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Reactions of (Aryl)(chloro)methyl *p*-Tolyl Sulfoxides with Tetrasulfur Tetranitride (S_4N_4): Formation and Characterization of 3,5-Diaryl-1,2,4,6-thiatriazine 1-Oxides

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Abstract—The reactions of (aryl)(chloro)methyl *p*-tolyl sulfoxides **2** with tetrasulfur tetranitride (S_4N_4) in *p*-dioxane at reflux gave 3,5-diaryl-1,2,4,6-thiatriazine 1-oxides, 3,5-diaryl-1,2,4-thiadiazoles, and 1-amino-3,5-diaryl-1,2,4,6-thiatriazine 1-oxides. For the first time, the structures of 3,5-diaryl-1,2,4,6-thiatriazine 1-oxides were unequivocally characterized based on X-ray crystallography of 3,5-di(3,4-dimethylphenyl)-1,2,4,6-thiatriazine 1-oxide. Treatment of the thiatriazine 1-oxides with *m*-CPBA gave 2,6-diaryl-4-(3-chlorophenyl)-1,3,5-triazines. Mechanisms are proposed for the formation of thiatriazine 1-oxides and 1,3,5-triazines.

Introduction

Much attention has been focused on exploiting the potential synthetic utility of tetrasulfur tetranitride (S_4N_4) through the reaction with a variety of organic compounds with a fundamental functional group.[1] Although various sulfur and nitrogen-containing heterocyclic compounds could be prepared in a single step, reactions involving S_4N_4 often gave a diverse range of products in relatively low yields. Very recently we have achieved success in reactions with α-halogeno ketoximes and α,α-dihalogeno ketoximes from which, respectively, 3,5-diaroyl-1,2,4-thiadiazoles[2] and 3-aryl-4-halo-1,2,5-thiadiazoles[3] were obtained in good yields. It was envisaged that the α-halogen atom to the oxime functionality contributed to the increase in product yields and caused the reactions to occur relatively cleanly, presumably by acting as a leaving group as suggested in the proposed mechanism. In order to understand further the significance of the leaving group at the α-position to the functionality which may act as a nucleophilic center, the title compounds **2** were treated with an equimolar amount of S_4N_4 in *p*-dioxane at reflux. The results are described herein.

Results and Discussion

The reactions of (aryl)(chloro)methyl *p*-tolyl sulfoxides with S_4N_4 (1 equiv.) in *p*-dioxane at reflux gave 3,5-diaryl-1,2,4,6-thiatriazine 1-oxides **3**, 3,5-diaryl-1,2,4-thiadiazoles **4**, 1-amino-3,5-diaryl-1,2,4,6-thiatriazines 1-oxides **5**, substituted benzaldehydes **6** and di-*p*-tolyl disulfide **7** (Scheme 1). Reaction time and yields of each product are summarized in Table 1.

Of the products **3**–**7**, the isolation of compounds **3** is significant in two ways: firstly, it represents the development of the first general synthetic method for 1,2,4,6-thiatriazine 1-oxides albeit in low yields, and secondly, it seems that the previously reported compound, assigned to be **3a** might be its tautomer in view of our data. A survey of the literature shows that there are two reports describing the isolation of 3,5-disubstituted 1,2,4,6-thiatriazine 1-oxides. The first report[4] involved the reaction of imidoylamidine with sulfur dichloride, yielding 1-chloro-1,2,4,6-thiatriazines which were converted into 1-oxo-1,2-dihydro-1,2,4,6-thiatriazines upon treatment with water. Only the melting points and elemental analyses of two compounds were reported. Subsequently, compound **3a** was reportedly isolated in 15–22%[5] and 32% yields[6] both in CH_2Cl_2, respectively, by treatment of 3,7-diphenyl-1,5,2,4,6,8-dithiatetrazocine with O_3. The structure of **3a** was characterized by spectroscopic and elemental analyses in the reports. Interestingly, all the reported data such as melting points, ^{1}H NMR, IR, and MS data are not in accord with our data. In addition, our data show that the ^{1}H NMR ($CDCl_3$, 300 MHz) spectra of **3a**, **3c**–**d**, and **3j** exhibited a singlet of NH protons at δ

Keywords: tetrasulfur tetranitride; α-chloro sulfoxides; thiatriazine 1-oxides; triazines.
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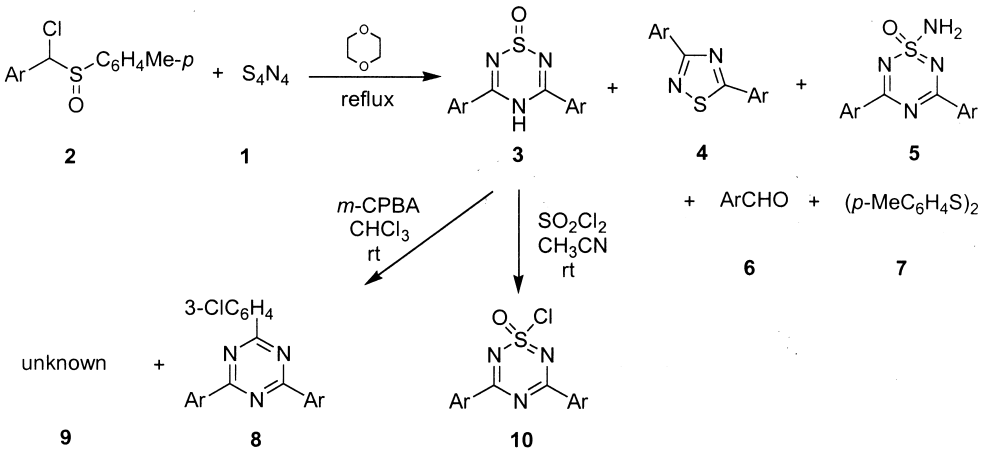


Scheme 1.

Table 1. Reaction time and yields of compounds **3**–**7** and **10**

Compound	Ar	Time (h)	Yield[a] (%)						
2			**3**	**4**	**5**	**6**	**7**	**10**	Mp[b] (°C)
a	Ph	17	**a** 38		**a** 18	trace	23	**a** 52	159–161
b	4-$MeOC_6H_4$	10	**b** 23			**b** 47	70	**b** 53	~180 (dec)
c	4-*t*-BuC_6H_4	13	**c** 12		**c** 8	**c** 18 (22)[c]	75	**c** 48	174–176
d	3,4-$Me_2C_6H_4$	7	**d** 22			**d**[d]	86	**d** 60	141–143
e	4-BrC_6H_4	7	**e** 12	**e** 11	**e** 13	**e** 13	28	[e]	
f	4-ClC_6H_4	10	**f** 20	**f** 33		**f** 31	80	[e]	
g	3-ClC_6H_4	10	**g** 12		**g** 22	**g** 22	76	[e]	
h	4-FC_6H_4	16	**h** 29	**h** 19	**h** 16		52	**h** 68	182–184
i	4-$O_2NC_6H_4$	7	**i** 50			**i** 28	41	**i** 66	~230 (dec)
j	6-MeC_5H_3N[f]	41	**j** 15				33		

[a] Isolated yields.
[b] Melting points of **10**, which were recrystallized from a mixture of CH_2Cl_2 and *n*-hexane except for **10a**, which was recrystallized from CH_3CN.
[c] Number in parenthesis represents the yields of *t*-butylbenzonitrile.
[d] A mixture of 3,4-dimethylbenzaldehyde and 3,4-dimethylbenzonitrile was obtained.
[e] A small amount of complex mixture.
[f] 6-Methylpyridin-2-yl.

