Reactions of 1-aryl-2,2-dihalogenoethanone oximes with tetrasulfur tetranitride (S_4N_4): a general method for the synthesis of 3-aryl-4-halogeno-1,2,5-thiadiazoles

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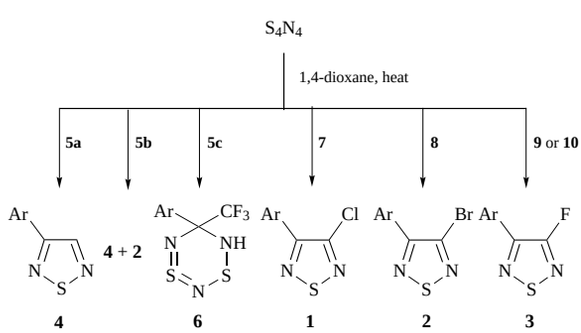
1-Aryl-2,2-dichloro-7, 1-aryl-2,2-dibromo-8, 1-aryl-2-bromo-2-fluoro-9 and 1-aryl-2-chloro-2-fluoro-ethanone oximes 10 have been prepared by allowing the corresponding ketones to react with hydroxylamine hydrochloride in EtOH at room temperature. Stereochemical assignments for the oximes were made on the basis of ^{1}H NMR spectroscopic evidence and an X-ray crystallographic analysis of 1-(3-chlorophenyl)-2,2-dichloroethanone oxime 7f. The 1-aryl-2,2-dihalogenoethanone oximes react with tetrasulfur tetranitride in refluxing 1,4-dioxane to give 3-aryl-4-chloro-1, 3-aryl-4-bromo-2, and 3-aryl-4-fluoro-1,2,5-thiadiazoles 3 in 69–98, 49–99, and 32–65% yields, respectively. A mechanism for the formation of the 1,2,5-thiadiazoles is proposed.

Introduction

3-Aryl-4-halogeno-1,2,5-thiadiazoles **1**–**3** have attracted much attention since the 3-chloro-, 3-fluoro, 3-aryl-4-chloro, and/or 3-aryl-4-fluoro-derivatives show herbicidal[1] or nematicidal effects.[2] The synthesis of 3-chloro- and 3-aryl-4-chloro-1,2,5-thiadiazoles has been extensively studied by Weinstock and co-workers[3] in a method involving the reaction of sulfur monochloride (S_2Cl_2) with α-aminoacetonitrile bisulfate, α-aminophenylacetonitrile hydrochloride, isonitrosophenylacetonitrile, or glyoxime in DMF at different reaction temperatures. This method has been widely utilized for the synthesis of 3-bromo- and 3-chloro-1,2,5-thiadiazoles. Alternatively, 3-aryl-4-chloro-**1** and 3-aryl-4-bromo-1,2,5-thiadiazoles **2** have been prepared by reactions of the corresponding 4-hydroxy compounds with phosphorous oxychloride[3] and phosphorus oxybromide,[4] respectively, and 3-aryl-4-fluoro-1,2,5-thidiazoles **3** by treating the corresponding chloro analogues with potassium fluoride at elevated temperature.[2]

Recently we reported a facile and much improved synthesis of 3-aryl-1,2,5-thiadiazoles **4**, by allowing 1-aryl-2-chloroethanone oximes **5a** to react with S_4N_4 in refluxing 1,4-dioxane;[5] no chlorine-containing 1,2,5-thiadiazoles **1** were detected. However, treatment of 1-aryl-2-bromoethanone oximes **5b** under the same conditions gave compounds **2** as the minor and compounds **4** as the major products (Scheme 1).



ArC(=NOH)CXYZ

5a X = Cl, Y = Z = H
5b X = Br, Y = Z = H
5c X = Y = Z = F
7 X = Y = Cl, Z = H
8 X = Y = Br, Z = H
9 X = Br, Y = F, Z = H
10 X = Cl, Y = F, Z = H

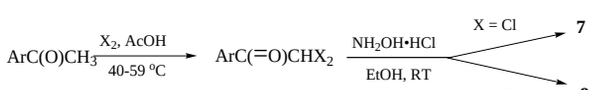
Scheme 1

In order to widen the scope of the reaction with α-halogeno ketoximes, the readily available 1-aryl-2,2,2-trifluoromethanone oximes **5c** were treated with S_4N_4 in refluxing 1,4-dioxane,[6] to give 5-aryl-5-trifluoromethyl-5*H*-1,3,2,4,6-dithiatriazines **6** as the major products. Because of this unexpected result together with the formation of **2** from the reactions of **5b** with S_4N_4, we have investigated on the reactions of the 1-aryl-2,2-dihalogenoethanone oximes **7**–**10** with S_4N_4 and describe herein over results.

Results and discussion

Synthesis of compounds 7–9

Although the synthesis and stereochemistry of *E*- and *Z*-**5a** and **5b** have been much studied,[7] the 1-aryl-2,2-dihalogenoethanone oximes **7**–**10** have received little attention, apart from 2,2-dichloro-1-phenylethanone oxime **7a** (Ar = Ph) a patent for which describes its importance as an anti-herbicide.[8] Since attempted synthesis of **7a** according to literature procedures failed, reactions under different conditions were studied,[9] and compounds **7** finally prepared *via* the 1-aryl-2,2-dichloroethanones **12**; the latter were prepared by chlorination of 1-arylethanones **11** according to a little modified literature procedures[10] in good to moderate yields (Scheme 2). Reaction



11 X = Cl, Br
12 X = Cl
13 X = Br

Scheme 2

times, yields, and melting points of compounds **7** are summarized in Table 1.

Of the compounds **12** prepared,[10] **12i** [Ar = 4-Cl_2CHC(O)C_6H_4], **12j** [Ar = 3-Cl_2CHC(O)C_6H_4], and **12k** [4-Cl_2CHC(O)biphenyl] are new. All of the compounds **7** except for **7a**[8] are new and their structures were assigned on the basis of spectroscopic data and elemental analyses.

The ^{1}H NMR spectra of compounds **7a**–**b**, **7d**, **7g**, **h** and **7j** exhibited two singlets at 6.48 and 7.40, 6.45 and 7.30, 6.41 and 7.60, 6.50 and 7.41, 6.48 and 7.37, 6.47 and 7.34 ppm, respectively, which were assigned to be methine proton signals of *E*- and *Z*-oximes in view of the reported chemical shifts of methylene protons of *Z*- (4.42 ppm) and *E*-2-bromo-1-phenylethanone oximes (4.30 ppm).[7] However, compounds **7c**,

Table 1 Reaction times, yields, and melting points of 1-aryl-2,2-dichloroethanone oximes **7**

Compd.	Ar	Time (*t*/h)	Yield (%)[a]	Mp (*T*/ °C)
7a	C_6H_5	24	86	Liquid[b]
7b	4-MeC_6H_4	24	81	Liquid[b]
7c	4-$O_2NC_6H_4$	34	73	112–114[c]
7d	3-$O_2NC_6H_4$	47	58	Liquid[b]
7e	4-BrC_6H_4	48	85	92–94[c]
7f	4-ClC_6H_4	49	82	98–100[d]
7g	4-FC_6H_4	27	84	Liquid[b]
7h	3-Cl,4-$MeOC_6H_3$	72	34	Liquid[d]
7i	4-$Cl_2CH(HON{=}C)C_6H_4$	72	82	170–172[e]
7j	3-$Cl_2CH(HON{=}C)C_6H_4$	72	53	Liquid[b]
7k	4′-$Cl_2CH(HON{=}C)$biphenyl-4-yl	72	86	133–135[e]

[a] Isolated yield. [b] *E*/*Z* mixture. [c,d,e] $CHCl_3$, CCl_4, and EtOH were used as solvents for recrystallization, respectively.

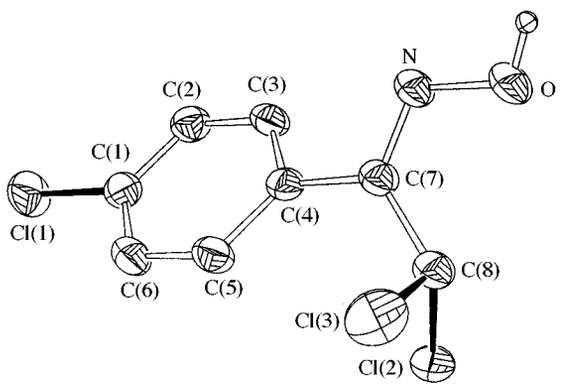


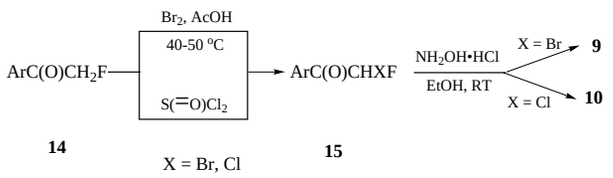
Fig. 1 ORTEP drawing of compound **7f**

7e, and **7f** exhibited only a singlet at 7.58, 7.50, and 7.42 ppm. Therefore, they were assigned as *Z*-oximes. This was confirmed by a X-ray single crystallographic analysis of compound **7f** for which Fig. 1 shows an ORTEP drawing and Tables 2 and 3, respectively, list selected bond distances and angles.

