforded **1b**.Yield: 1.81 g (87%), colourless solid, mp 166–168 °C; UV (λ_{max}): 258 nm (CH_3OH); IR (KBr): 3097, 2921, 2563, 1614, 1446, 1348, 1225 cm^{-1}; ^{1}H NMR ($CDCl_3$/DMSO-d_6, 200 MHz): δ 2.35 (s, 3H, CH_3), 5.36 (s, 2H, CH_2), 6.95–7.42 (m, 8H, ArH), 13.77 (s, 1H, SH). ^{13}C NMR ($CDCl_3$/DMSO-d_6,50 MHz): δ 21.6, 46.0, 123.1, 127.5, 128.2, 129.1, 129.9, 132.2, 141.4, 152.4 (C═N), 169.1 (C═S); ^{13}C NMR-DEPT-135 ($CDCl_3$/DMSO-d_6, 50 MHz): δ 21.6 ($CH_3\uparrow$), 45.9 ($CH_2\downarrow$), 127.4, 128.1, 129.1, 129.8 (all CH). MS: *m*/*z* (%)=315 (M^+, 5), 317 (M+2, 2), 280 (100), 247 (2), 125 (30), 117 (8), 102 (4), 89 (14), 77 (6). Anal. calcd for $C_{16}H_{14}N_3SCl$ (315.820): C, 60.84; H, 4.46; N, 13.30. Found: C, 60.97; H, 4.75; N, 13.03. The structure of the compound **1b** was further confirmed by XRD.[12]

4.1.3. 5-(*p*-Anisyl)-4-(2-chlorobenzyl)-1,2,4-triazole-3-thione (1c). Treatment of 2-chlorobenzyl isothiocyanate (1.3 g, 8.0 mmol) with *p*-anisic hydrazide (1.47 g, 8.0 mmol) in ethanol afforded the thiosemicarbazide, which on refluxing in 10% K_2CO_3 for 7 h, furnished **1c**. Yield: 2.12 g (80%), colourless solid, mp 195–197 °C; UV (λ_{max}): 260 nm (CH_3OH); IR (KBr): 3107, 2945, 2588, 1608, 1515, 1350, 1257, 1174 cm^{-1}; ^{1}H NMR ($CDCl_3$/DMSO-d_6, 400 MHz): δ 3.79 (s, 3H, OCH_3), 5.34 (s, 2H, CH_2), 6.86–7.62 (m, 8H, ArH), 13.91 (s, 1H, SH). ^{13}C NMR ($CDCl_3$/DMSO-d_6,100 MHz): δ 44.74 (CH_2), 54.49 (OCH_3), 113.53, 116.96, 126.28, 126.42, 127.69, 128.10, 128.65, 129.96, 130.91, 131.97, 150.98, 160.46 (C–OCH_3), 167.61 (C═S). MS: *m*/*z* (%)=331 (M^+, 6), 333 (M+2, 2), 296 (100), 281 (4), 265 (3), 163 (4), 133 (10), 125 (28), 89 (14), 77 (6). Anal. calcd for $C_{16}H_{14}N_3OSCl$ (331.820): C, 57.91; H, 4.25; N, 12.66. Found: C, 58.10; H, 4.43; N, 12.81.

4.1.4. 4-(2-Bromobenzyl)-5-(*o*-tolyl)-1,2,4-triazole-3-thione (1d). Refluxing a mixture of 2-bromobenzyl isothiocyanate (1.7 g, 7.5 mmol) and *o*-toluic hydrazide (1.2 g, 7.5 mmol) in ethanol yielded the thiosemicarbazide, which on treatment with 10% K_2CO_3 for 8 h, furnished **1d**. Yield: 2.23 g (83%), colourless solid, mp 188–190 °C; UV (λ_{max}): 253 nm (CH_3OH); IR (KBr): 3087, 2927, 2578, 1598, 1453, 1338, 1247 cm^{-1}; ^{1}H NMR($CDCl_3$, 400 MHz): δ 2.07 (s, 3H, CH_3), 5.25 (s, 2H, CH_2), 6.95–7.42 (m, 8H, ArH), 12.40 (s, 1H, SH). ^{13}C NMR($CDCl_3$, 100 MHz); δ 19.44 (CH_3), 47.34 (CH_2), 122.50, 124.55, 126.05, 127.63, 128.35, 129.27, 129.58, 130.76, 131.09, 132.67, 133.92, 138.27, 151.84, 168.18 (C═S). MS: *m*/*z* (%)=359 (M^+)(361-trace), 280 (100), 171 (10), 169 (10), 163, (2), 117 (6), 89 (12), 77 (4). Anal. calcd for $C_{16}H_{14}N_3SBr$ (360.271): C, 53.34; H, 3.91; N, 11.66. Found: C, 53.57; H, 3.78; N, 11.82.