11.7–13.0 ppm, except for **3b**, which exhibited the corresponding signal at δ 7.75 ppm. The ^{1}H NMR spectra of **3e**–**g** and **3h**–**i** were measured in DMSO-d_6–$CDCl_3$ due to the solubility problem, which showed no NH proton signals. In the ^{13}C NMR spectrum of each compound, except for compounds **3f** and **3g**, the number of signals was equivalent to half of the total number of carbons of the compound, which is indicative of symmetric structure. IR (KBr) spectra exhibited a band at 1020–1161 cm^{-1}, corresponding to S=O stretching vibrations. The FAB MS of each compound was in good agreement with its molecular weight. However, compounds **3e**–**g** are unstable in air. Attempts to obtain pure compounds for analysis and spectroscopic data were unsuccessful. The X-ray crystal structure of **3d**[14] supports our view of the structure of **3** (Fig. 1). Fig. 1 shows that the structure of the six-membered 1,2,4,6-thiatriazine ring is not planar as demonstrated by torsional angles (°): N(2)–S–N(1)–C(1), −37.7(2); N(1)–S–N(2)–C(2), 35.7(2); S–N(1)–C(1)–N(3), 15.5(3); S–N(1)–C(1)–C(11), −167.37(17); C(2)–N(3)–C(1)–N(1), 16.6(4); C(2)–N(3)–C(1)–C(11), −160.7(2); S–N(2)–C(2)–N(3), −11.4(3); S–N(2)–C(2)–C(21), 173.32(17); C(1)–N(3)–C(2)–N(2), −18.9(4); C(1)–N(3)–C(2)–C(21), 156.5(2).

For further structural identification, we have prepared 3,5-diaryl-1-chloro-1-oxo-1,2,4,6-thiatriazines **10**[7] by chlorination of **3** with SO_2Cl_2 in CH_3CN in 48 to 68% yields (Scheme 1). Yields and melting points of **10** are summarized

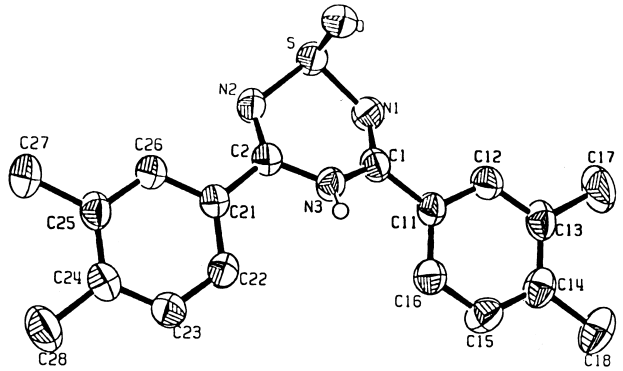
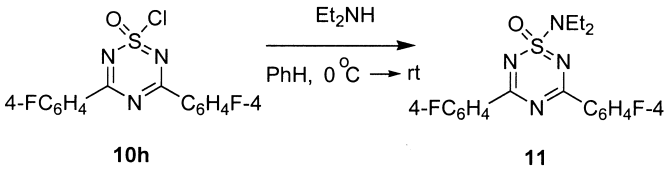
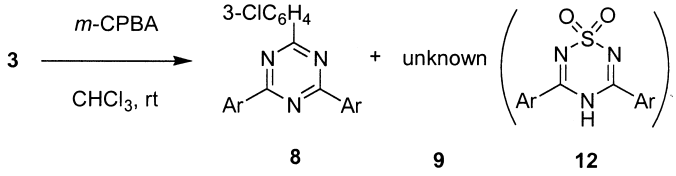


Figure 1. ORTEP drawing of **3d**. Selected bond distances [Å] and angles [°] **3d**: S–O 1.4886(19), S–N1 1.690(2), S–N2 1.992(2), N1–C1 1.301(3), N2–C2 1.305(3), N3–C2 1.379(3), N3–C1 1.382(3), C1–C11 1.481(3), C2–C21 1.486(3), O–S–N1 105.98 (10), N1–S–N2 102.78 (10), C1–N1–S 117.00 (16), C2–N2–S 117.40 (16), C2–N3–C1 122.0 (2), N1–C1–N3 123.0 (2) N1–C1–C11 120.2 (2), N3–C1–C11 116.7 (2), N2–C2–N3 122.8 (2), N2–C2–C21 119.9 (2), N3–C2–C21 117.1 (2),



Scheme 2.



Scheme 3.

in Table 1. Treatment of **10h** with Et_2NH in benzene at 0°C, followed by raising the temperature to room temperature gave 1-(diethylamino)-3,5-di(4-fluorophenyl)-1-oxo-1,2,4,6-thiatriazine (**11**) in 82% yield (Scheme 2).

Compound **11** is analogous to 1-(alkylamino)-3-(trichloromethyl)-1-oxo-5-phenyl-1,2,4,6-thiatriazine, which was prepared from 1-chloro-3-(trichloromethyl)-1-oxo-5-phenyl-1,2,4,6-thiatriazine and alkylamines.[4] Apart from the reported compounds, i.e., 1-(alkylamino)-1-oxo-1,2,4,6-thiatriazines having different substituents at C-3 and C-5, compound **11** is characterized by having the same aryl groups at C-3 and C-5.

In order to confirm the possible involvement of **10** as intermediates for the formation of **5**, compound **3a** was treated with SCl_2, which might be formed as a side product (vide infra, Scheme 4), in *p*-dioxane for 14 h at reflux. TLC showed three spots (R_f=0, 0.9 (major), and 0.95, EtOAc–*n*-hexane=1:3). However, none of the spots corresponded to **10a**. Chromatography of the reaction mixture gave a small amount of solids, which were not converted to **5a** by treatment with either NH_3 or $NaNH_2$ in *p*-dioxane at reflux.

Unexpectedly, the reaction of compound **3a** together with *m*-CPBA in $CHCl_3$ at room temperature gave 2-(3-chlorophenyl)-4,6-diphenyl-1,3,5-triazine (**8a**) (Ar=Ph) and an unknown compound **9a** (Scheme 3). No 3,5-diphenyl-1,2,4,6-thiatriazine 1,1-dioxides (**12a**) (Ar=Ph) were isolated. Similarly, the reactions of selected compounds **3** gave compounds **8** as well as unknown compounds analogous to compounds **9a**. Reaction time, yields and melting points of **8** are summarized in Table 2.