1-Aryl-2,2-dibromoethanone oximes **8** were prepared from 1-aryl-2,2-dibromoethanones **13** under the same conditions as for compounds **7** in good to moderate yields (Scheme 2). Compounds **13** prepared according to the literature procedures[11] are known except for **13g** (Ar = 4-FC_6H_4, X = Br), **13i** (Ar = 3-$MeOC_6H_4$, X = Br), **13k** [Ar = 4-$Br_2CHC(O)C_6H_4$, X = Br], **13l** [Ar = 3-$Br_2CHC(O)C_6H_4$, X = Br], and **13m** (Ar = 4-Br_2CH-C(O)biphenyl, X = Br). Reaction times, yields, and melting points for compounds **8** are summarized in Table 4.

For compounds **8a**, **8d**, **8g**, and **8l**, the presence of two singlets at 6.59 and 7.44, 6.42 and 7.59, 6.46 and 7.24, and 6.43 and 7.29 ppm, respectively suggested that, as with compounds **7**, each product was a mixture of *E*- and *Z*-oximes. Other compounds **8** exhibited a singlet in the range of 7.18–8.16 ppm, indicating the formation of a single isomer, *i.e.* *Z*-oximes.

Similarly, 1-aryl-2-bromo-**9** and 2-chloro-2-fluoro-ethanone oximes **10** were prepared *via* the corresponding 1-aryl-2-halogeno-2-fluoroethanones **15** which were, in turn, prepared by treatment of 1-aryl-2-fluoroethanones **14**[12] with bromine or thionyl chloride, respectively, according to literature procedures[13] (Scheme 3). Yields of **15** decreased with reaction



Scheme 3

Table 2 Selected bond lengths (Å) for compound **7f**[a]

Cl(1)–C(1)	1.736(3)	N–C(7)	1.282(4)
Cl(2)–C(8)	1.768(3)	C(4)–C(7)	1.481(4)
Cl(3)–C(8)	1.787(3)	C(7)–C(8)	1.502(4)
O–N	1.389(3)		

[a] Crystallographic numbering scheme, see Fig. 1.

Table 3 Selected bond angles (°) for compound **7f**[a]

C(7)–N–O	113.9(2)	N–C(7)–C(8)	121.1(2)
C(3)–C(4)–C(5)	118.7(3)	C(4)–C(7)–C(8)	123.1(2)
C(3)–C(4)–C(7)	119.8(2)	C(7)–C(8)–Cl(2)	112.1(2)
C(5)–C(4)–C(7)	121.6(3)	C(7)–C(8)–Cl(3)	110.1(2)
N–C(7)–C(4)	115.8(2)	Cl(2)–C(8)–Cl(3)	110.1(2)

[a] Crystallographic numbering scheme, see Fig. 1.

Table 4 Reaction times, yields, and melting points of 1-aryl-2,2-dibromoethanone oximes **8**

Compd.	Ar	Time (*t*/h)	Yield (%)[a]	Mp (*T*/°C)
8a	C_6H_5	48	61	Liquid[b]
8b	4-MeC_6H_4	72	58	105–107[c]
8c	4-$O_2NC_6H_4$	72	72	125–127[c]
8d	3-$O_2NC_6H_4$	48	75	Liquid[b]
8e	4-BrC_6H_4	48	80	100–101[c]
8f	4-ClC_6H_4	86	82	108–109[d]
8g	4-FC_6H_4	48	84	Liquid[b]
8h	4-$MeOC_6H_4$	36	74	97–99[d]
8i	3-$MeOC_6H_4$	63	66	80–82[d]
8j	$C_{10}H_8$	96	61	97–98[c]
8k	4-$Br_2CH(HON{=}C)C_6H_4$	72	76	176–178[d]
8l	3-$Br_2CH(HON{=}C)C_6H_4$	72	93	Liquid[b]
8m	4′-$Br_2CH(HON{=}C)$biphenyl-4-yl	72	80	173–175[d]

[a] Isolated yield. [b] *E*/*Z* mixture. [c,d] CCl_4 and EtOH were used as solvents for recrystallization, respectively.

temperatures >50 °C, whereas the reaction proceeded very slowly at <40 °C. Reaction times and yields of **9**, **10**, and **15** are summarized in Table 5.

All of compounds **15** prepared are known, whereas compounds **9** and **10** are new. ^{1}H NMR spectra of **9a** and **10** show two singlets at 6.71 and 7.54 ppm due to the methine protons for the *E*- and *Z*-forms. For compounds **7**–**10**, it has been found that where they exist as solids they appear to be solely *Z*-isomers, whereas products which are oils are mixtures of *E*- and *Z*-geometrical isomers showing a preference for the latter form. The formation of *Z*-isomers in preference to *E*-isomers may be due to the ease of formation of hydrogen bonding between the OH group and the halogen atoms of α,α-dihalogeno ketoximes.

Reactions of 1-aryl-2,2-dihalogenoethanone oximes 7–10 with S_4N_4

The reactions of **7** and **8** with S_4N_4 in refluxing 1,4-dioxane gave **1** and **2**, respectively. Compounds **9** and **10** reacted with S_4N_4 to give **3** under the same reaction conditions. The reactions of **7** and **8** were quenched when no spot corresponding to **7** ($R_F \cong 0.09$, C_6H_6) and **8** ($R_F \cong 0.20$, C_6H_6) was observed on TLC, whereas those of **9** ($R_F \cong 0.08$, C_6H_6) and **10** ($R_F \cong 0.07$, C_6H_6) were quenched when the spot corresponding to S_4N_4 ($R_F = 0.51$, C_6H_6–hexane, 1 : 1) had disappeared on TLC by the time the colour of the solution became reddish brown. Reaction times, yields and melting points of compounds **1**–**3** are summarized in Tables 6, 8, and 10, respectively, and their analytical IR, and ^{1}H NMR data are summarized in Tables 7, 9, and 11, respectively.

Of the compounds listed in Table 7, compounds **2a** and **2f** were reported to be prepared by treating 3-hydroxy-4-phenyl- and 3-(4-chlorophenyl)-4-hydroxy-1,2,5-thiadiazoles with phosphorus oxybromide in 61 and 85% yields,[4] respectively.

Table 5 Reaction times, yields, and melting points of 1-aryl-2-bromo-**9** and 2-chloro-2-fluoro-ethanone oximes **10**, and 1-aryl-2-halogeno-2-fluoroethanones **15**

Compound	Ar	X	Time (*t*/h)	Yield (%)[a]	Compound	Time (*t*/h)	Yield (%)[a]	Mp (*T*/°C)
15a	C_6H_5	Br	7	78	**9a**	48	84	Liquid[b]
15b	4-MeC_6H_4	Br	5	73	**9b**	48	91	94–96[c]
15c	4-BrC_6H_4	Br	9	71	**9c**	3	89	101–103[c]
15d	C_6H_5	Cl	15	49	**10**	24	71	Liquid[b]

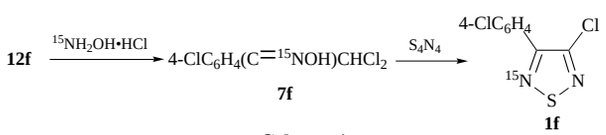
[a] Isolated yield. [b] *E*/*Z* mixture. [c] $CHCl_3$ was used as a solvent for recrystallization.

Table 6 Reaction times, yields, and melting points of 3-aryl-4-chloro-1,2,5-thiadiazoles **1**

Compound	Ar	Time (*t*/h)	Yield (%)[c]	Mp (*T*/°C)
1a	C_6H_5	4	98	31–33[c] (lit.,[2] 31.5–32.5)
1b	4-MeC_6H_4	3	74	Liquid (lit.,[2] 27–28)
1c	4-$O_2NC_6H_4$	3	85	101–103[c]
1d	3-$O_2NC_6H_4$	4	94	97–98[c]
1e	4-BrC_6H_4	6	97	69–71[c] (lit.,[2] 74–75.5)
1f	4-ClC_6H_4	6	98	38–39[c] (lit.,[2] 37.5–38.5)
1g	4-FC_6H_4	3	98	35–37[c] (lit.,[2] 35–36.5)
1h	3-Cl-, 4-$MeOC_6H_3$	12	84	83–85[c]
1i	4-Y-C_6H_4[b]	3	78	129–131[d]
1j	3-Y-C_6H_4[b]	3	69	124–125[d]
1k	4-Y-biphenyl[b]	5	91	159–161[d]

[a] Isolated yield. [b] Y = 3-chloro-1,2,5-thiadiazol-4-yl. [c,d] Hexane and EtOH were used as solvents for recrystallization, respectively.