4.1.5. 5-Benzyl-4-(2-chlorobenzyl)-1,2,4-triazole-3-thione (1e). The thione **1e** was prepared by refluxing the thiosemicarbazide, obtained from 2-chlorobenzyl isothiocyanate (1.83 g, 10 mmol) and benzyl hydrazide (1.5 g, 10 mmol), in 10% K_2CO_3 for 7 h. Yield: 2.29 g (73%), colourless solid, mp 150–152 °C; UV (λ_{max}): 256 nm (CH_3OH); IR (KBr): 3083, 2918, 1588, 1448, 1347, 1239 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.89 (s, 2H, CH_2), 5.29 (s, 2H, CH_2), 6.83 (d, J=7.6 Hz, 1H, H_6–ArH), 7.08–7.39 (m, 8H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 32.03 (C–CH_2), 44.27 (N–CH_2), 127.15, 127.28, 127.57, 128.45, 128.85, 129.11, 129.63, 131.58, 132.10, 132.82, 151.66, 168.30. MS: *m*/*z* (%)=315 (M^+, 16), 317 (M+2, 6), 280 (100), 247 (8), 163 (10), 125 (80), 89 (12), 77 (4). Anal. calcd for $C_{16}H_{14}N_3SCl$ (315.820): C, 60.84; H, 4.46; N, 13.30. Found: C, 61.10; H, 4.73; N, 13.12.

4.1.6. 4-(2-Chlorobenzyl)-5-(2-chlorophenyl)-1,2,4-triazole-3-thione (1f). The thiosemicarbazide, obtained from 2-chlorobenzyl isothiocyanate (1.07 g, 5.8 mmol) and *o*-chlorobenzhydrazide (1 g, 5.8 mmol), was refluxed in 10% K_2CO_3 for 8 h to afford **1f**. Yield: 1.76 g (85%), colourless solid, mp 190–192 °C; UV (λ_{max}): 257 nm (CH_3OH); IR (KBr): 3085, 2948, 2598, 1607, 1437, 1338, 1249 cm^{-1}; ^{1}H NMR (CDCl$_3$/DMSO-d_6 200 MHz): δ 5.31 (s, 2H, CH$_2$), 6.97–7.45 (m, 8H, ArH), 13.90 (s, 1H, SH). ^{13}C NMR (CDCl$_3$/DMSO-d_6, 50 MHz): δ 44.8, 125.5, 127.1, 128.7, 129.1, 129.3, 129.9, 131.7, 132.4, 132.7, 132.8, 134.4, 149.4, 168.5 (C=S). MS: *m/z* (%)=335 (M$^+$, 5), 337 (M+2, 3), 300 (100)[302, 38], 280 (10), 163 (4), 137 (12)[139, 4], 125 (44), 102 (12), 89 (20), 77 (8). Anal. calcd for $C_{15}H_{11}N_3SCl_2$ (336.238): C, 53.85; H, 3.29; N, 12.49. Found: C, 53.82; H, 3.41; N, 12.66.

4.1.7. 4-(2-Bromobenzyl)-5-(2-chlorophenyl)-1,2,4-triazole-3-thione (1g). Treatment of 2-bromobenzyl isothiocyanate (1.33 g, 5.8 mmol) with *o*-chloro benzhydrazide (1 g, 5.8 mmol) in ethanol afforded the thiosemicarbazide, which on refluxing in 10% K_2CO_3 for 7 h furnished **1g**. Yield: 1.71 g (78%), colourless solid, mp 182–184 °C; UV (λ$_{max}$): 257 nm (CH$_3$OH); IR (KBr): 3097, 2948, 2578, 1612, 1436, 1332, 1238 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz); δ 5.34 (s, 2H, CH$_2$), 6.98–7.46 (m, 8H, ArH), 12.17 (s, 1H, SH). ^{13}C NMR (CDCl$_3$, 100 MHz); δ 47.56, 122.65, 124.84, 127.00, 127.62, 128.74, 129.38, 130.02, 131.58, 132.51, 132.66, 133.75, 134.45, 149.93, 168.54 (C=S). MS, *m/z* (%)=(379 (M$^+$), 381-trace), 300 (100)[302, 33], 169 (16)[171, 14], 163 (6), 137 (14)[139, 6], 102 (14), 90 (38), 77 (10). Anal. calcd for $C_{15}H_{11}N_3SClBr$ (380.690): C, 47.32; H, 2.91; N, 11.03. Found: C, 47.60; H, 3.10; N, 11.28.