Table 2. Reaction time, yields and melting points of compounds **8**

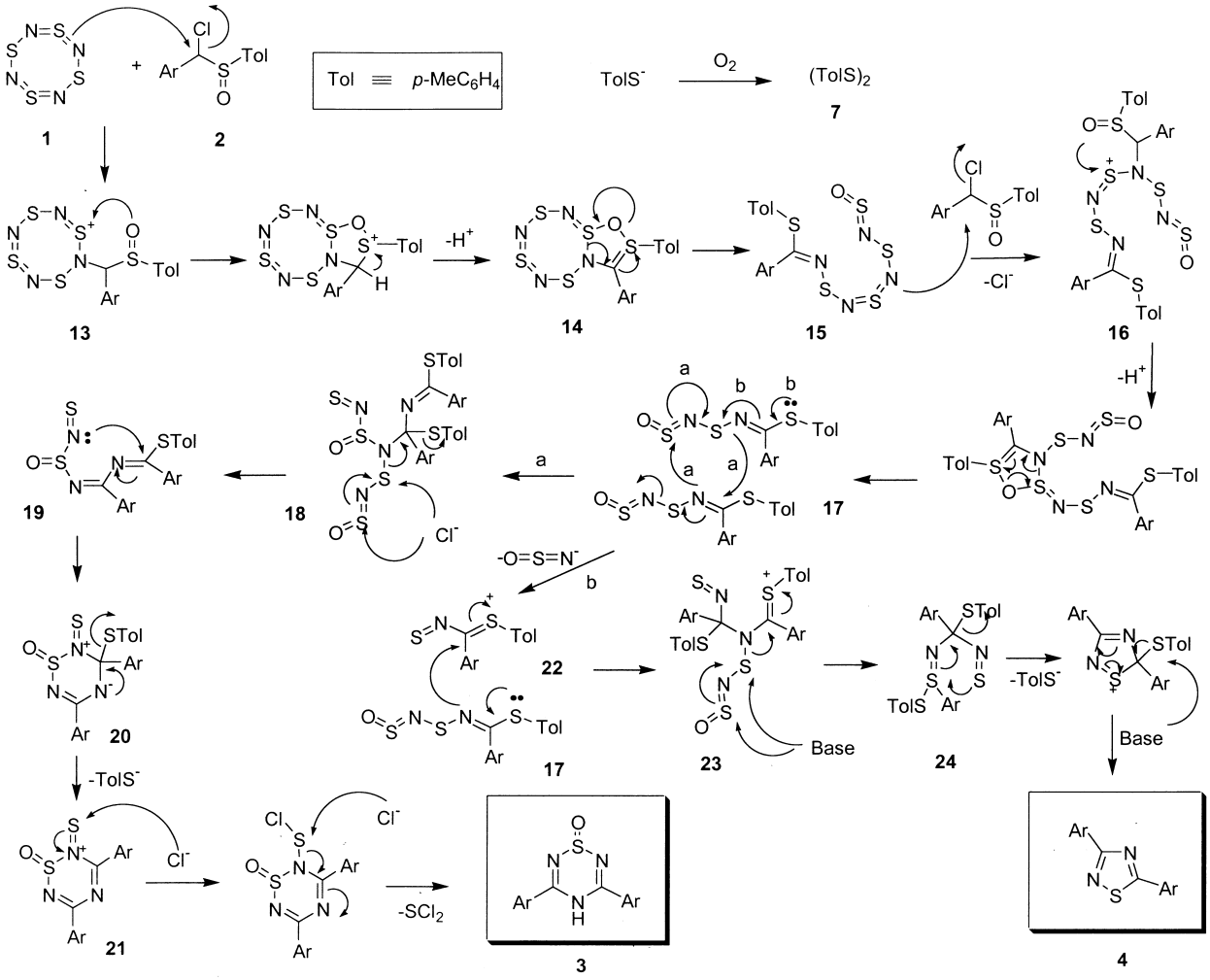
Compd	Time (h)	Compd	Yield[a] (%)	Mp[b] (°C)	Compd[c] (mg)
3a	3	**8a**	38	194–195	**9a** (21)
3c	3	**8c**	30	143–145	**9c** (12)
3d	3	**8d**	25	179–180	**9d** (16)
3g	5	**8g**	33	218–219	**9g** [d]
3h	4[e]	**8h**	28	225–226	**9h** (38)

[a] Isolated yields.
[b] Recrystallized from *n*-hexane.
[c] Recrystallized from a mixture of EtOAc and *n*-hexane. Compounds **9** did not melt at 300°C.
[d] Complex mixtures.
[e] A mixture of $CHCl_3$ and MeOH (10:1) was used as a reaction solvent.

The structures of **8** were determined based on the structure of **8g**, which was independently prepared by following the procedure in the literature.[8] The physical and the spectroscopic data of **8g** were in good agreement with those of the authentic sample obtained from 3-chlorobenzonitrile and $NaNH_2$. In spite of the existence of several methods for the synthesis of 2,4,6-trialkyl (or triaryl)-1,3,5-triazines bearing the same alkyl (or aryl) groups,[9] to the best of our knowledge, the oxidation of **3** with *m*-CPBA is the first method for 1,3,5-triazines having two identical aryl groups together with one 3-chlorophenyl group. Interestingly, the latter must originate from *m*-CPBA.

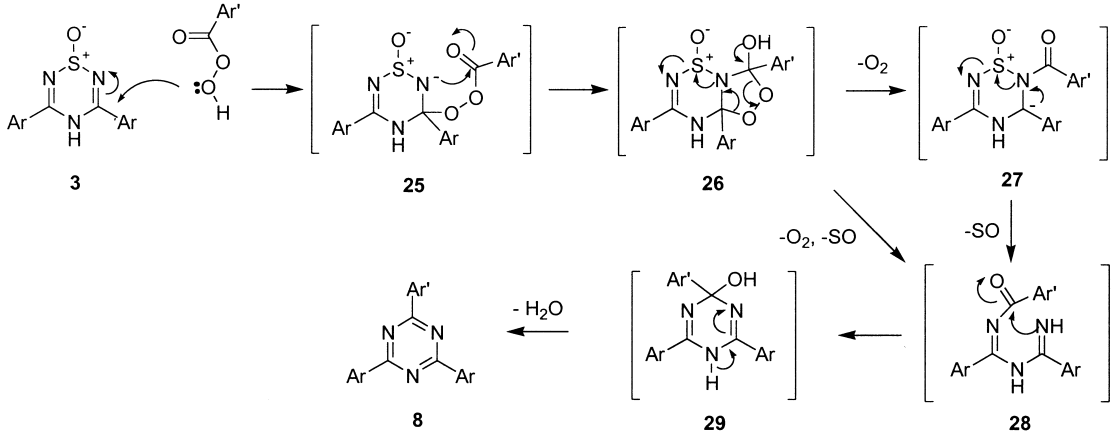
In order to obtain mechanistic information, compound **2b** was treated with S_4N_4 in the presence of 4-bromobenzonitrile for 12 h under the same conditions as for those without 4-bromobenzonitrile. From the reaction mixture, only **3b** was obtained in 21% yield. Neither 3-(4-methoxyphenyl)-5-(4-bromophenyl)-1,2,4,6-thiatriazine 1-oxide nor **3e** was detected. The result indicates that benzonitrile derivatives may not be involved in the formation of **3**. The fact that a significant amount (0–53%) of S_4N_4 was recovered from 1:1 reactions of α-chloromethyl sulfoxides **2** and S_4N_4 suggests that two moles of **2** are needed for the reaction with 1 mol of **1**. Based on the observations, the following mechanism is proposed for the formation of compounds **3**, **4**, and **7** (Scheme 4).

Displacement of a chloride ion from **2** by a nucleophilic attack of S_4N_4 to give an intermediate **13**, followed by the formation of an S–O bond, concomitant with deprotonation, would give an intermediate **14**. This compound undergoes bond reorganization, causing an oxygen transfer to the S_4N_4 moiety to give an intermediate **15**. At this stage, the intermediate **15** would be expected to react with one more α-chloromethyl sulfoxide molecule in a similar fashion to the previous steps, i.e. displacement of the chloride ion, deprotonation, cyclization, and bond reorganization, to give two molecules of imido thioester **17**. It would be expected that the intermediate **17** undergoes two types of reactions: cleavage of the S–N bond to give the S_2NO-nucleophile moiety, possibly assisted by nucleophiles such



Scheme 4.

as Cl^- and NH_3, and the *p*-tolylthiolate ion giving a new imido thioester **19** (path a). Intramolecular cyclization by nucleophilic attack of N═S nitrogen on the carbon of the imido thioester, concomitant with extrusion of the *p*-tolylthiolate ion, would yield **21** via the cyclic intermediate **20**. Desulfurization of **21**, presumably by loss of SCl_2 would yield **3**. Alternatively, one molecule of the imido thioester **17** may be activated by loss of OSN^- to give a sulfonium ion **22** (path b), which may be attacked by another molecule of **17** to yield a new sulfonium ion **23**. Cleavage of the S–N bond by nucleophilic attack on either sulfur atom of the O═S═N═S moiety would give an intermediate **24**, which undergoes intramolecular cyclization, concomitant with loss of the *p*-tolylthio group giving compounds **4**. Compound **7** is expected to be formed by the oxidation of *p*-tolylthiolate in the presence of oxygen



Scheme 5.