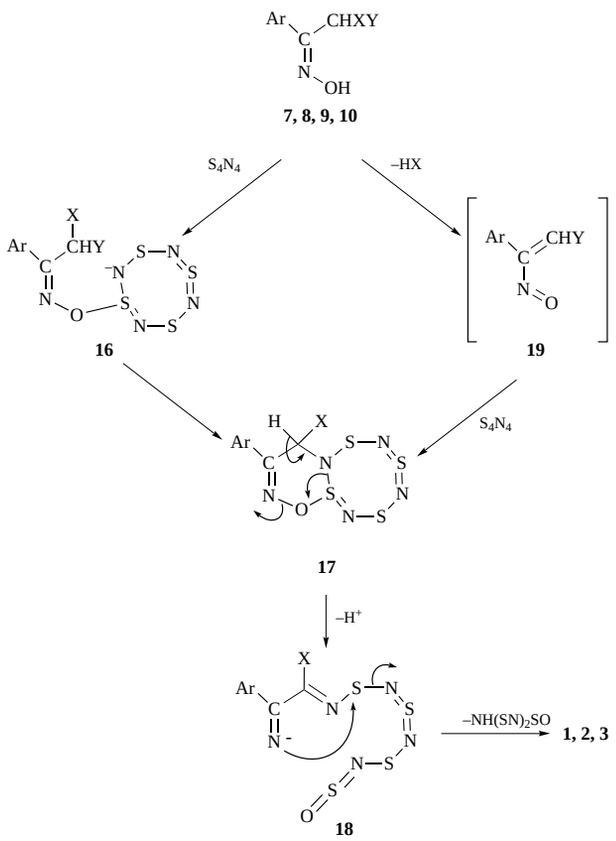
The mechanism for the formation of compounds **1**–**3** is uncertain as shown in a variety of the reactions with S_4N_4 previously studied.[14] In order to determine the source of nitrogen atoms of compounds **1**–**3**, ^{15}N-labelled hydroxylamine hydrochloride ($^{15}NH_2OH$ HCl, 99 atom%) was used to prepare the ^{15}N-labelled oxime **7f**, from which **1f** was obtained (Scheme 4).



Scheme 4

Mass spectral data for **1f** obtained from the ^{15}N-labelled oxime **7f** shows the fragments having mass number (*m*/*z*) 231 (97.6%, M^+) and 233 (76.5%, $M^+ + 2$), whereas that of **1f** obtained from ^{15}N-unlabelled oxime **7f** shows the fragments of mass number (*m*/*z*) 230 (97.6%, M^+) and 232 (82.1, $M^+ + 2$). The results indicate clearly that ^{15}N atom of **7f** is involved as one of the nitrogen atoms of 1,2,5-thiadiazole ring. Since the mass spectra of **1f** formed *via* ^{15}N-labelled and ^{15}N-unlabelled oximes **7f** show the fragments having (*m*/*z*) 138 and 137, corresponding to the molecular weight of ^{15}N-labelled and ^{15}N-unlabelled 4-chlorobenzonitriles, respectively, the N-5 atom of **1f** is thought to originate from the oxime nitrogen atom.

On the basis of these results, we propose the following pathway in which nucleophilic attack of the hydroxy group of dihalogeno ketoximes **7**–**10** on the tetravalent sulfur atom of S_4N_4 gives the intermediate **16**; subsequently, nucleophilic displacement of the halogen atom on this by the amide ion gives a cyclic intermediate **17**. Deprotonation of this, followed by cleavage of the N–S and N–O bonds gives an imide ion **18**, which then cyclizes to give **1** and HS_3N_3O. Alternatively, formation of the intermediate **17** might be explained on the basis of [4 + 2] cycloaddition between S_4N_4 and the nitroso olefin **19**[15] which is believed to be readily formed in the presence of base existing in the reaction mixtures (Scheme 5).



Scheme 5

The incorporation of an oxime nitrogen into the 1,2,5-thiadiazoles is in contrast with the proposed mechanism for the formation of 3,4-diphenyl-1,2,5-thiadiazole by reaction of benzil monooxime with S_4N_4, in which the =NOH group was completely eliminated and the two nitrogen atoms of 1,2,5-thiadiazole originate from S_4N_4.[16]

In conclusion, the geometry of 1-aryl-2,2-dihalogenoethanone oximes has been assigned on the basis of ^1H NMR spectroscopic data and a X-ray single crystallographic analysis in which solid oximes appear to be *Z*-isomers. However, oily liquid oximes exist as a mixture of *E*- and *Z*-isomers, showing preference for the latter. We have demonstrated the synthetic utility of S_4N_4 by isolation of excellent yields of 1,2,5-thiadiazoles having a chlorine **1** or a bromine atom **2** at C-3 from the reactions with 1-aryl-2,2-dichloro- **7** and 1-aryl-2,2-dibromo-ethanone oximes **8**, respectively. Similarly compounds **3** were obtained from the reactions with 1-aryl-2-bromo-**9** and 1-aryl-2-chloro-2-fluoro-ethanone oximes **10** in fair yields. It has been shown that the 2-nitrogen atom of **1** has its origin in the oxime nitrogen atom of **7**.

Experimental

All melting points were determined on a Fisher–Johns melting point apparatus and are uncorrected. IR spectra were obtained on a Shimadzu IR-470 IR spectrophotometer for samples of

Table 7 Analytical, IR, and ^{1}H NMR data for 3-aryl-4-chloro-1,2,5-thiadiazoles **1**

Compound (Formula)	Found (%) (Required) C	H	N	S	ν_{max}[a]/cm^{-1}	δ_H ($CDCl_3$; 80 MHz)	*m/z* (EI)
1c ($C_8H_4ClN_3O_2S$)	39.7 (39.8)	1.7 (1.7)	17.4 (17.4)	13.3 (13.3)	1597, 1517, 1350, 1161, 979, 739, 704	8.44 (4 H, dd, *J* 15.8, 9.2, ArH)	241 (100%, M^+), 243 (37.3, $M^+ + 2$), 211 (60.6), 213 (23.1), 195 (27.4), 197 (10.4), 180 (7.0), 160 (29.9)
1d ($C_8H_4ClN_3O_2S$)	39.75 (39.8)	1.7 (1.7)	17.4 (17.4)	13.3 (13.3)	1523, 1338, 1258, 1174, 998, 899, 877, 835, 810, 765, 717, 666	7.64 (1 H, t, *J* 7.9, ArH), 8.34 (2 H, d, *J* 7.9, ArH), 8.83 (1 H, s, ArH)	241 (100%, M^+), 243 (37.9, $M^+ + 2$), 211 (22.6), 213 (8.3), 195 (51.9), 197 (19.3), 180 (9.3), 160 (26.2)
1h ($C_9H_6Cl_2N_2OS$)	41.4 (41.4)	2.3 (2.3)	10.7 (10.7)	12.25 (12.2)	1590, 1504, 1343, 1280, 1159, 1062, 1018, 992, 813, 733, 698	3.83 (3 H, s, MeO), 7.00 (1 H, d, *J* 8.7, ArH), 7.89 (1 H, d, *J* 8.7, ArH), 8.02 (1 H, s, ArH)	260 (100%, M^+), 262 (69.2, $M^+ + 2$), 264 (14.2, $M^+ + 4$), 245 (40.9), 247 (26.5), 199 (20.2), 167 (17.4)
1i ($C_{10}H_4Cl_2N_4S_2$)	38.1 (38.1)	1.3 (1.3)	17.7 (17.8)	20.4 (20.3)	1351, 1171, 880, 853, 839, 820, 561	8.10 (4 H, s, ArH)	314 (100, M^+), 316 (73.9, $M^+ + 2$), 318 (17.4, $M^+ + 4$), 253 (63.0), 255 (26.6), 221 (19.8), 160 (28.5)
1j ($C_{10}H_4Cl_2N_4S_2$)	38.1 (38.1)	1.3 (1.3)	17.75 (17.8)	20.4 (20.3)	3067, 1339, 1304, 1251, 1170, 969, 826, 799	7.59 (1 H, t, *J* 14, ArH), 8.18 (2 H, d, *J* 14, ArH), 8.66 (1 H, s, ArH)	314 (100%, M^+), 316 (73.7, $M^+ + 2$), 318 (17.0, $M^+ + 4$), 253 (54.9), 255 (22.3), 221 (15.8), 160 (30.2)
1k ($C_{16}H_8Cl_2N_4S_2$)	49.0 (49.1)	2.05 (2.1)	14.3 (14.3)	16.4 (16.4)	3079, 3046, 1607, 1458, 1350, 932, 799, 780	7.74 (4 H, d, *J* 8.2, ArH), 8.06 (4 H, d, *J* 8.2, ArH)	390 (100%, M^+), 392 (76.3, $M^+ + 2$), 394 (20.5, $M^+ + 4$), 297 (65.5), 263 (30.9), 236 (51.9), 204 (72.6)

[a] IR spectra for **1c**–**h** were taken neat and KBr was used for those of **1i**–**k**

Table 8 Reaction times, yields, and melting points of 3-aryl-4-bromo-1,2,5-thiadiazoles **2**

Compd.	Ar	Time (*t*/h)	Yield (%)[a]	Mp (*T*/°C)
2a	C_6H_5	3	95	57–59[c] (lit.,[4] 59–60)
2b	4-MeC_6H_4	3	92	27–29[c]
2c	4-$O_2NC_6H_4$	3	99	101–102[c]
2d	3-$O_2NC_6H_4$	3	98	102–103[c]
2e	4-BrC_6H_4	4	97	82–84[c]
2f	4-ClC_6H_4	3	96	66–67[c] (lit.,[4] 60–61)
2g	4-FC_6H_4	3	98	58–60[c]
2h	4-$MeOC_6H_4$	3	94	75–77[c]
2i	3-$MeOC_6H_4$	5	95	Liquid
2j	2-Naphthyl	4	86	70–71[c]
2k	4-Y-C_6H_4[b]	12	93	135–137[d]
2m	3-Y-C_6H_4[b]	3	49	128–129[d]
2n	4-Y-biphenyl-4-yl[b]	5	86	176–178[d]

[a] Isolated yield. [b] Y = 3-bromo-1,2,5-thiadiazol-4-yl. [c,d] Hexane and EtOH were used as solvents for recrystallization, respectively.