4.2. Photochemical synthesis of substituted 1,2,4-triazolo [3,4-*b*]-1,3-(4*H*)-benzothiazines 2a–e and desulfurized 1,2,4-triazoles 3a–d,f,g from thiones 1a–g

4.2.1. Irradiation of (1a). (i) An acetonitrile solution (150 mL) of 4-(2-chlorobenzyl)-5-phenyl-1,2,4-triazole-3-thione **1a** (0.3 g, 0.9 mmol) containing 30 mL of aqueous 2 M NaOH was flushed with nitrogen for 1 h and irradiated at 254 nm in an Applied Photophysics multilamp reactor (MLR) for 18 h. After completion of the reaction, checked by TLC, the solvent was removed under reduced pressure from the two-phase mixture and it was extracted with ethyl acetate. The ethyl acetate layer was separated; the aqueous layer was neutralized with dil. HCl, and extracted with ethyl acetate. The ethyl acetate portions were combined together, evaporated and the residue obtained was chromatographed over a column of silica gel; elution with ethyl acetate–petroleum ether (1:1) furnished the photosubstituted 3-phenyl-1,2,4-triazolo [3,4-*b*]-1,3(4*H*)-benzothiazine **2a** (41%). In addition 4-(2-chlorobenzyl)-3-phenyl-1,2,4-triazole **3a** (10%) was obtained in the petroleum ether–ethyl acetate (3:7) elusion. The spectral and analytical data of compounds **2a** and **3a** were reported earlier.[6]

4.3. Irradiation of (1b)

Irradiation of an acetonitrile (150 mL) solution of 4-(2-chlorobenzyl)-5-(*p*-tolyl)-1,2,4-triazole-3-thione **1b** (0.3 g, 1.0 mmol) containing 2 M NaOH (30 mL), after flushing with nitrogen, in multilamp reactor for 17 h, followed by usual workup as mentioned above and chromatographic separation afforded triazolo benzothiazine **2b** and triazole **3b**.

4.3.1. 3-(*p*-Tolyl)-1,2,4-triazolo-[3,4-*b*]-1,3(4*H*)-benzothiazine (2b). Yield: 0.12 g (47%), colourless solid, mp 204–206 °C; UV (λ$_{max}$): 261, 243 nm (CH$_3$OH); IR (KBr): 1593, 1473, 748 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.45 (s, 3H, CH$_3$), 5.20 (s, 2H, CH$_2$), 7.22–7.60 (m, 8H, ArH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 21.44, 47.61, 123.32, 127.30, 127.89, 127.92, 128.51, 129.07, 129.44, 129.82, 130.20, 140.64, 147.55, 154.06. MS: *m*/*z* (%)=279 (M$^+$, 100), 278 (22), 263 (3), 207 (2), 161 (14), 135 (22), 134 (44), 121 (25), 117 (12), 116 (14), 108 (12), 102 (4), 90 (20), 89 (24), 77 (12). Anal. calcd for $C_{16}H_{13}N_3S$ (279.360): C, 68.78; H, 4.69; N, 15.04. Found: C, 68.49; H, 4.93; N, 15.25.

4.3.2. 4-(2-Chlorobenzyl)-3-(*p*-tolyl)-1,2,4-triazole (3b). Yield: 0.021 g (8%), colourless solid, mp 130–132 °C; UV (λ$_{max}$): 236 nm (CH$_3$OH); IR (KBr) 1603, 1517, 1473 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.40 (s, 3H, CH$_3$), 5.29 (s, 2H, CH$_2$), 6.87 (d, *J*=7.32 Hz, 1H, C$_6$–ArH), 7.23–7.47 (m, 7H, ArH), 8.16 (s, 1H, C$_5$–H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 21.39, 46.53, 123.47, 127.63, 128.38, 128.57, 129.67, 130.02, 130.06, 132.76, 132.84, 140.49 144.33 (C$_5$–H), 154.50 (C=N). MS: *m*/*z* (%)=283 (M$^+$, 68)[285, M+2, 20], 248 (100), 166 (3), 165 (4), 138 (2), 131 (4), 125 (92)[127, 32], 117 (5), 116 (6), 104 (4), 103 (24), 90 (12), 89 (34), 77 (36). Anal. calcd for $C_{16}H_{14}N_3Cl$ (283.754): C, 67.72; H, 4.97; N, 14.80. Found: C, 67.87; H, 5.10; N, 15.02.