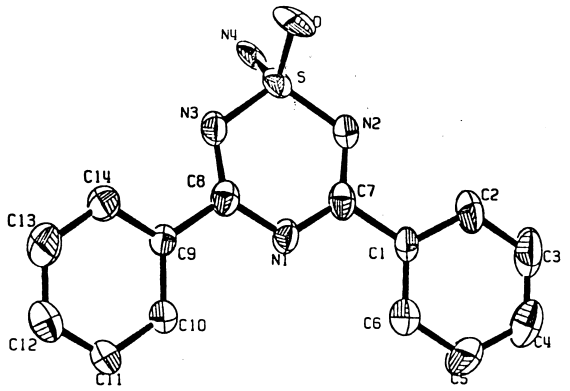


Figure 2. ORTEP drawing of **5a**. Selected bond distances [Å] and angles [°] **5a**: S–O 1.438(5), S–N3 1.578(6), S–N4 1.578(9), S–N2 1.599(6), C7–N1 1.335(9), C8–N1 1.342(9), C7–N2 1.332(10), C8–N3 1.318(10), O–S–N4 106.1(4), O–S–N3 113.1(4), O–S–N2 110.3(4), N4–S–N3 106.9(4), N4–S–N2 110.2(4), N3–S–N2 110.1(3), N2–C7–N1 126.8(7), N2–C7–C1 116.0(6), N1–C7–C1 117.2(7), N3–C8–N1 127.6(7), N3–C8–C9 116.0(6), N1–C8–C9 116.4(6), C7–N1–C8 118.6(7), C7–N2–S 118.3(5), C8–N3–S 118.5(5).

under basic conditions.[11] Heating **2a** in wet *p*-dioxane for 12 h at reflux gave benzaldehyde and **7** in 77 and 58% yields, respectively. However, the reaction of **2c** even in dried *p*-dioxane under the same conditions afforded **6c** and **7** in 82 and 66% yields, respectively. The results suggest that **6** is unlikely to be formed by hydrolysis of **2**. Hydrolysis of various imido thioesters is also unlikely because they are known to resist hydrolysis under basic conditions.[12]

The formation of 1,3,5-triazines **8** may be understood by assuming a nucleophilic attack of *m*-CPBA on the imino carbon of **3** to give an intermediate **25**, which subsequently undergoes intramolecular cyclization by nucleophilic attack on the carbonyl carbon of *m*-CPBA moiety, yielding an intermediate **26** (Scheme 5). Subsequent elimination of O_2, followed by loss of SO would give *N*-3-chlorobenzoylimine **28**, which undergoes cyclization, followed by loss of H_2O, giving **8**. Alternatively, the intermediate **28** may be formed by a stepwise mechanism via the formation of intermediate **27**.

Of compounds **4e**, **4f**, and **4h**, only **4e** is known and its melting point is in accord with the value in the literature.[10] The structure of compounds **5** was determined based on spectroscopic data along with X-ray crystallography of **5a**[15] (Fig. 2).

Conclusions

The reactions of (aryl)(chloro)methyl *p*-tolyl sulfoxides with tetrasulfur tetranitride in *p*-dioxane at reflux afforded 3,5-diaryl-1,2,4,6-thiatriazine 1-oxides, whose structures were unequivocally characterized based on the spectroscopic and analytical data including X-ray crystallographic analysis of **3d**, which shows that the six-membered ring is not planar. The previously reported compound which was assigned to be **3a** is conceived to be planar 1-hydroxy-1,2,4,6-thiatriazine, a tautomer of **3a**, by judging every spectroscopic and analytical data reported.

Experimental

General

The ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$, DMSO-d_6, or $CDCl_3$–DMSO–d_6 solution containing Me_4Si as an internal standard. IR spectra were recorded in KBr or thin films on KBr plates. FAB MS spectra and elemental analyses were measured by the Inter-University Center for Natural Science Research Facilities, SNU. Column chromatography was performed using silica gel (70–230 mesh). Melting points are uncorrected.

(Aryl)(chloro)methyl *p*-tolyl sulfoxides (**2**) were prepared by treatment of arylmethyl *p*-tolyl sulfoxides with *N*-chlorosuccinimide according to the standard literature procedure.[13] Tetrasulfur tetranitride (**1**) was prepared by the documented procedure.[1,2]

General procedure for the reaction of (aryl)(chloro)-methyl *p*-tolyl sulfoxides (2) with tetrasulfur tetranitride (1)

A mixture of **2** (0.72–2.16 mmol) and S_4N_4 (0.72–2.16 mmol) in *p*-dioxane (15–20 mL) was heated for an appropriate time at reflux by the time the spot corresponding to **2** had disappeared on TLC (R_f=0.6, EtOAc–*n*-hexane=1:3). Removal of the solvent in vacuo gave a residue, which was chromatographed on a silica gel column (2×13 cm). Elution with *n*-hexane gave a trace amount of sulfur. Subsequent elution with a mixture of benzene and *n*-hexane (1:5) gave di-*p*-tolyl disulfide (**7**). Elution with the same solvent mixture (1:3) gave unreacted **1** and 3,5-diaryl-1,2,4-thiadiazoles (**4**). Elution with a mixture of EtOAc and *n*-hexane (1:8) gave substituted benzaldehydes (**6**). Elution next with a mixture of EtOAc and *n*-hexane (1:3) gave 1-amino-3,5-diaryl-1,2,4,6-thiatriazine 1-oxides (**5**). In the case of the reactions with **2a**, **2b**, **2d**, **2f**, and **2i** where no **5** was isolated, elution with a mixture of EtOAc and *n*-hexane (1:3) gave unknown mixtures. Subsequent elution with a mixture of EtOAc and *n*-hexane (2:1) gave 3,5-diaryl-1,2,4,6-thiatriazine 1-oxides **3a**, **3e**, and **3j**. However, compounds **3f**–**h** and **3i** were eluted with EtOAc and acetone, respectively. Reaction time and yields of **3**–**7** are summarized in Table 1.

3,5-Diphenyl-1,2,4,6-thiatriazine 1-oxide (3a). It was prepared by the general procedure from (chloro)(phenyl)-methyl *p*-tolyl sulfoxide (**2a**) and S_4N_4: mp 178–180°C (CH_2Cl_2–*n*-hexane) (lit.[5] 156–158°C); ^1H NMR ($CDCl_3$) δ 7.48 (t, J=7.4 Hz, 4H), 7.65 (d, J=7.4 Hz, 2H), 7.74 (d, J=7.4 Hz, 4H), 11.8 (s, 1H); ^1H NMR (DMSO-d_6) δ 7.60–7.74 (m, 6H), 7.93–8.21 (m, 4H), 12.81 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 128.5, 128.7, 131.1, 133.4, 154.8; IR (KBr) 3360, 1606, 1558, 1065 cm^{-1}; IR (Nujol mull) 1603, 1555, 1062 cm^{-1}; FAB MS *m*/*z*) 270 ($(M+1)^+$, 100%), 222 ($(M+1)^+-SO$, 6.9), 136 ($(C_6H_5CNS+1)^+$, 26), 104 ($(C_6H_5CN+1)^+$, 27). Anal. Calcd for $C_{14}H_{11}N_3OS$: C, 62.43; H, 4.12; N, 15.60; S, 11.91. Found: C, 62.28; H, 4.09; N, 15.43; S, 11.69.

3,5-Di(4-methoxyphenyl)-1,2,4,6-thiatriazine 1-oxide (3b).

It was prepared by the general procedure from (chloro)(4-methoxyphenyl)methyl *p*-tolyl sulfoxide (**2b**) and S_4N_4: mp 151–153°C (CH_2Cl_2–*n*-hexane); ^{1}H NMR ($CDCl_3$–DMSO-d_6) δ 3.85, (s, 6H), 6.92 (d, J=8.7 Hz, 4H), 7.75 (s, 1H), 7.87 (d, J=8.7 Hz, 4H); ^{13}C NMR ($CDCl_3$–DMSO-d_6) δ 55.8, 113.9, 126.0, 129.9, 161.8, 163.1; IR (KBr) 3328, 1628, 1596, 1020 cm^{-1}; FAB MS (*m*/*z*) 330 ($(M+1)^+$, 67%), 282 ($(M+1)^+-SO$, 5.2), 166 ($(CH_3OC_6H_4CNS+1)^+$, 32), 134 ($(CH_3OC_6H_4CN+1)^+$, 13). Anal. Calcd for $C_{16}H_{15}N_3OS$: C, 58.34; H, 4.59; N, 12.76; S, 9.74. Found: C, 58.18; H, 4.38; N, 12.59; S, 9.62.