KBr pellets or thin films. ^{1}H NMR spectra were determined on a Brüker 80 MHz spectrometer using tetramethylsilane as internal standard; *J* values are given in Hz. Mass spectra were obtained by electron impact at 70 eV at the Inter-University Center for Natural Sciences Research Facilities. Elemental analyses were determined by the Korea Basic Science Center. Column chromatography was performed on silica gel (Merck, 70-230, ASTM).

Tetrasulfur tetranitride was prepared by the reaction of sulfur monochloride with ammonia gas at room temperature.[17] 1-Aryl-2,2-dichloroethanones **12** were prepared according to literature procedures[10] except for the amount of chlorine gas employed (7–10 equiv.) and the reaction temperature (40–59 °C): 2,2-dichloro-1-phenylethanone **12a**,[18] liquid (Found: C, 50.75; H, 3.2; Cl, 37.0. $C_8H_6Cl_2O$ requires C, 50.9; H, 3.2; Cl, 37.5%); ν_{max}(KBr)/cm^{-1} 1705 (C=O): δ_H($CDCl_3$; 80 MHz) 6.84 (1 H, s, $CHCl_2$), 7.53 (3 H, m, Ph) and 8.08 (2 H, m, Ph); 2,2-dichloro-1-(4-methylphenyl)ethanone **12b**, mp 55–56 °C (from CCl_4) (lit.,[10] 54.5–55.3 °C); 2,2-dichloro-1-(4-nitrophenyl)-ethanone **12c**, mp 27–28 °C (from CCl_4) (lit.,[10] 27–28 °C); 2,2-*dichloro*-1-(3-*nitrophenyl*)*ethanone* **12d**, pale yellow oil (Found: C, 41.0; H, 2.15; Cl, 30.2; N, 5.9. $C_8H_5Cl_2NO_3$ requires C, 41.1; H, 2.15; Cl, 30.3; N, 6.0%); ν_{max}(KBr)/cm^{-1} 1699 (C=O); δ_H($CDCl_3$; 80 MHz) 6.63 (1 H, s, $CHCl_2$), 7.76 (1 H, t, *J* 8, ArH), 8.48 (2 H, d, *J* 8, ArH) and 8.89 (1 H, s, ArH); 1-(4-bromophenyl)-2,2-dichloroethanone **12e**, mp 61–62 °C (from CCl_4) (lit.,[10] 61.6–62 °C); 1-(4-*chlorophenyl*)-2,2-*dichloro-ethanone* **12f**, mp 47–48 °C (from CCl_4) (Found: C, 42.95; H, 2.3; Cl, 47.8. $C_8H_5Cl_3O$ requires C, 43.0; H, 2.25; Cl, 47.6); ν_{max}(KBr)/cm^{-1} 1701 (C=O); δ_H($CDCl_3$; 80 MHz) 6.58 (1 H, s, $CHCl_2$) and 7.67 (4 H, dd, *J* 31, 8, ArH); 2,2-*dichloro*-1-(4-*fluorophenyl*)*ethanone* **12g**, mp 38–40 °C (from CCl_4) (Found: C, 46.4; H, 2.4; Cl, 34.3. $C_8H_5Cl_2FO$ requires C, 46.4; H, 2.4; Cl, 34.25); ν_{max}(KBr)/cm^{-1} 1702 (C=O); δ_H($CDCl_3$; 80 MHz) 6.62 (1 H, s, $CHCl_2$), 7.17 (1 H, t, *J* 9, ArH) and 8.08 (2 H, m, ArH); 1-(3-chloro-4-methoxyphenyl)-2,2-dichloroethanone **12h**, mp 71–73 °C (from CCl_4) (lit.,[19] 72–73 °C); 1,4-*bis*(*dichloro-acetyl*)*benzene* **12i**, mp 154–156 °C (from $CHCl_3$) (Found: C, 40.0; H, 2.0; O, 10.7. $C_{10}H_6Cl_4O_2$ requires C, 40.0; H, 2.0; O, 10.7%); ν_{max}(KBr)/cm^{-1} 1690 (C=O); δ_H($CDCl_3$–[$^2H_6$]-DMSO); 80 MHz) 7.81 (2 H, s, $CHCl_2$), 8.23 (4 H, s, ArH); 1,3-*bis*(*dichloroacetyl*)*benzene* **12j**, oil (Found: C, 40.0; H, 2.0; O, 10.8. $C_{10}H_6Cl_4O_2$ requires C, 40.0; H, 2.0; O, 10.7%); ν_{max}(KBr)/cm^{-1} 1700 (C=O); δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 7.60 (2 H, s, 2CH), 7.70 (1 H, t, *J* 8, ArH), 8.33 (2 H, d, *J* 8, ArH) and 8.75 (1 H, s, ArH); 4,4′-*bis*(*dichloroacetyl*)*biphenyl* **12k** mp 162–164 °C (from $CHCl_3$) (Found: C, 51.15; H, 2.7; O, 8.6. $C_{16}H_{10}Cl_4O_2$ requires C, 51.1; H, 2.7; O, 8.5%); ν_{max}(KBr)/cm^{-1} 1693 (C=O); δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 7.80 (2 H, s, $CHCl_2$), 7.49 and 7.83 (8 H, 2 d, *J* 8.3, ArH). 1-Aryl-2,2-dibromoethanones **13** were prepared by the literature methods[11]: 2,2-dibromo-1-phenylethanone **13a** mp 36–37 °C (from CCl_4) (lit.,[11] 36 °C); 2,2-dibromo-1-(4-methylphenyl)-ethanone **13b**, mp 99–100 °C (from CCl_4) (lit.,[11] 98–99 °C); 2,2-dibromo-1-(4-nitrophenyl)ethanone **13c**, mp 54–55 °C (from CCl_4) (lit.,[11] 54–55 °C); 2,2-dibromo-1-(3-nitrophenyl)ethanone **13d**, mp 54–55 °C (from CCl_4) (lit.,[11] 55–56 °C; 1-(4-bromophenyl)-2,2-dibromoethanone **13e**, mp 91–92 °C (from CCl_4) (lit.,[11] 93–94 °C); 1-(4-chlorophenyl)-2,2-dibromoethanone **13f**, mp 92–93 °C (from CCl_4) (lit.,[11] 93–94 °C); 2,2-*dibromo*-1-(4-*fluorophenyl*)*ethanone* **13g**, oil (Found: C, 32.5; H, 1.7; O, 5.4.

Table 9 Analytical, IR, and ^{1}H NMR data for 3-aryl-4-bromo-1,2,5-thiadiazoles **2**