4.4. Irradiation of (1c)

5-(*p*-Anisyl)-4-(2-chlorobenzyl)-1,2,4-triazole-3-thione **1c** (0.35 g, 1.1 mmol) in acetonitrile (150 mL) containing 2 M NaOH (30 mL) was irradiated using a multilamp reactor (254 nm) for 20 h. Usual workup followed by chromatographic separation furnished the respective triazolo benzothiazine **2c** and triazole **3c**.

4.4.1. 3-(*p*-Anisyl)-1,2,4-triazolo-[3,4-*b*]-1,3(4*H*)-benzothiazine (2c). Yield: 0.12 g (38%), colourless solid, mp 166–168 °C; UV (λ$_{max}$): 260, 206 nm (CH$_3$OH); IR (KBr): 1614, 1467, 1245, 1031, 746 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.85 (s, 3H, OCH$_3$), 5.42 (s, 2H, CH$_2$), 6.95 (d, *J*=8.76 Hz, 2H, ArH), 7.26–7.40 (m, 4H, ArH), 8.00 (d, *J*=8.8 Hz, 2H, ArH). MS: *m*/*z* (%)=295 (M$^+$, 100), 294 (90), 279 (56), 223 (4), 161 (20), 135 (21), 134 (80), 133 (21), 121 (35), 108 (10), 102 (11), 90 (42), 89 (41), 77 (23). Anal. calcd for $C_{16}H_{13}N_3SO$ (295.359): C, 65.06; H, 4.43; N, 14.22. Found: C, 65.25; H, 4.68; N, 14.38.

4.4.2. 3-(*p*-Anisyl)-4-(2-chlorobenzyl)-1,2,4-triazole (3c). Yield: 0.047 g (15%), colourless solid, mp 156–158 °C; UV (λ$_{max}$): 248 nm (CH$_3$CN); IR (KBr): 1583, 1503, 1450, 1358, 1259 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.84 (s, 3H, OCH$_3$), 5.28 (s, 2H, CH$_2$), 6.87 (d, *J*=7.8 Hz, 1H, C$_6$–ArH), 6.97 (m, 2H, ArH), 7.23–7.51 (m, 5H, ArH), 8.16 (s, 1H, C$_5$–H). MS: *m*/*z* (%)=299 (M$^+$, 71)[301, M+2, 25], 264 (72), 236 (11), 221 (5), 131 (3), 165 (11), 125 (100), 127 (32), 104 (2), 103 (10), 90 (20), 89 (36), 77 (10). Anal. calcd for $C_{16}H_{14}N_3ClO$ (299.754): C, 64.10; H, 4.70; N, 14.01. Found: C, 64.37; H, 4.89; N, 14.20.

4.5. Irradiation of (1d)

4.5.1. 3-(*o*-Tolyl)-1,2,4-triazolo-[3,4-*b*]-1,3(4*H*)-benzothiazine (2d). (i) Irradiation of an acetonitrile (150 mL) solution of 4-(2-bromobenzyl)-5-(*o*-tolyl)-1,2,4-triazole-3-thione **1d** (0.3 g, 1.1 mmol) containing 2 M NaOH (30 mL) in a multilamp reactor for 11 h, and chromatographic separation afforded **2d**. Yield: 0.15 g (50%), colourless solid, mp 173–175 °C; UV (λ_{max}): 259, 231 nm (CH$_3$OH); IR (KBr): 1585, 1470, 746 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.63 (s, 3H, CH$_3$), 5.46 (s, 2H, CH$_2$), 7.25–7.91 (m, 8H, ArH). ^{13}C NMR (CDCl$_3$, 100 MHz); δ 21.67, 50.68, 125.72, 127.30, 128.04, 128.42, 128.65, 128.98, 129.44, 131.11, 137.07, 147.20, 151.65, 153.15. MS: *m*/*z* (%)=279 (M$^+$, 100), 278 (10), 264 (4), 161 (3), 135 (20), 134 (16), 121 (52), 117 (14), 116 (15), 108 (5), 102, (2), 90 (14), 89 (22), 77 (14). Anal. calcd for C$_{16}$H$_{13}$N$_3$S (279.360): C, 68.78; H, 4.69; N, 15.04. Found: C, 68.52; H, 4.97; N, 15.32.