3,5-Di(4-*t*-butylphenyl)-1,2,4,6-thiatriazine 1-oxide (3c). It was prepared by the general procedure from (4-*t*-butylphenyl)(chloro)methyl *p*-tolyl sulfoxide (**2c**) and S_4N_4: mp 185–187°C (CH_2Cl_2–*n*-hexane); ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 18H), 7.42 (d, J=8.3 Hz, 4H), 7.65 (d, J=8.3 Hz, 4H), 11.7 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 31.5, 35.6, 126.1, 126.8, 128.5, 130.1, 157.5; IR (KBr) 3344, 1600, 1580, 1062 cm^{-1}; FAB MS (*m*/*z*) 382 ($(M+1)^+$, 100%), 334 ($(M+1)^+-SO$, 5.7), 192 ($((CH_3)_3CC_6H_4CNS+1)^+$, 2.4), 160 ($((CH_3)_3CC_6H_4CN+1)^+$, 55). Anal. Calcd for $C_{22}H_{27}N_3OS$: C, 69.26; H, 7.13; N, 11.01; S, 8.40. Found: C, 69.34; H, 7.08; N, 11.12; S, 8.28.

3,5-Di(3,4-dimethylphenyl)-1,2,4,6-thiatriazine 1-oxide (3d). It was prepared by the general procedure from (chloro)(3,4-dimethylphenyl)methyl *p*-tolyl sulfoxide (**2d**) and S_4N_4: mp 194–195°C (CH_2Cl_2–*n*-hexane); ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 6H), 2.35 (s, 6H), 7.20 (d, J=7.9 Hz, 2H), 7.41 (s, 2H), 7.50 (d, J=7.9 Hz, 2H), 11.76 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 20.1, 20.3, 126.4, 130.0, 130.1, 130.8, 137.4, 142.5, 156.0; IR (KBr) 3200, 1584, 1555, 1062 cm^{-1}; FAB MS (*m*/*z*) 326 ($(M+1)^+$, 100%), 278 ($(M+1)^+-SO$, 6.8), 165 ($((CH_3)_2C_6H_3CNS+1)^+$, 23), 132 ($((CH_3)_2C_6H_3CN+1)^+$, 40). Anal. Calcd for $C_{18}H_{19}N_3OS$: C, 66.43; H, 5.88; N, 12.91; S, 9.85. Found: C, 66.39; H, 5.82; N, 12.88; S, 9.68.

3,5-Di(4-bromophenyl)-1,2,4,6-thiatriazine 1-oxide (3e). It was prepared by the general procedure from (4-bromophenyl)(chloro)methyl *p*-tolyl sulfoxide (**2e**) and S_4N_4: mp (dec) 203–205°C (acetone–*n*-hexane); ^{1}H NMR (DMSO-d_6) δ 7.79 (d, J=8.5 Hz, 4H), 8.13 (d, J=8.5 Hz, 4H); ^{13}C NMR (DMSO-d_6) δ 127.0, 131.3, 132.4, 133.0, 158.0; IR (KBr) 3328, 1619, 1587, 1075 cm^{-1}; FAB MS (*m*/*z*) 426 ($(M+1)^+$, 1.9%), 428 ($(M+1)^+$+2, 3.1), 430 ($(M+1)^+$+4, 1.6), 378 ($(M+1)^+-SO$, 0.3), 214 ($(BrC_6H_4CNS+1)^+$, 1.3), 182 ($(BrC_6H_4CN+1)^+$, 2.0).

3,5-Di(4-chlorophenyl)-1,2,4,6-thiatriazine 1-oxide (3f). It was prepared by the general procedure from (chloro)(4-chlorophenyl)methyl *p*-tolyl sulfoxide (**2f**) and S_4N_4: ^{1}H NMR (DMSO-d_6) δ 7.43 (d, J=8.0 Hz, 4H), 7.75 (d, J=8.0 Hz, 4H); IR (KBr) 3326, 1605, 1581, 1065 cm^{-1}; HRFAB MS (*m*/*z*) 337.9927 $(M+1)^+$ ($C_{14}H_9Cl_2N_3OS$ requires 336.9843).

3,5-Di(3-chlorophenyl)-1,2,4,6-thiatriazine 1-oxide (3g). It was prepared by the general procedure from (chloro)(3-chlorophenyl)methyl *p*-tolyl sulfoxide (**2g**) and S_4N_4: ^{1}H NMR (DMSO-d_6) δ 7.47 (dd, J=7.79, 7.87 Hz, 4H), 7.56 (d, J=7.87 Hz, 4H), 8.12 (d, J=7.79 Hz, 4H), 8.21 (s, 4H); IR (KBr) 3326, 1612, 1580, 1072 cm^{-1}; HRFAB MS (*m*/*z*) 337.9933 $(M+1)^+$ ($C_{14}H_9Cl_2N_3OS$ requires 336.9843).

3,5-Di(4-fluorophenyl)-1,2,4,6-thiatriazine 1-oxide (3h). It was prepared by the general procedure from (chloro)(4-fluorophenyl)methyl *p*-tolyl sulfoxide (**2h**) and S_4N_4: mp 198–199°C (CH_2Cl_2–*n*-hexane); ^{1}H NMR (DMSO-d_6) δ 7.19–7.25 (m, 4H), 8.21–8.27 (m, 4H); ^{13}C NMR (DMSO-d_6) δ 116.6 (J=22 Hz), 127.9, 132.2 (J=9.3 Hz), 165.7 (J=251 Hz), 167.7; IR (KBr) 3189, 1610, 1585, 1061 cm^{-1}; FAB MS (*m*/*z*) 306 ($(M+1)^+$, 54%), 258 ($(M+1)^+-SO$, 4.0), 154 ($(FC_6H_4CNS+1)^+$, 100), 122 ($(FC_6H_4CN+1)^+$, 25). Anal. Calcd for $C_{14}H_9F_2N_3OS$: C, 55.08; H, 2.97; N, 13.76; S, 10.50. Found: C, 54.76; H, 3.28; N, 13.59; S, 11.05.

3,5-Di(4-nitrophenyl)-1,2,4,6-thiatriazine 1-oxide (3i). It was prepared by the general procedure from (chloro)(4-nitrophenyl)methyl *p*-tolyl sulfoxide (2i) and S_4N_4: mp (dec) 198–200°C (acetone–*n*-hexane); ^{1}H NMR (DMSO-d_6) δ 8.31 (d, J=8.6 Hz, 4H), 8.58 (d, J=8.6 Hz, 4H); ^{13}C NMR (DMSO-d_6) δ 124.0, 129.4, 146.9, 149.4, 159.5; IR (KBr) 3376, 1520, 1337, 1011 cm^{-1}; FAB MS (*m*/*z*) 360 ($(M+1)^+$, 6.5%), 312 ($(M+1)^+-SO$, 1.4), 181 ($(O_2NC_6H_4CNS+1)^+$, 3.3), 149 ($(O_2NC_6H_4CN+1)^+$, 15). Anal. Calcd for $C_{14}H_9N_5O_5S$: C, 46.80; H, 2.52; N, 19.49; S, 8.92. Found: C, 46.68; H, 2.30; N, 19.28; S, 8.68.

3,5-Di(6-methylpyridin-2-yl)-1,2,4,6-thiatriazine 1-oxide (3j). It was prepared by the general procedure from (chloro)(6-methylpyridin-2-yl)methyl *p*-tolyl sulfoxide (**2j**) and S_4N_4: mp 218–220°C (CH_2Cl_2–*n*-hexane); ^{1}H NMR ($CDCl_3$) δ 2.73 (s, 6H), 7.43 (d, J=7.80 Hz, 2H), 7.87 (dd, J=7.78, 7.80 Hz, 2H), 8.30 (d, J=7.78 Hz, 2H), 12.99 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 24.3, 119.5, 126.2, 137.4, 149.0, 157.4, 167.1; IR (KBr) 3250, 1642, 1587, 1551, 1113 cm^{-1}; FAB MS (*m*/*z*) 300 ($(M+1)^+$, 100%), 252 ($(M+1)^+-SO$, 4.1), 151 ($(C_6H_6NCNS+1)^+$, 2.8), 119 ($(C_6H_6NCN+1)^+$, 42). Anal. Calcd for $C_{14}H_{13}N_5OS$: C, 56.17; H, 4.38; N, 23.40; S, 10.71. Found: C, 55.98; H, 4.19; N, 23.28; S, 10.58.