Compound (Formula)	Found (%) (Required) C	H	N	S	ν_{max}[a]/cm^{-1}	δ_H($CDCl_3$; 80 MHz)	*m/z* (EI)
2a ($C_8H_5BrN_2S$)	39.8 (39.85)	2.1 (2.1)	11.6 (11.6)	13.4 (13.3)	3060, 1442, 1353, 1147, 966, 835	7.48 (3 H, m, PhH), 7.92 (2 H, m, PhH)	240 (46.6%, M^+), 242 (50.3, $M^+ + 2$), 135 (100)
2b ($C_9H_7BrN_2S$)	42.4 (42.4)	2.8 (2.8)	11.0 (11.0)	12.6 (12.6)	3025, 1615, 1521, 1451, 1410, 1349, 1253, 1189, 1160, 1141, 1040, 1028, 982, 820	2.42 (3 H, s, Me), 7.56 (4 H, dd, *J* 42, 8, ArH)	254 (57.2%, M^+), 256 (44.0, $M^+ + 2$), 149 (100)
2c ($C_8H_4BrN_3O_2S$)	33.6 (33.6)	1.4 (1.4)	14.7 (14.7)	11.2 (11.2)	1597, 1517 (s), 1349 (s), 1331, 1313, 1297, 1163, 981, 860, 853, 835, 716	8.23 (4 H, dd, *J* 14, 8, ArH)	285 (29.2%, M^+), 287 (27.5, $M^+ + 2$), 160 (100)
2d ($C_8H_4BrN_3O_2S$)	33.6 (33.6)	1.4 (1.4)	14.7 (14.7)	11.2 (11.2)	3091, 1613, 1532, 1491, 1344, 1262, 1162, 1094, 1078, 1011, 826, 803, 723	7.67 (1 H, t, *J* 7, ArH), 8.32 (2 H, d, *J* 7, ArH), 8.83 (1 H, s, ArH)	285 (31.6%, M^+), 287 (29.5, $M^+ + 2$), 160 (100)
2e ($C_8H_4Br_2N_2S$)	30.0 (30.0)	1.3 (1.3)	8.7 (8.75)	10.05 (10.0)	1590, 1498, 1450, 1398, 1350, 1142, 958, 813	7.69 (4 H, dd, *J* 17, 8, ArH)	318 (44.0%, M^+), 320 (89.3, $M^+ + 2$), 322 (39.9, $M^+ + 4$), 213 (100), 215 (95.1)
2f ($C_8H_4BrClN_2S$)	34.8 (34.9)	1.45 (1.5)	10.1 (10.2)	11.7 (11.6)	1597, 1502, 1451, 1348, 1145, 1092, 1019, 967, 827	8.25 (4 H, dd, *J* 18, 7, ArH)	274 (18.2%, M^+), 276 (22.8, $M^+ + 2$), 169 (100)
2g ($C_8H_4BrFN_2S$)	37.0 (37.1)	1.55 (1.6)	10.8 (10.8)	12.4 (12.4)	3086, 1602, 1517, 1452, 1348, 1237, 1161, 963, 835	7.14 (2 H, m, ArH), 7.87 (2 H, m, ArH)	258 (73.0%, M^+), 260 (73.8, $M^+ + 2$), 153 (100), 137 (23.1), 139 (23.8), 121 (30.9)
2h ($C_9H_7BrN_2OS$)	39.8 (39.9)	2.6 (2.6)	10.3 (10.3)	11.9 (11.8)	1453, 1349, 1302, 1258, 1181, 1143, 1030, 963, 822	3.86 (3 H, s, OMe), 7.36 (4 H, dd, *J* 17, 8, ArH)	270 (99.2%, M^+), 272 (100, $M^+ + 2$), 165 (71.7), 150 (22.8), 133 (45.6)
2i ($C_9H_7BrN_2OS$)	39.85 (39.9)	2.6 (2.6)	10.3 (10.3)	11.9 (11.8)	3009, 1603, 1585, 1460, 1361, 1250, 1150, 1052, 1003, 863, 791	3.87 (3 H, s, MeO), 7.03 (1 H, m, ArH), 7.47 (3 H, m, ArH)	270 (60.9%, M^+), 272 (63.6, $M^+ + 2$), 165 (100)
2j ($C_{12}H_7BrN_2S$)	49.4 (49.5)	2.4 (2.4)	9.5 (9.6)	11.1 (11.0)	3056, 1593, 1475, 1331, 1140, 1106, 982, 931, 858, 813, 749	7.50 (2 H, m, ArH), 7.85 (4 H, m, ArH), 8.47 (1 H, s, ArH)	290 (16.2%, M^+), 292 (15.3, $M^+ + 2$), 153 (100)
2k ($C_{10}H_4Br_2N_4S_2$)	29.75 (29.7)	1.0 (1.0)	13.8 (13.9)	15.9 (15.9)	3042, 1590, 1465, 1338, 967, 840, 742	8.06 (4 H, s, ArH)	402 (51.2%, M^+), 404 (100, $M^+ + 2$), 406 (56.7, $M^+ + 4$), 297 (47.8), 299 (51.0), 265 (11.6), 267 (11.7), 160 (33.9)
2l ($C_{10}H_4Br_2N_4S_2$)	29.8 (29.7)	1.0 (1.0)	13.8 (13.9)	15.9 (15.9)	3072, 1342 (s), 1315, 1251, 1168, 966, 821, 794, 689, 534	7.63 (1 H, t, *J* 15, ArH), 8.12 (2 H, d, *J* 15, ArH), 8.46 (1 H, s, ArH)	402 (48.2%, M^+), 404 (100, $M^+ + 2$), 406 (52.2, $M^+ + 4$), 297 (48.7), 299 (50.0), 265 (21.8), 267 (25.8), 160 (56.1)
2m ($C_{16}H_8Br_2N_4S_2$)	40.1 (40.0)	1.7 (1.7)	11.6 (11.7)	13.4 (13.35)	3088, 3045, 1603, 1466, 1349, 928, 819, 789	7.89 (8 H, dd, *J* 13.6, 8.3, ArH)	480 (49.6%, M^+), 482 (100, $M^+ + 2$), 484 (54.0, $M^+ + 4$), 376 (50.2), 378 (49.3), 344 (24.1), 346 (26.2), 204 (46.7)

[a] IR spectra of **2a**–**j** were taken neat and KBr was used for those of **2k**–**m**.

Table 10 Reaction times, yields, and melting points of 3-aryl-4-fluoro-1,2,5-thiadiazoles **3**

Compound	Ar	Time (*t*/h)	Yield (%)[a]	Mp (*T*/°C)[b]
3a	C_6H_5	5	32	45–46 (lit.,[2] 45)
3b	4-MeC_6H_4	3	47	56–57
3c	4-BrC_6H_4	3	61	76–77
3d	C_6H_5	3	65	45–46 (lit.,[2] 45)

[a] Isolated yields. [b] CCl_4 was used as a solvent for recrystallization.

$C_8H_5Br_2FO$ requires C, 32.5; H, 1.7; O, 5.4%); ν_{max}(KBr)/cm^{-1} 1693 (C=O); δ_H($CDCl_3$; 80 MHz) 6.61 (1 H, s, $CHBr_2$), 7.14 (2 H, t, *J* 8.3, ArH) and 8.16 (2 H, dd, *J* 8.3, 3.5, ArH); 2,2-dibromo-1-(4-methoxyphenyl)ethanone **13h**, mp 92–93 °C (from CCl_4) (lit.,[20] 92–93 °C); 2,2-*dibromo*-1-(3-*methoxyphenyl*)*ethanone* **13i**, oil (Found: C, 35.05; H, 2.6; O, 10.4. $C_9H_8Br_2O_2$ requires C, 35.1; H, 2.6; O, 10.4%); ν_{max}(KBr)/cm^{-1} 1693 (C=O); δ_H($CDCl_3$; 80 MHz) 3.26 (3 H, s, MeO), 6.59 (1 H, s, $CHBr_2$) and 6.61–7.11 (4 H, m, ArH); 2,2-dibromo-1-(2-naphthyl)ethanone **13j**, mp 100–102 °C (from CCl_4) (lit.,[11] 101–102 °C); 1,4-*bis*(*dibromoacetyl*)*benzene* **13k**, mp 166–168 °C (from $CHCl_3$) (Found: C, 25.15; H, 1.3; O, 6.7. $C_{10}H_5Br_4O_2$ requires C, 25.1; H, 1.3; O, 6.7%); ν_{max}(KBr)/cm^{-1} 1690 (C=O); δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 7.81 (2 H, s, $CHBr_2$) and 8.23 (4 H, s, ArH); 1,3-*bis*(*dibromoacetyl*)*benzene* **13l**, mp 54–55 °C (from $CHCl_3$) (Found: C, 25.1; H, 1.3; O, 6.8. $C_{10}H_6Br_4O_2$ requires C, 25.1; H, 1.3; O, 6.7%); ν_{max}(KBr)/cm^{-1} 1693 (C=O); δ_H($CDCl_3$)–[$^2H_6$]-DMSO; 80 MHz) 7.59 (2 H, s, $CHBr_2$), 7.69 (1 H, t, *J* 8, ArH), 8.32 (2 H, d, *J* 8, ArH) and 8.75 (1 H, s, ArH); 4,4′-*bis*-(*dibromoacetyl*)*biphenyl* **13m**, mp 216–217 °C (from $CHCl_3$) (Found: C, 34.6; H, 1.8; O, 5.8. $C_{16}H_{10}Br_4O_2$ requires C, 34.7; H, 1.8; O, 5.8%); ν_{max}(KBr)/cm^{-1} 1690 (C=O); δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 7.79 (2 H, s, $CHBr_2$) and 7.50 and 7.80 (8 H, 2 d, *J* 8.2, ArH).

General procedure for the preparation of 1-aryl-2,2-dichloroethanone oximes 7

To a solution of **12** (6–12 mmol) in EtOH (30 ml) was added hydroxylamine hydrochloride (18–36 mmol). The mixture was stirred for an appropriate time at room temperature. The hydrochloride salt disappeared slowly as the reaction proceeded and a clean solution resulted. After solvent removal, water (30 ml) was added to the reaction mixture to give white solids **7**, which were filtered off and recrystallized from $CHCl_3$. When, upon addition of water, yellowish white liquids formed at the bottom of the flask, the mixtures were extracted with EtOAc (100 ml × 2) an the extracts dried ($MgSO_4$). Evaporation of the extracts gave residues which were chromatographed (silica gel column: 2 × 10 cm) with benzene as eluent to give compounds **7** contaminated with **12**. The crude oximes **7c** and **7e** were recrystallized from $CHCl_3$ and that of **7f** from CCl_4. Yields, reaction times and melting points of compounds **7** are summarized in Table 1.