4.6. Irradiation of (1e)

4.6.1. 3-Benzyl-1,2,4-triazolo-[3,4-*b*]-1,3(4*H*)-benzothiazine (2e). The compound **2e** was obtained on irradiation of 5-benzyl-4-(2-chlorobenzyl)-1,2,4-triazole-3-thione **1e** (0.25 g 0.8 mmol) in acetonitrile (150 mL) containing 2 M NaOH (30 mL) using multilamp reactor for 21 h, followed by chromatographic separation. Yield: 0.10 g (45%), colourless solid, mp 162–164 °C; UV (λ_{max}): 257, 208 nm (CH$_3$OH); IR (KBr): 1595, 1475, 748 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.37 (s, 2H, CH$_2$), 4.81 (s, 2H, CH$_2$), 7.09–7.42 (m, 9H, ArH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 31.45, 46.69, 127.39, 127.52, 127.89, 128.39, 129.17, 135.10, 147.50, 153.20. MS: *m*/*z* (%)=279 (M$^+$, 100), 278 (28), 161 (12), 135 (78), 134 (20), 121 (24), 117 (15), 116 (13), 108 (6), 102 (6), 90 (25), 89 (32), 77 (24). Anal. calcd for C$_{16}$H$_{13}$N$_3$S (279.360): C, 68.78; H, 4.69; N, 15.04. Found: C, 68.98; H, 4.90; N, 15.30.

4.7. Irradiation of 1f

4.7.1. 4-(2-Chlorobenzyl)-3-(2-chlorophenyl)-1,2,4-triazole (3f). The irradiation of 4-(2-chlorobenzyl)-5-(2-chlorophenyl)-1,2,4-triazole-3-thione **1f** (0.2 g, 0.6 mmol) in acetonitrile (150 mL) containing 2 M NaOH (30 mL) using multilamp reactor (254 nm) for 32 h, and usual workup followed by chromatographic separation using petroleum ether–ethyl acetate mixture (1:9) furnished the respective triazole **3f**. Yield: 0.085 g (47%), colourless solid, mp 100–102 °C; UV (λ_{max}): 267 nm (CH$_3$OH); IR (KBr): 1613, 1583, 1453 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.12 (s, 2H, CH$_2$), 6.88 (dd, J=7.6, 1.6 Hz, 1H, C$_6$–ArH), 7.14–7.50 (m, 7H, ArH), 8.25 (s, 1H, C$_5$–H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 47.00, 126.55, 127.42, 127.62, 130.09, 130.27, 130.32, 130.60, 132.22, 132.86, 133.91, 134.58, 144.18 (C$_5$–H), 152.45 (C=N). MS: *m*/*z* (%)=303 (M$^+$, 38)[305, M+2, 22] [307, M+4, 8], 268 (68)[270, 30], 242 (4), 166 (4), 165 (3), 138 (6), 131 (5), 125 (100)[127, 30], 104 (30), 103 (8), 90 (14), 89 (33), 77 (12). Anal. calcd for C$_{15}$H$_{11}$N$_3$Cl$_2$ (304.172): C, 59.22; H, 3.64; N, 13.81. Found: C, 59.42; H, 3.83; N, 13.63.

4.8. Irradiation of 1g

4.8.1. 4-(2-Bromobenzyl)-3-(2-chlorophenyl)-1,2,4-triazole (3g). Irradiation of an acetonitrile (150 mL) solution of 4-(2-bromobenzyl)-5-(2-chlorophenyl)-1,2,4-triazole-3-thione **1g** (0.3 g, 0.8 mmol) containing 2 M NaOH (30 mL), (after flushing with nitrogen) in multilamp reactor for 13 h, followed by chromatographic separation afforded triazole **3g**. Yield: 0.13 g (48%), colourless solid, mp 128–130 °C; UV (λ_{max}): 267 nm (CH$_3$OH); IR (KBr): 1601, 1591, 1447 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.13 (s, 2H, CH$_2$), 6.90 (dd, J=7.32, 2.44 Hz, 1H, C$_6$–ArH), 7.16–7.56 (m, 7H, ArH), 8.22 (s, 1H, C$_5$–H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 49.01, 123.55, 126.36, 127.15, 127.97, 129.83, 130.00, 130.46, 131.93, 132.63, 133.37, 133.57, 134.31, 143.89 (C$_5$–H), 152.13 (C=N). MS: *m*/*z* (%)=347 (M$^+$, 40), 349 (M+2, 53), 351 (M+4, 13), 268 (100) [270 (30)], 233 (4), 206 (4), 176 (12), 169 (75)[170 (74)], 137 (3), 131 (10), 104 (18), 103 (5), 90 (76), 89 (55), 77 (12). Anal. calcd for C$_{15}$H$_{11}$N$_3$ClBr (348.624): C, 51.67; H, 3.18; N, 12.05. Found: C, 51.88; H, 3.40; N, 12.30.