3,5-Di(4-bromophenyl)-1,2,4-thiadiazole (4e). Mp 167–169°C (*n*-hexane); ^{1}H NMR ($CDCl_3$) δ 7.64 (d, J=8.7 Hz, 2H), 7.42 (d, J=8.7 Hz, 2H), 7.92 (d, J=8.7 Hz, 2H), 8.23 (d, J=8.7 Hz, 2H); IR (KBr) 3056, 1577, 1452 cm^{-1}; MS (*m*/*z*) 394 (M^+, 21%), 215 (100), 181 (28), 134 (11). Anal. Calcd for $C_{14}H_8Br_2N_2S$: C, 42.45; H, 2.04; N, 7.07; S, 8.10. Found: C, 42.28; H, 2.01; N, 7.18; S, 8.30.

3,5-Di(4-chlorophenyl)-1,2,4-thiadiazole (4f). Mp 160–161°C (CH_2Cl_2–*n*-hexane) (lit.[9] 161–162°C); ^{1}H NMR ($CDCl_3$) δ 7.40 (d, J=8.4 Hz, 2H), 7.42 (d, J=8.4 Hz, 2H), 7.92 (d, J=8.4 Hz, 2H), 8.23 (d, J=8.4 Hz, 2H); IR (KBr) 3056, 1587, 1456 cm^{-1}; MS (*m*/*z*) 306 (M^+, 26%), 169 (100), 137 (28), 102 (11). Anal. Calcd for $C_{14}H_8Cl_2N_2S$: C, 54.74; H, 2.62; N, 9.12; S, 10.44. Found: C, 54.59; H, 2.60; N, 9.05; S, 10.28.

3,5-Di(4-fluorophenyl)-1,2,4-thiadiazole (4h). Mp 189–190°C (CH_2Cl_2–*n*-hexane); ^{1}H NMR ($CDCl_3$) δ 7.17–7.28 (m, 4H), 8.04–8.08 (m, 2H), 8.37–8.42 (m, 2H); IR (KBr)

3056, 1590, 1465 cm^{-1}; MS (*m*/*z*) 274 (M^+, 54%), 153 (100), 121 (31). Anal. Calcd for $C_{14}H_8F_2N_2S$: C, 61.30; H, 2.94; N, 10.21; S, 11.69. Found: C, 61.25; H, 2.93; N, 10.16; S, 11.48.

1-Amino-3,5-diphenyl-1,2,4,6-thiatriazine 1-oxide (5a). Mp 242–243°C (CH_2Cl_2–*n*-hexane); ^1H NMR ($CDCl_3$–DMSO-d_6) δ 7.47–7.58 (m, 6H), 7.62 (s, 2H), 8.51 (d, *J*=7.8 Hz, 4H); ^{13}C NMR ($CDCl_3$–DMSO-d_6) δ 128.9, 129.2, 133.1, 136.7, 169.6; IR (KBr) 3328, 3232, 1491, 1417, 1251 cm^{-1}; FAB MS (*m*/*z*) 285 (($M+1)^+$, 76%), 136 (($C_6H_5CNS+1)^+$, 67), 104 (($C_6H_5CN+1)^+$, 18). Anal. Calcd for $C_{14}H_{12}N_4OS$: C, 59.14; H, 4.25; N, 19.70; S, 11.28. Found: C, 59.08; H, 4.19; N, 19.58; S, 11.09.

1-Amino-3,5-di(*t*-butylphenyl)-1,2,4,6-thiatriazine 1-oxide (5c). Mp 230–201°C (CH_2Cl_2–*n*-hexane); ^1H NMR ($CDCl_3$) δ 1.37 (s, 18H), 5.20 (s, 2H), 7.51 (d, *J*=8.6 Hz, 4H), 8.42 (d, *J*=8.6 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 31.1, 35.0, 125.2, 128.7, 133.4, 156.1, 169.5; IR (KBr) 3392, 3280, 1475, 1417, 1257 cm^{-1}; FAB MS (*m*/*z*) 397 (($M+1)^+$, 100%), 192 ((($CH_3)_3CC_6H_4CNS+1)^+$, 0.3), 160 ((($CH_3)_3CC_6H_4CN+1)^+$, 43*)*. Anal. Calcd for $C_{22}H_{28}N_4OS$: C, 66.63; H, 7.12; N, 14.13; S, 8.09. Found: C, 66.58; H, 7.01; N, 14.04; S, 7.98.

1-Amino-3,5-di(4-bromophenyl)-1,2,4,6-thiatriazine 1-oxide (5e). Mp (dec) 224–226°C (CH_2Cl_2–*n*-hexane); ^1H NMR (DMSO-d_6) δ 7.63 (d, *J*=8.6 Hz, 4H), 7.75 (s, 2H), 8.37 (d, *J*=8.6 Hz, 4H); ^{13}C NMR (DMSO-d_6) δ 127.2, 130.3, 131.4, 135.0, 168.4; IR (KBr) 3360, 3216, 1577, 1478, 1417, 1248 cm^{-1}; FAB MS (*m*/*z*) 441 (($M+1)^+$, 48%), 443 (($M+1)^+$+2, 100), 445 (($M+1)^+$+4, 58), 214 (($BrC_6H_4CNS+1)^+$, 0.6), 182 (($BrC_6H_4CN+1)^+$, 36). Anal. Calcd for $C_{14}H_{10}Br_2N_4OS$: C, 38.08; H, 2.28; N, 12.67; S, 7.25. Found: C, 38.14; H, 2.31; N, 12.59; S, 7.08.

1-Amino-3,5-di(3-chlorophenyl)-1,2,4,6-thiatriazine 1-oxide (5g). Mp 200–201°C (CH_2Cl_2–*n*-hexane); ^1H NMR ($CDCl_3$) δ 5.30 (s, 2H), 7.47 (dd, *J*=8.0, 8.4 Hz, 2H), 7.59 (d, *J*=8.4 Hz, 2H), 8.40 (d, *J*=8.0 Hz, 2H), 8.48 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 127.4, 129.0, 130.0, 132.8, 134.6, 138.2, 168.8; IR (KBr) 3376, 3264, 1491, 1430, 1276 cm^{-1}; FAB MS (*m*/*z*) 353 (($M+1)^+$, 100%), 355 (($M+1)^+$+2, 70), 357 (($M+1)^+$+4, 15), 170 (($ClC_6H_4CNS+1)^+$, 0.9), 138 (($ClC_6H_4CN+1)^+$, 34). Anal. Calcd for $C_{14}H_{10}Cl_2N_4OS$: C, 47.60; H, 2.85; N, 15.86; S, 9.08. Found: C, 47.48; H, 2.78; N, 15.79; S, 8.96.

1-Amino-3,5-di(4-fluorophenyl)-1,2,4,6-thiatriazine 1-oxide (5h). Mp 260–261°C (CH_2Cl_2–*n*-hexane); ^1H NMR ($CDCl_3$–DMSO-d_6) δ 6.66 (s, 2H), 7.13–7.18 (m, 4H), 8.49–8.54 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 115.6 (*J*=22 Hz), 131.7 (*J*=9.2 Hz), 131.8, 166.2 (*J*=255 Hz), 169.9; IR (KBr) 3363, 3236, 1601, 1501, 1434, 1267 cm^{-1}; FAB MS (*m*/*z*) 321 (($M+1)^+$, 88%), 154 (($FC_6H_4CNS+1)^+$, 100), 122 (($FC_6H_4CN+1)^+$, 20). Anal. Calcd for $C_{14}H_{10}F_2N_4OS$: C, 52.50; H, 3.15; N, 17.49; S, 10.01. Found: C, 52.89; H, 3.74; N, 17.20; S, 10.34.