Table 11 Analytical, IR, and ^{1}H NMR data for 3-aryl-4-fluoro-1,2,5-thiadiazoles **3**

Compd. (Formula)	Found (%) (Required) C	H	N	S	ν_{max}[a]/cm^{-1}	δ_H($CDCl_3$; 80 MHz)	*m/z* (EI)
3b ($C_9H_7FN_2S$)	55.6 (55.7)	3.6 (3.6)	14.4 (14.4)	16.6 (16.5)	3072, 1613, 1510, 1435, 1302, 1284, 1190, 1037, 823, 736	2.35 (3 H, s, Me), 7.54 (4 H, dd, *J* 49, 8, ArH)	194 (100%, M^+), 149 (1.06), 116 (2.2)
3c ($C_8H_4BrFN_2S$)	37.05 (37.1)	1.55 (1.6)	10.8 (10.8)	12.4 (12.4)	3071, 1588, 1495, 1445, 1309, 1124, 958, 810	7.66 (4 H, dd, *J* 22, 8, ArH)	258 (100%, M^+), 260 (94.7, $M^+ + 2$), 215 (2.43), 197 (12.1), 182 (4.3)

[a] IR spectra were taken neat.

2,2-Dichloro-1-phenylethanone oxime 7a. *E*/*Z* mixture (46 : 54) (Found: C, 47.0; H, 3.5; N, 6.9. $C_8H_7Cl_2NO$ requires C, 47.1; H, 3.5; N, 6.9%); ν_{max}(neat)/cm^{-1} 3296 (OH), 3056 and 1599; δ_H($CDCl_3$; 80 MHz) 6.48 and 7.40 (1 H, 2 s, $CHCl_2$), 7.36 (3 H, m, ArH), 7.71 (2 H, m, ArH) and 9.61 (1 H, s, br, OH); *m/z* (EI) 203 (100%, M^+), 205 (66.2, $M^+ + 2$) and 207 (9.8, $M^+ + 4$).

2,2-Dichloro-1-(4-methylphenyl)ethanone oxime 7b. *E*/*Z* mixture (41 : 59) (Found: C, 49.6; H, 4.2; N, 6.4. $C_9H_9Cl_2NO$ requires C, 49.6; H, 4.2; N, 6.4%); ν_{max}(neat)/cm^{-1} 3296 (OH), 3040 and 1603; δ_H($CDCl_3$; 80 MHz) 2.33 (3 H, s, Me), 6.45 and 7.30 (1 H, 2 s, $CHCl_2$), 7.38 (4 H, dd, *J* 16, 8, ArH) and 8.82 (1 H, s, OH); *m/z* (EI) 217 (100%, M^+), 219 (67.3, $M^+ + 2$) and 221 (11.4, $M^+ + 4$).

2,2-Dichloro-1-(4-nitrophenyl)ethanone oxime 7c. *Z*-form (Found: C, 38.5; H, 2.45; N, 11.2, $C_8H_6Cl_2N_2O_3$ requires C, 38.6; H, 2.4; N, 11.25%); ν_{max}(neat)/cm^{-1} 3216 (OH), 3040, 1600, 1520s and 1346s; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 7.58 (1 H, s, $CHCl_2$), 8.12 (4 H, dd, *J* 20, 7, ArH) and 13.07 (1 H, s, OH); *m/z* (EI) 248 (100%, M^+), 250 (65.9, $M^+ + 2$) and 252 (10.5, $M^+ + 4$).

2,2-Dichloro-1-(3-nitrophenyl)ethanone oxime 7d. *E*/*Z* mixture (36 : 64) (Found: C, 38.65; H, 2.5; N, 11.2. $C_8H_6Cl_2N_2O_3$ requires C, 38.6; H, 2.4; N, 11.25%); ν_{max}(neat)/cm^{-1} 3392 (OH), 3040, 1610, 1520s and 1345s; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 6.41 and 7.60 (1 H, 2 s, $CHCl_2$), 7.97 (4 H, m, ArH) and 9.50 and 10.12 (1 H, 2 s, OH); *m/z* (EI) 248 (100%, M^+), 250 (63.8, $M^+ + 2$) and 252 (8.9, $M^+ + 4$).

1-(4-Bromophenyl)-2,2-dichloroethanone oxime 7e. *Z*-form (Found: C, 33.9; H, 2.1; N, 4.9. $C_8H_6BrCl_2NO$ requires C, 34.0; H, 2.1; N, 4.95%); ν_{max}(neat)/cm^{-1} 3312 (OH), 3040 and 1587; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 7.50 (1 H, s, $CHCl_2$), 7.52 (4 H, dd, *J* 20, 8, ArH), 12.42 (1 H, s, OH); *m/z* (EI) 281 (100%, M^+), 283 (163.2, $M^+ + 2$), 285 (74.8, $M^+ + 4$), 287 (9.7, $M^+ + 6$).

1-(4-Chlorophenyl)-2,2-dichloroethanone oxime 7f. *Z*-form (Found: C, 40.5; H, 2.5; N, 5.9. $C_8H_6Cl_3NO$ requires C, 40.3; H, 2.5; N, 5.9%); ν_{max}(neat)/cm^{-1} 3295 (OH), 3040 and 1588; δ_H($CDCl_3$; 80 MHz). 7.42 (1 H, s, $CHCl_2$), 7.45 (4 H, dd, *J* 23, 8, ArH) and 9.23 (1 H, s, br, OH); *m/z* (EI) 237 (100%, M^+), 239 (97.5, $M^+ + 2$) and 241 (30.8, $M^+ + 4$).

2,2-Dichloro-1-(4-fluorophenyl)ethanone oxime 7g. *E*/*Z* mixture (16 : 84) (Found: C, 43.2; H, 2.7; N, 6.3. $C_8H_6Cl_2FNO$ requires C, 43.3; H, 2.7; N, 6.3%); ν_{max}(neat)/cm^{-1} 3264 (OH), 3040 and 1597; δ_H($CDCl_3$; 80 MHz) 6.50 and 7.41 (1 H, 2 s, $CHCl_2$), 6.99 (2 H, m, ArH), 7.76 (2 H, m, ArH), 9.83 and 10.23 (1 H, 2 s, br, OH); *m/z* (EI) 221 (100%, M^+), 223 (65.5, $M^+ + 2$) and 225 (11.1, $M^+ + 4$).

1-(3-Chloro-4-methoxyphenyl)-2,2-dichloroethanone oxime 7h. *E*/*Z* mixture (31 : 69) (Found: C, 40.2; H, 3.0; N, 5.2. $C_9H_8Cl_3NO_2$ requires C, 40.3; H, 3.0; N, 5.2%); ν_{max}(neat)/cm^{-1} 3360 (OH), 3024 and 1594; δ_H($CDCl_3$; 80 MHz) 3.83 (3 H, s, MeO), 6.48 and 7.37 (1 H, 2 s, $CHCl_2$), 6.91 and 6.95 (1 H, 2 d, *J* 8.8, 8.2, ArH), 7.60 (2 H, m, ArH) and 8.50 (1 H, s, br, OH); *m/z* (EI) 267 (100%, M^+), 269 (96.7, $M^+ + 2$) and 271 (32.1, $M^+ + 4$).

1,4-Bis(dichloroacetyl)benzene dioxime 7i. *Z*-form (Found: C, 36.4; H, 2.45; N, 8.5; O, 9.8. $C_{10}H_8Cl_4N_2O_2$ requires C, 36.4; H, 2.4; N, 8.5; O, 9.7%); ν_{max}(KBr)/cm^{-1} 3280 (OH), 3042 and 1610; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 7.18 (2 H, s, $CHCl_2$), 7.50 (2 H, s, ArH), 7.84 (2 H, s, ArH), 11.93 (1 H, s, OH) and 12.70 (1 H, s, OH).

1,3-Bis(dichloroacetyl)benzene dioxime 7j. *E*/*Z* mixture (33 : 67) (Found: C, 36.45; H, 2.45; N, 8.5; O, 9.6. $C_{10}H_8Cl_4N_2O_2$ requires C, 36.4; H, 2.4; N, 8.5; O, 9.7%); ν_{max}(KBr)/cm^{-1} 3290 (OH), 3026 and 1600; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 6.47 and 7.34 (2 H, 2 s, 2 × $CHCl_2$), 7.33 (2 H, m, ArH), 8.45 (2 H, m, ArH) and 11.34 and 12.01 (2 H, 2 s, OH).

4,4′-Bis(dichloroacetyl)biphenyl dioxime 7k. *Z*-form (Found: C, 47.4; H, 3.0; N, 6.8; O, 7.8. $C_{16}H_{12}Cl_4N_2O_2$ requires C, 47.3; H, 3.0; N, 6.9; O, 7.9%); ν_{max}(KBr)/cm^{-1} 3280 (OH), 3042 and 1602; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 7.70 (2 H, s, $CHCl_2$), 7.49 (4 H, d, *J* 8.2, ArH), 7.79 (4 H, 2 d, *J* 8.2, ArH), 11.97 (1 H, s, OH) and 12.63 (1 H, s, OH).