4.9. General procedure for the synthesis of substituted 1,2,4-triazole-3-thiones 4a–g

A mixture of acid hydrazide (1 equiv.) and aryl isothiocyanate (1 equiv.) was refluxed in K$_2$CO$_3$ solution (100 mL, 10%) for 6–8 h, cooled, filtered and the filtrate washed with ether. The aqueous layer was neutralized with cold, dil. HCl (in the case of **4d** pH=7 was maintained). The separated solid was filtered and washed with water to get the corresponding triazole-3-thione. The product was recrystallized from ethyl acetate. The triazole-3-thione **4e** was prepared from the respective thiosemicarbazide, obtained from the corresponding acid hydrazide and isothiocyanate.

The spectral and analytical data for compounds **4a–e** were reported earlier.[16]

4.9.1. 4-(2-Chlorophenyl)-5-phenyl-1,2,4-triazole-3-thione (4f). The thione **4f** was prepared by refluxing a mixture of 2-chlorophenyl isothiocyanate (1.0 g, 5 mmol) and benzoic hydrazide 0.68 g (5 mmol) in 10% K$_2$CO$_3$ for 8 h. Yield: 1.03 g (72%), colourless solid, mp 224–226 °C (lit.[1] mp 222 °C).

4.9.2. 4,5-Di-(2-chlorophenyl)-1,2,4-triazole-3-thione (4g). A mixture of 2-chlorobenzhydrazide (1.0 g, 5 mmol) and 2-chlorophenyl isothiocyanate (1.0 g, 5 mmol) was refluxed for 8 h in K$_2$CO$_3$ solution. Yield: 1.2 g (74%), colourless solid, mp 252–254 °C; UV (λ_{max}): 257 and 219 nm (MeOH); IR (KBr): 3100, 2900, 2598, 1495, 1350, 1274, 1240 cm^{-1}; ^{1}H NMR (CDCl$_3$/200 MHz,): δ 7.24–7.53 (m, 8H, ArH), 12.10 (s, 1H, SH). ^{13}C NMR (CDCl$_3$/50 MHz,): δ 124.62, 125.67, 127.85, 128.40, 128.69, 129.01, 129.45, 129.88, 130.24, 130.53, 132.24, 147.48, 167.01; ^{13}C NMR-DEPT 90 (CDCl$_3$/50 MHz,): δ 124.63, 125.68, 127.86, 128.42, 128.68, 129.46, 129.88, 130.27 (all CH). MS: *m*/*z* (%)=321 (M$^+$,13), (323, M+2), (325, M+4), 288 (40), 286 (100), 149 (90), 137 (5), 125 (11), 111 (11), 90 (11), 75 (18). Anal. calcd for C$_{14}$H$_9$Cl$_2$N$_3$S (322.212): C, 52.18; H, 2.81; N, 13.04. Found: C, 52.09; H, 2.79; N, 13.08. The structure of the compound **4g** was further confirmed by XRD.[17]

4.10. General procedure for the photochemical desulfurization of triazole-3-thiones 1a–d and 4a–g

A methanolic solution (180 mL) of triazole-3-thione and benzophenone (1.2 equiv.) was flushed with nitrogen for 1 h and irradiated in a multilamp reactor (254 nm). After completion of the reaction, checked by TLC, the solvent was removed under reduced pressure. The residue obtained was chromatographed over a column of silica gel. Elution with petroleum ether–ethyl acetate afforded the desulfurized triazoles.

4.10.1. 3-Phenyl-4-(*p*-tolyl)-1,2,4-triazole (5a). Irradiation of a solution of **4a** (0.3 g, 1.1 mmol) and benzophenone (0.24 g, 1.3 mmol) in methanol (180 mL) using MLR for 38 h, followed by chromatographic separation, afforded **5a**. Yield: 42%.