General procedure for the preparation of 2,6-diaryl-4-(3-chlorophenyl)-1,3,5-triazines 8

To a solution of **3** (0.074–0.22 mmol) in $CHCl_3$ (6–10 mL) was added *m*-CPBA (57–86%, 0.11–0.45 mmol). The mixture was stirred for an appropriate time at room temperature. After removal of the solvent in vacuo, the residue was chromatographed on a silica gel column (2×8 cm). Elution with a mixture of benzene and *n*-hexane (1:4) gave **8**. Elution with a mixture of EtOAc and acetone gave an unknown mixture **9**. Attempted purification of **9** by recrystallization from a mixture of acetone and *n*-hexane has been unsatisfactory. A mixture of $CHCl_3$ and MeOH (10:1) was used as a solvent for the reaction of **3h**. Reaction time and yields of **8** and **9**, and melting points of **8** are summarized in Table 2.

2-(3-Chlorophenyl)-4,6-diphenyl-1,3,5-triazine (8a). Mp 194–195°C (CH_2Cl_2–*n*-hexane); ^1H NMR ($CDCl_3$) δ 7.53 (dd, *J*=7.7, 7.8 Hz, 1H), 7.58–7.66 (m, 7H), 8.68 (d, *J*=7.7 Hz, 1H), 8.76–8.82 (m, 5H); IR (KBr) 3056, 1584, 1516, 1440, 1360, 1020, 755, 684 cm^{-1}; MS (*m*/*z*) 343 (M^+, 60%), 137 (63), 103 (100). Anal. Calcd for $C_{21}H_{14}ClN_3$: C, 73.36; H, 4.10; N, 12.22. Found: C, 73.00; H, 4.09; N, 12.27.

2-(3-Chlorophenyl)-4,6-di(4-*t*-butylphenyl)-1,3,5-triazine (8c). Mp 143–145°C (*n*-hexane); ^1H NMR ($CDCl_3$) δ 1.43 (s, 18H), 7.53 (dd, *J*=7.7, 7.8 Hz, 1H), 7.59 (d, *J*=7.7 Hz, 1H), 7.62 (d, *J*=8.5 Hz, 4H), 8.67 (d, *J*=7.8 Hz, 1H), 8.69 (d, *J*=8.5 Hz, 4H), 8.75 (s, 1H); IR (KBr) 3056, 2944, 1571, 1507, 1360, 1014, 819, 787 cm^{-1}. Anal. Calcd for $C_{29}H_{30}ClN_3$: C, 76.38; H, 6.63; N, 9.21. Found: C, 76.19; H, 6.55; N, 9.13.

2-(3-Chlorophenyl)-4,6-di(3,4-dimethylphenyl)-1,3,5-triazine (8d). Mp 179–180°C (*n*-hexane); ^1H NMR ($CDCl_3$) δ 2.40 (s, 6H), 2.45 (s, 6H), 7.34 (d, *J*=8.0 Hz, 2H), 7.52 (dd, *J*=7.6, 7.9 Hz, 1H), 7.59 (d, *J*=7.9 Hz, 1H), 8.50 (d, *J*=8.0 Hz, 2H), 8.51 (s, 2H), 8.66 (d, *J*=7.6 Hz, 1H), 8.74 (s, 1H); IR (KBr) 3040, 1510, 1344, 1020, 780 cm^{-1}; MS (*m*/*z*) 399 (M^+, 18%), 207 (10), 139 (100), 111 (18). Anal. Calcd for $C_{25}H_{22}ClN_3$: C, 75.08; H, 5.54; N, 10.51. Found: C, 75.16; H, 5.51; N, 10.38.

2,4,6-Tri(3-chlorophenyl)-1,3,5-triazine (8g). Mp 218–219°C (CH_2Cl_2–*n*-hexane); ^1H NMR ($CDCl_3$) δ 7.55 (t, *J*=7.7 Hz, 3H), 7.63 (d, *J*=7.7 Hz, 3H), 8.66 (d, *J*=7.7 Hz, 3H), 8.72 (s, 3H); IR (KBr) 3056, 1619, 1516, 1440, 1350, 1065, 1024, 771, 710, 672 cm^{-1}. Anal. Calcd for $C_{21}H_{12}Cl_3N_3$: C, 61.12; H, 2.93; N, 10.18. Found: C, 60.04; H, 2.88; N, 10.06.

2-(3-Chlorophenyl)-4,6-di(4-fluorophenyl)-1,3,5-triazine (8h). Mp 225–226°C (*n*-hexane); ^1H NMR ($CDCl_3$) δ 7.23–7.29 (m, 4H), 7.52 (dd, *J*=7.8, 7.9 Hz, 1H), 7.60 (d, *J*=7.8 Hz, 1H), 8.62 (d, *J*=7.9 Hz, 1H), 8.69 (s, 1H), 8.74–8.79 (m, 4H); IR (KBr) 3088, 1593, 1516, 1408, 1356, 1011, 819, 784 cm^{-1}; MS (*m*/*z*) 379 (M^+, 47%), 137 (51), 121 (100). Anal. Calcd for $C_{21}H_{12}ClF_2N_3$: C, 66.41; H, 3.18; N, 11.06. Found: C, 66.29; H, 3.15; N, 11.08.

Unknown compound 9a. ^1H NMR (DMSO-d_6) δ 7.43–7.52 (m, 6H), 8.27 (d, *J*=7.9 Hz, 4H); ^{13}C NMR (DMSO-d_6) δ 128.5, 128.8, 131.8, 137.3, 165.1; IR (KBr) 1500, 1446, 1401, 1132 cm^{-1}; FAB MS (*m*/*z*) 329 (M^+, 100%).

Unknown compound 9c. ^{1}H NMR (DMSO-d_6) δ 1.36 (s, 18H), 7.49 (d, J=7.9 Hz, 4H), 8.15 (d, J=7.9 Hz, 4H); IR (KBr) 1491, 1411, 1392, 1132 cm^{-1}.

Unknown compound 9d. ^{1}H NMR (DMSO-d_6) δ 2.25 (s, 6H), 2.28 (s, 6H), 7.21 (d, J=7.6 Hz, 2H), 8.05 (d, J=7.6 Hz, 2H), 8.07 (s, 2H); IR (KBr) 1497, 1404, 1385, 1132 cm^{-1}.

Unknown compound 9h. ^{1}H NMR (DMSO-d_6) δ 7.24–7.31 (m, 4H), 8.32–8.37 (m, 4H); IR (KBr) 1494, 1417, 1392, 1136 cm^{-1}; FAB MS (m/z) 365 (M^+, 59%).

Preparation of 2,4,6-tri(3-chlorophenyl)-1,3,5-triazine 8g

To a solution of 3-chlorobenzonitrile (848 mg, 6.16 mmol) in diethyl ether (20 mL) was added $NaNH_2$ (50% in toluene, 2.41 g, 30.8 mmol). The mixture was heated to reflux condition through overnight. TLC (R_f=0.75, CH_2Cl_2–n-hexane=2:1) showed the spot with the same R_f value as that of **8g** obtained from the reaction of **3g** with m-CPBA. Removal of the solvent, followed by work-up gave **8g** (87 mg, 10%).

General procedure for the preparation of 3,5-diaryl-1-chloro-1-oxo-1,2,4,6-thiatriazines 10

To a solution of **3** (0.058–0.095 mmol) in CH_3CN (5–10 mL) was added sulfuryl chloride (0.058–0.095 mmol). The mixture was stirred for 0.5 h at room temperature and worked up when no spot corresponding to **3** had observed on TLC (R_f=0.2, EtOAc–n-hexane=1:1). Yields and melting points of **10a**–**d** and **10h**–**i** are summarized in Table 1.