General procedure for the preparation of 3-aryl-4-chloro-1,2,5-thiadiazoles 1

To a solution of **7** (0.63–2.3 mmol) in 1,4-dioxane (10–15 ml) was added S_4N_4 (0.63–2.3 mmol). The mixture was heated at reflux until no spot corresponding to **7** was observed on TLC ($R_F \cong 0.09$, C_6H_6), after which the solvent was removed *in vacuo*. The residue was extracted with $CHCl_3$ (150 ml) and the extracts were evaporated. Chromatography of the residue on a silica gel column (2 × 12 cm) using hexane (200 ml) as eluent gave sulfur and a minute amount of unknown compounds. Elution with hexane–benzene (3 : 1; 120 ml) gave compounds **1**. Elution with the same solvent mixture (1 : 1; 100 ml) gave unchanged S_4N_4. Reaction times, yields, and melting points of compounds **1** prepared are summarized in Table 6 and their analytical, IR and ^{1}H NMR data in Table 7.

General procedure for the preparation of 1-aryl-2,2-dibromoethanone oximes 8

The experimental procedures are basically the same as those for the preparation of **7**. Reaction times, yields, and melting points of compounds **8** are summarized in Table 8.

2,2-Dibromo-1-phenylethanone oxime 8a. *E*/*Z* mixture (29 : 71) (Found: C, 32.8; H, 2.4; N, 4.75. $C_8H_7Br_2NO$ requires C, 32.8; H, 2.4; N, 4.8%); ν_{max}(neat)/cm^{-1} 3298 (OH), 3046, 1491, 1399, 1281, 996, 950, 845, 781 and 694; δ_H($CDCl_3$; 80 MHz) 6.59 and 7.44 (1 H, 2 s, $CHBr_2$), 7.42 (3 H, m, ArH), 7.73 (2 H, m, ArH) and 9.23 and 9.77 (1 H, 2 s, OH).

2,2-Dibromo-1-(4-methylphenyl)ethanone oxime 8b. *Z*-form (Found: C, 35.2; H, 2.95; N, 4.5. $C_9H_9Br_2NO$ requires C, 35.2; H, 2.95; N, 4.6%); ν_{max}(neat)/cm^{-1} 3297 (OH), 3040 and 1600; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 2.35 (3 H, s, Me), 6.65 (1 H, s, $CHBr_2$), 7.58 (4 H, dd, *J* 54, 8, ArH) and 10.03 (1 H, s, OH); *m/z* (EI) 305 (14.4% M^+), 307 (27.2, $M^+ + 2$), 309 (13.0, $M^+ + 4$) and 134 (100).

2,2-Dibromo-1-(4-nitrophenyl)ethanone oxime 8c. *Z*-form (Found: C, 28.5; H, 1.8; N, 8.3. $C_8H_6Br_2N_2O_3$ requires C, 28.4; H, 1.8; N, 8.3%); ν_{max}(neat)/cm^{-1} 3296 (OH), 3030, 1602, 1570s and 1347s; δ_H($CDCl_3$)–[$^2H_6$]-DMSO; 80 MHz) 7.54 (1 H, s,

$CHBr_2$), 8.11 (4 H, dd, *J* 22, 8, ArH) and 10.87 (1 H, s, OH); *m/z* (EI) 338 (0.8%, M^+), 340 (1.2, $M^+ + 2$), 342 (0.7, $M^+ + 4$) and 117 (100).

2,2-Dibromo-1-(3-nitrophenyl)ethanone oxime 8d. *E*/*Z* mixture (36:64) (Found: C, 28.4; H, 1.8; N, 8.3. $C_8H_6Br_2N_2O_3$ requires C, 28.4; H, 1.8; N, 8.3%); ν_{max}(neat)/cm^{-1} 3408 (OH), 3088, 1613, 1592s and 1350s; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 6.42 and 7.59 (1 H, 2 s, $CHBr_2$), 7.96 (4 H, m, ArH), 9.29 and 9.88 (1 H, 2 s, OH); *m/z* (EI) 338 (3.2%, M^+), 340 (4.8, $M^+ + 2$), 342 (2.6, $M^+ + 4$) and 117 (100).

1-(4-Bromophenyl)-2,2-dibromoethanone oxime 8e. *Z*-form (Found: C, 25.8; H, 1.6; N, 3.8. $C_8H_6Br_3NO$ requires C, 25.8; H, 1.6; N, 3.8%); ν_{max}(KBr)/cm^{-1} 3280 (OH), 3041 and 1588; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 7.45 (1 H, s, $CHBr_2$), 7.66 (4 H, dd, *J* 21, 8, ArH) and 11.10 (1 H, s, OH); *m/z* (EI) 368 (1.5%, M^+), 370 (5.1, $M^+ + 2$), 372 (6.1, $M^+ + 4$), 374 (1.7, $M^+ + 6$) and 182 (100).

1-(4-Chlorophenyl)-2,2-dibromoethanone oxime 8f. *Z*-form (Found: C, 29.3; H, 1.85; N, 4.3. $C_8H_6Br_3NO$ requires C, 29.35; H, 1.85; N, 4.3%); ν_{max}(KBr)/cm^{-1} 3292 (OH), 3040 and 1591; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 7.42 (1 H, s, $CHBr_2$), 7.59 (4 H, dd, *J* 35, 8.4, ArH) and 12.59 (1 H, s, OH); *m/z* (EI) 325 (4.0%, M^+), 327 (6.7, $M^+ + 2$), 329 (4.8, $M^+ + 4$) and 136 (100).

2,2-Dibromo-1-(4-fluorophenyl)ethanone oxime 8g. *E*/*Z* mixture (34:66) (Found: C, 30.9; H, 1.9; N, 4.55. $C_8H_6Br_2FNO$ requires C, 30.9; H, 1.9; N, 4.5%); ν_{max}(neat)/cm^{-1} 3288 (OH), 3040 and 1598; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 6.46 and 7.24 (1 H, 2 s, $CHBr_2$), 6.45 (4 H, m, ArH) and 8.63 and 9.40 (1 H, 2 s, OH); *m/z* (EI) 309 (2.0%, M^+), 311 (5.5, $M^+ + 2$), 313 (3.5, $M^+ + 4$) and 151 (100).

2,2-Dibromo-1-(4-methoxyphenyl)ethanone oxime 8h. *Z*-form (Found: C, 33.4; H, 2,8; N, 4.3. $C_9H_9Br_2NO$ requires C, 33.5; H, 2.8; N, 4.3%); ν_{max}(KBr)/cm^{-1} 3296 (OH), 3039 and 1603; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 3.87 (3 H, s, MeO), 7.47 (1 H, s, $CHBr_2$), 7.51 (4 H, dd, *J* 70, 8, ArH) and 10.63 (1 H, s, OH); *m/z* (EI) 321 (3.5%, M^+), 323 (3.9, $M^+ + 2$), 325 (2.9, $M^+ + 4$) and 135 (100).

2,2-Dibromo-1-(3-methoxyphenyl)ethanone oxime 8i. *Z*-form (Found: C, 33.4; H, 2.8; N, 4.4. $C_9H_9Br_2NO$ requires C, 33.5; H, 2.8; N, 4.3%); ν_{max}(KBr)/cm^{-1} 3302, 1600, 1507, 1437, 1299, 1189, 1020, 961 and 832; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 3.87 (3 H, s, MeO), 7.09 (1 H, m, ArH), 7.48 (1 H, s, $CHBr_2$), 7.52 (3 H, m, ArH) and 9.72 (1 H, s, OH); *m/z* (EI) 321 (1.9%, M^+), 323 (2.3, $M^+ + 2$), 325 (1.7, $M^+ + 4$) and 135 (100).

2,2-Dibromo-1-(2-naphthyl)ethanone oxime 8j. *Z*-form (Found: C, 40.1; H, 2.65; N, 4.05. $C_{12}H_9Br_2NO$ requires C, 40.0; H, 2.6; N, 4.1%); ν_{max}(KBr)/cm^{-1} 3280 (OH), 3072 and 1597; δ_H($CDCl_3$–[$^2H_6$]-acetone; 80 MHz) 7.45 (2 H, m, ArH), 7.83 (4 H, m, ArH), 8.16 (1 H, s, $CHBr_2$), 8.68 (1 H, s, ArH) and 10.85 (1 H, s, OH); *m/z* (EI) 341 (2.7%, M^+), 343 (3.0, $M^+ + 2$), 345 (2.5, $M^+ + 4$) and 153 (100).