An ethanolic solution of **4a** (0.5 g, 1.9 mmol) in the presence of a catalytic amount of Raney Ni (in absolute ethanol was refluxed for 23 h). After completion of the reaction, the solution was filtered, concentrated and purified over silica gel column to get **5a**.Yield: 0.12 g, 47%, mp, mixture mp and superimposable IR was found to be consistent with **5a** obtained from the photolysis of **4a**.

4.10.2. 3,4-Di-(*p*-tolyl)-1,2,4-triazole (5b). A solution of **4b** (0.4 g, 1.4 mmol) and benzophenone (0.31 g, 1.7 mmol) in methanol (180 mL) was irradiated using MLR for 40 h. After completion of the reaction, followed by chromatographic separation afforded **5b**. Yield: 59%.

The thione **4b** (0.6 g, 2.1 mmol) in 17% aq.HNO_3 (50 mL) was refluxed for 5 h. After completion of the reaction, it was cooled to room temperature and then neutralized with dil. NaOH. The solid obtained was filtered, washed with water and recrystallized from ethyl acetate to isolate the desulfurized product (0.29 g, 55%), which was compared with the desulfurized triazole **5b**, obtained under photolytic condition by mp, mixture mp and superimposable IR.

4.10.3. 4-(1-Naphthyl)-3-(*o*-tolyl)-1,2,4-triazole (5c). Photolysis of **4c** (0.3 g, 0.9 mmol) and benzophenone (0.2 g, 1.1 mmol) in methanol (180 mL) using MLR for 30 h, followed by chromatographic separation, afforded **5c**. Yield: 70%.

4.10.4. 3-(4-Pyridyl)-4-(*p*-tolyl)-1,2,4-triazole (5d). Irradiation of **4d** (0.3 g, 1.1 mmol) and benzophenone (0.24 g, 1.3 mmol) in methanol (180 mL) using MLR for 43 h, followed by chromatographic separation furnished **5d**. Yield: 30%.

4.10.5. 4-Benzyl-3-phenyl-1,2,4-triazole (5e). Irradiation of a mixture of **4e** (0.3 g, 1.1 mmol) and benzophenone (0.24 g, 1.3 mmol) in methanol (180 mL) using MLR for 33 h, furnished **5e**. Yield: 57%.

The structures of triazoles **5a–e** were confirmed by mp, mixture mp and superimposable IR with those obtained under TFR condition, which has been reported earlier.[16]

4.10.6. 4-(2-Chlorophenyl)-3-phenyl-1,2,4-triazole (5f). Photolysis of 4-(2-chlorophenyl)-5-phenyl-1,2,4-triazole-3-thione **4f** (0.25 g, 0.8 mmol) and benzophenone (0.19 g, 1.0 mmol) in methanol (180 mL) using MLR for 50 h, followed by chromatographic separation, afforded **5f**. Yield: 0.11 g (52%), colourless solid, mp 98–100 °C; UV (λ_{max}): 236, 208 nm (MeOH); IR (KBr): 1524, 1434 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.25–7.60 (m, 9H, ArH), 8.30 (s, 1H, C_5–H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 126.24, 127.97, 128.18, 128.62, 129.01, 130.02, 130.97, 131.28, 131.67, 132.47, 144.62, (C_5–H) 153.45 (C=N). MS: *m/z* (%)=255 (M^+, 100)[257, M+2, 34], 254 (41)[256, 33], 220 (98), 193 (8), 166 (6), 165 (5), 152 (30)[154, 11], 138 (14)[140, 6], 125 (32)[127, 10], 103 (10), 90 (51), 89 (23), 77 (26). Anal. calcd for $C_{14}H_{10}N_3Cl$ (255.701): C, 65.76; H, 3.94; N, 16.43. Found: C, 65.97; H, 4.12; N, 16.71.