1-Chloro-1-oxo-3,5-diphenyl-1,2,4,6-thiatriazine (10a). Mp 159–161°C (CH_3CN); ^{1}H NMR ($CDCl_3$) δ 7.58 (t, J=7.4 Hz, 4H), 7.71 (t, J=7.4 Hz, 2H), 8.57 (d, J=7.4 Hz, 4H); IR (KBr) 3056, 1587, 1468, 1414, 1302, 1174, 1139, 1084, 1017, 966, 838 cm^{-1}; FAB MS (m/z) 304 ($(M+1)^+$, 33%), 136 ($(C_6H_5CNS+1)^+$, 75), 104 ($(C_6H_5CN+1)^+$, 6.6). Anal. Calcd for $C_{14}H_{10}ClN_3OS$: C, 55.35; H, 3.32; N, 13.83; S, 10.56. Found: C, 55.16; H, 3.30; N, 13.79; S, 10.34.

1-Chloro-3,5-di(4-methoxyphenyl)-1-oxo-1,2,4,6-thiatriazine (10b). Mp (dec) ~180°C (CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 3.93 (s, 6H), 7.23 (d, J=8.98 Hz, 4H), 8.50 (d, J=8.98 Hz, 4H); IR (KBr) 3056, 2928, 1433, 1401, 1376, 1302, 1254, 1164, 1126, 1020, 960, 841 cm^{-1}; FAB MS (m/z) 364 ($(M+1)^+$, 24%), 166 ($(CH_3OC_6H_4CNS+1)^+$, 7.0), 134 ($(CH_3OC_6H_4CN+1)^+$, 48). Anal. Calcd for $C_{16}H_{14}ClN_3O_3S$: C, 52.82; H, 3.88; N, 11.55; S, 8.81. Found: C, 52.74; H, 3.69; N, 11.38; S, 8.67.

3,5-Di(4-*t*-butylphenyl)-1-chloro-1-oxo-1,2,4,6-thiatriazine (10c). Mp 174–176°C (CH_2Cl_2–n-hexane); ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 18H), 7.60 (d, J=8.3 Hz, 4H), 8.50 (d, J=8.3 Hz, 4H); IR (KBr) 3056, 2944, 1596, 1433, 1376, 1305, 1260, 1100, 1011, 966, 838 cm^{-1}; FAB MS (m/z) 416 ($(M+1)^+$, 21%), 192 ($((CH_3)_3C_6H_4CNS+1)^+$, 2.8), 160 ($((CH_3)_3C_6H_4CN+1)^+$, 100). Anal. Calcd for $C_{22}H_{26}ClN_3OS$: C, 63.52; H, 6.30; N, 10.10; S, 7.71. Found: C, 63.48; H, 6.35; N, 10.02; S, 7.58.

1-Chloro-3,5-di(3,4-dimethylphenyl)-1-oxo-1,2,4,6-thiatriazine (10d). Mp 141–143°C (CH_2Cl_2–n-hexane); ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 12H), 7.33 (d, J=7.8 Hz, 2H), 8.29 (d, J=7.8 Hz, 2H), 8.30 (s, 2H); IR (KBr) 3056, 2960, 1600, 1452, 1401, 1372, 1302, 1100, 998, 758 cm^{-1}; FAB MS (m/z) 360 ($(M+1)^+$, 85%), 164 ($((CH_3)_2C_6H_3CNS+1)^+$, 2.7), 132 ($((CH_3)_2C_6H_3CN+1)^+$, 46). Anal. Calcd for $C_{18}H_{18}ClN_3OS$: C, 60.07; H, 5.04; N, 11.68; S, 8.91. Found: C, 60.19; H, 5.00; N, 11.74; S, 8.80.

1-Chloro-3,5-di(4-fluorophenyl)-1-oxo-1,2,4,6-thiatriazine (10h). Mp 182–184°C (CH_2Cl_2–n-hexane); ^{1}H NMR ($CDCl_3$) δ 7.25–7.28 (m, 4H), 8.57–8.62 (m, 4H); IR (KBr) 3056, 1590, 1504, 1449, 1420, 1395, 1369, 1305, 1228, 1139, 960, 848 cm^{-1}; FAB MS (m/z) 340 ($(M+1)^+$, 6.8%), 154 ($(FC_6H_4CNS+1)^+$, 42), 122 ($(FC_6H_4CN+1)^+$, 16). Anal. Calcd for $C_{14}H_8ClF_2N_3OS$: C, 49.49; H, 2.37; N, 12.37; S, 9.44. Found: C, 49.61; H, 2.31; N, 12.19; S, 9.25.

1-Chloro-3,5-di(4-nitrophenyl)-1-oxo-1,2,4,6-thiatriazine (10i). Mp (dec) ~230°C (CH_2Cl_2–n-hexane); ^{1}H NMR ($CDCl_3$) δ 8.39 (d, J=8.8 Hz, 4H), 8.73 (d, J=8.8 Hz, 4H); IR (KBr) 3056, 1596, 1520, 1456, 1420, 1337, 1302, 1100, 1081, 1004, 966, 867 cm^{-1}; FAB MS (m/z) 394 ($(M+1)^+$, 28%), 181 ($(O_2NC_6H_4CNS+1)^+$, 12), 149 ($(O_2NC_6H_4CN+1)^+$, 56). Anal. Calcd for $C_{14}H_8ClN_5O_5S$: C, 42.70; H, 2.05; N, 17.79; S, 8.14. Found: C, 42.56; H, 2.04; N, 17.64; S, 8.01.

1-(Diethylamino)-3,5-di(4-fluorophenyl)-1-oxo-1,2,4,6-thiatriazine 11. To a solution of 1-chloro-3,5-di(4-fluorophenyl)-1-oxo-1,2,4,6-thiatriazine (**10h**) (42 mg, 0.124 mmol) in benzene (5 mL) at an ice temperature was added diethylamine (23 mg, 0.310 mmol). The mixture was warmed to room temperature and then stirred for 3 h. Water (10 mL) was added to the mixture and the reaction mixture was extracted with ether (3×10 mL). The extracts were dried over $MgSO_4$. Removal of the solvent gave a residue, which was chromatographed on a silica gel (2×6 cm). Elution with EtOAc gave **11** (38 mg, 82%): mp 159–160°C (CH_2Cl_2–n-hexane); ^{1}H NMR ($CDCl_3$) δ 1.24 (t, J=7.1 Hz, 6H), 3.21 (q, J=7.1 Hz, 4H), 7.14–7.21 (m, 4H), 8.50–8.55 (m, 4H); IR (KBr) 2944, 1593, 1484, 1420 cm^{-1}; Anal. Calcd for $C_{18}H_{18}F_2N_4OS$: C, 57.43;H, 4.82; N, 14.88; S, 8.52. Found: C, 57.35; H, 4.79; N, 14.78; S, 8.30.

Reaction of 2b with S_4N_4 in the presence of 4-bromobenzonitrile

A mixture of **2b** (864 mg, 2.93 mmol), **1** (594 mg, 3.23 mmol), and 4-bromobenzonitrile (267 mg, 1.47 mmol) in p-dioxane (20 mL) was refluxed for 12 h. TLC of the reaction mixture showed a spot corresponding to **3b** (R_f=0.7, EtOAc). The mixture was worked up as described in the general procedure for **3**. ^{1}H NMR spectrum of the fraction containing the spot did not indicate the presence of **3** having p-bromophenyl moiety. From the reaction mixture was isolated **3b** in 21% yield.

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14. Crystal data for $C_{18}H_{19}N_3OS$ **3d**: M=325.42, monoclinic, a=9.0127(3), b=17.0053(5), c=11.0069(2) Å, α=90.00, β=92.38, γ=90.00°, V=1685.50 Å^3, space group $P21/n$, Z=4, 9649 reflections measured, 3395 unique (R_{int}=0.0600), $R1$=0.0497, $wR2$=0.1239, *Good* F=1.017, largest diff. peak 0.224e Å^{-3}.
15. Crystal data for $C_{14}H_{12}N_4OS$ **5a**: M=284.34, monoclinic, a=9.897(5), b=4.708(4), c=28.44(4) Å, α=90.00, β=90.72, γ=90.00°, V=1325.12 Å^3, space group $P21/C$, Z=4, 2292 reflections measured, 1824 unique (R_{int}=0.0438), $R1$=0.1040, $wR2$=0.2359, *Good* F=1.125, largest diff. peak 0.73e Å^{-3}.