4.10.7. 3,4-Di-(2-chlorophenyl)-1,2,4-triazole (5g). Irradiation of 4,5-di-(2-chlorophenyl)-1,2,4-triazole-3-thione **4g** (0.25 g, 0.8 mmol) and benzophenone (1.2 equiv., 0.17 g) in absolute methanol (180 mL), at 254 nm in MLR for 65 h, furnished **5g** after chromatographic separation. Yield: 0.12 g (60%), colourless solid, mp 138–140 °C; UV (λ_{max}): 268 and 222 nm (MeOH); IR (KBr): 1500 (C=N) cm^{-1}; ^1H NMR (DMSO-d_6/CD_3CN/200 MHz): δ 7.30–7.50 (m, 8H, ArH), 8.75 (s, 1H). ^{13}C NMR (DMSO-d_6/CD_3CN/50 MHz): δ 126.52, 127.71, 128.67, 129.84, 130.28, 130.96, 132.01, 132.75, 133.25, 134.28, 145.49 (C_5–CH); ^{13}C NMR-DEPT-135, (DMSO-d_6/CD_3CN/50 MHz): δ 127.71, 128.67, 129.84, 130.28, 130.95, 132.01, 132.76, 133.25, 145.49 (C_5–CH) (all CH). MS: *m/z* (%)=289 (M^+, 25), (291, M+2), (293, M+4), 254 (41), 256 (23) 152 (37), 138 (13), 125 (44), 111 (35), 90 (62), 75 (100), 63 (70), 50 (45). Anal. calcd for $C_{14}H_9Cl_2N_3$ (290.146): C, 57.95; H, 3.12; N, 14.48. Found: C, 58.05; H, 3.25; N, 14.38.

A solution of **4g** (0.5 g, 1.5 mmol) and catalytic amount of Raney Ni in absolute ethanol was refluxed for 26 h. After completion of the reaction, the solution was filtered, concentrated and purified over silica gel column to get **5g**. Yield: 0.1 g, 22%, mp, mixture mp and superimposable IR was found to be consistent with **5g** obtained from the photolysis of **4g**.

4.10.8. 4-(2-Chlorobenzyl)-3-phenyl-1,2,4-triazole (3a). A methanolic solution of **1a** (0.3 g, 0.9 mmol) containing benzophenone (0.12 g, 1 mmol) after flushing with nitrogen was irradiated, in multilamp reactor for 62 h. After completion of the reaction, chromatographic separation afforded triazole **3a**.

4.10.9. 4-(2-Chlorobenzyl)-3-(*p*-tolyl)-1,2,4-triazole (3b). Irradiation of a methanolic solution of **1b** (0.4 g, 1.3 mmol) and benzophenone (0.28 g, 1.5 mmol) using MLR for 53 h, afforded **3b**.

4.10.10. 3-(*p*-Anisyl)-4-(2-chlorobenzyl)-1,2,4-triazole (3c). Irradiation of a mixture of **1c** (0.4 g, 1.2 mmol) and benzophenone (0.26 g, 1.4 mmol) in methanol (180 mL) using MLR for 47 h, furnished **3c**. Yield: 48%.

The structure of triazoles **3a–c** were confirmed by mp, mixture mp and superimpossable IR with those obtained under base mediated photolytic condition.

4.10.11. 4-(2-Bromobenzyl)-3-(*o*-tolyl)-1,2,4-triazole (3d). (ii) A methanolic solution (180 mL) of thione **1d** (0.2 g, 0.6 mmol) containing benzophenone (0.12 g, 0.7 mmol) was flushed with nitrogen and irradiated in a multilamp reactor for 48 h. After completion of the reaction monitored by TLC, the solvent was removed under reduced pressure; the residue obtained was chromatographed over a column of silica gel. Elution with ethyl acetate afforded desulfurized triazole **3d**. Yield: 0.13 g (71%), colourless solid, mp 108–110 °C; UV (λ_{max}): 266 nm (CH_3OH); IR (KBr): 1602, 1581, 1462 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.16 (s, 3H, CH_3), 5.06 (s, 2H, CH_2), 6.78 (d, J=7.32 Hz, 1H, C_6–ArH), 7.16–7.55 (m, 7H, ArH), 8.30 (s, 1H, C_5–H). ^{13}C NMR ($CDCl_3$, 100 MHz); δ 19.59, 48.57, 123.25, 125.83, 127.89, 129.61, 129.94, 130.27, 130.33, 130.62, 133.22, 133.69, 138.55, 143.56 (C_5–H), 153.57 (C=N). MS: *m/z* (%)=327 (M^+, 15)[329, M+2, 16], 326[328], 312 (7), 248 (100), 172 (6), 169 (20)[171, 23], 158 (59), 131 (4), 117 (7), 116 (8), 104 (8), 103 (14), 90 (30), 89 (24), 77 (27). Anal. calcd for $C_{16}H_{14}N_3Br$ (328.205): C, 58.55; H, 4.29; N, 12.80. Found: C, 58.80; H, 4.41; N, 12.93.

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