1,4-Bis(dibromoacetyl)benzene dioxime 8k. (Found: C, 23.6; H, 1.6; N, 5.6; O, 6.4. $C_{10}H_8Br_4N_2O_2$ requires C, 23.65; H, 1.6; N, 5.5; O, 6.3%); ν_{max}(KBr)/cm^{-1} 3280 (OH), 3042 and 1610; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 7.18 (2 H, s, 2 × $CHBr_2$), 7.50 (2 H, s, ArH), 7.84 (2 H, s, ArH), 11.93 (1 H, s, OH) and 12.70 (1 H, s, OH).

1,3-Bis(dibromoacetyl)benzene dioxime 8l. (Found: C, 23.7; H, 1.6; N, 5.5; O, 6.2. $C_{10}H_8Br_4N_2O_2$ requires C, 23.65; H, 1.6; N, 5.5; O, 6.3%); ν_{max}(neat)/cm^{-1} 3296s, 3040, 2880, 1435, 1377, 1264, 1045, 979, 806 and 714; δ_H($CDCl_3$; 80 MHz) 6.43 (1 H, s, $CHBr_2$), 7.29 (1 H, s, $CHBr_2$), 7.30 (2 H, m, ArH), 8.40 (2 H, m, ArH), 9.21 (1 H, s, OH) and 9.89 (1 H, s, OH).

4,4′-Bis(dibromoacetyl)biphenyl dioxime 8m. (Found: C, 33.0; H, 2.1; N, 4.75; O, 5.45. $C_{16}H_{12}Br_4N_2O_2$ requires C, 32.9; H, 2.1; N, 4.8; O, 5.5%); ν_{max}(KBr)/cm^{-1} 3285 (OH), 3040 and 1608; δ_H($CDCl_3$–[$^2H_6$]-DMSO; 80 MHz) 7.66 (8 H, dd, *J* 24, 8.3, ArH), 7.75 (2 H, s, 2 × $CHBr_2$), 11.93 (1 H, s, OH) and 12.52 (1 H, s, OH).

General procedure for the preparation of 3-aryl-4-bromo-1,2,5-thiadiazoles 2

To a solution of **8** (1.0–3.6 mmol) in 1,4-dioxane (15 ml) was added S_4N_4 (1.0–4.2 mmol). The mixture was heated at reflux until no spot corresponding to **8** was observed on TLC ($R_F \cong 0.2$, C_6H_6). After solvent removal *in vacuo* from the reaction mixture, the residue was chromatographed on a silica gel column (2 × 10 cm, 70–230 mesh). Hexane (200 ml) as eluent gave sulfur and hexane–benzene (4:1; 200 ml) gave unchanged S_4N_4; subsequently the same mixture (2:1; 200 ml) gave compounds **2**. Reaction times, yields, and melting points of compounds **2** are summarized in Table 8 and their analytical, IR, and ^{1}H NMR data in Table 9.

General procedure for the preparation of 1-aryl-2-bromo-2-fluoroethanones[8] 14

To a solution of the appropriate 1-aryl-2-fluoroethanone[9] **13** (5.7–8.0 mmol) in glacial acetic acid (15–30 ml) was added bromine (7.5–8.2 mmol). The mixture was stirred for 5–10 h at 40–50 °C and quenched when no spot corresponding to **13** appeared on TLC ($R_F \cong 0.4$, ethyl acetate–*n*-hexane, 1:4). The reaction mixture was worked up as described in the literature. Reaction times and yields of **14** are summarized in Table 5. 2-Bromo-2-fluoro-1-phenylethanone **14a**, mp 55–56 °C (lit.,[13] 55 °C); 2-*bromo*-2-*fluoro*-1-(4-*methylphenyl*)*ethanone* **14b**, mp 64–66 °C (Found: C, 46.7; H, 3.95; Br, 34.8. C_9H_8BrFO requires C, 46.8; H, 3.9; Br, 34.6%); ν_{max}(KBr)/cm^{-1} 1698 (CO); δ_H($CDCl_3$; 80 MHz) 2.41 (3 H, s, Me), 6.67 (d, 1 H, *J* 51, CHBrF) and 7.75 (4 H, dd, *J* 39, 8, ArH); *m/z* (EI) 230 (51.6%, M^+), 232 (52.9, $M^+ + 2$), 151 (32.6) and 91 (100); 2-*bromo*-2-*fluoro*-1-(4-*bromophenyl*)*ethanone* **14c**, mp 96–98 °C (Found: C, 32.4; H, 1.7; Br, 54.2. $C_8H_5Br_2FO$ requires C, 32.5; H, 1.7; Br, 54.0%); ν_{max}(KBr)/cm^{-1} 1702 (C=O); δ_H($CDCl_3$; 80 MHz) 6.69 (1 H, d, *J* 51, CHBrF) and 7.99 (4 H, d, *J* 8.4, ArH); *m/z* (EI) 294 (23.8%, M^+), 296 (47.1, $M^+ + 2$), 298 (19.2, $M^+ + 4$), 215 (100) and 217 (98.2); 2-chloro-2-fluoro-1-phenylethanone **14d**, mp 45–46 °C (lit.,[13] 45 °C).

General procedure for the preparation of 1-aryl-2-bromo-9 and 1-aryl-2-chloro-2-fluoroethanone oximes 10

The experimental procedures are basically the same as those for the preparation of **7** except for quenching of the reaction by addition of water to the mixture when no spot corresponding to **13** had appeared on TLC ($R_F \cong 0.4$, ethyl acetate–hexane, 1:4). Reaction times, yields, and melting points of **9** and **10** are summarized in Table 5.

2-Bromo-2-fluoro-1-phenylethanone oxime 9a. *Z*-form (Found: C, 41.4; H, 3.0; N, 6.0. C_8H_7BrFNO requires C, 41.4; H, 3.0; N, 6.0%); ν_{max}(neat)/cm^{-1} 3312 (OH), 3072, 1452, 1382, 1314, 1159, 1095, 1066, 954, 772 and 398; δ_H($CDCl_3$–[$^2H_6$]-acetone; 80 MHz) 7.35 (3 H, m, PhH), 7.56 (1 H, d, *J* 48, CHBrF), 7.64 (2 H, m, PhH) and 10.12 (1 H, s, OH).

2-Bromo-2-fluoro-1-(4-methylphenyl)ethanone oxime 9b. *Z*-form (Found: C, 43.7; H, 3.7; N, 5.8. C_9H_9BrFNO requires C, 43.9; H, 3.7; N, 5.7%); ν_{max}(neat)/cm^{-1} 3296 (OH), 1607, 1514, 1475, 1443, 1094, 1063, 957, 820 and 746; δ_H($CDCl_3$–[$^2H_6$]-acetone; 80 MHz) 2.35 (3 H, s, Me), 7.50 (1 H, d, *J* 50, CHBrF), 7.61 (4 H, dd, *J* 43, 8, ArH) and 11.12 (1 H, s, OH); *m/z* (EI) 245 (20.4%, M^+), 247 (17.4, $M^+ + 2$) and 123 (100).

2-Bromo-2-fluoro-1-(4-bromophenyl)ethanone oxime 9c. *Z*-form (Found: C, 30.85; H, 1.9; N, 4.5. $C_8H_6Br_2FNO$ requires C, 30.9; H, 1.9; N, 4.5%); ν_{max}(neat)/cm^{-1} 3298 (OH), 1603, 1509, 1430, 1045, 972, 896, 880 and 753; δ_H($CDCl_3$–[$^2H_6$]-acetone; 80 MHz) 7.53 (1 H, d, *J* 48, CHBrF), 7.58 (4 H, dd, *J* 15, 8, ArH) and 10.94 (1 H, s, OH).

2-Chloro-2-fluoro-1-phenylethanone oxime 10. *E*/*Z* mixture (Found: C, 51.15; H, 3.8; N, 7.45; O, 8.6. C_8H_7ClFNO requires C, 51.2; H, 3.8; N, 7.5; O, 8.5%); ν_{max}(neat)/cm^{-1} 3312 (OH), 3072, 1572, 1470, 1101, 1066, 967 and 797; δ_H($CDCl_3$; 80 MHz) 6.71 and 7.54 (1 H, 2 d, *J* 48, CHClF), 7.62 (2 H, m, PhH), 7.34

(3 H, m, PhH), 9.59 and 10.04 (1 H, 2 s, OH); *m/z* (EI) 187 (31.8%, M^+), 189 (11.7, $M^+ + 2$), 120 (65.4) and 77 (100).

General procedure for the preparation of 3-aryl-4-fluoro-1,2,5-thiadiazoles 3

To a solution of **14** (1.5–1.6 mmol) in 1,4-dioxane (15 ml) was added S_4N_4 (1.5–1.6 mmol). The mixture was heated at reflux until no spot corresponding to **14** was observed on TLC ($R_F \cong 0.18$, C_6H_6). After removal of the solvent *in vacuo* from the reaction mixture, the residue was chromatographed on a silica gel column (2 × 10 cm). Hexane (200 ml) as eluent gave a sulfur and hexane–benzene (4 : 1; 200 ml) gave unchanged S_4N_4. Subsequent elution with the same solvent mixture (2 : 1; 200 ml) gave compounds **3**. Reaction times, yields, and melting points of compounds **3** are summarized in Table 10, and their analytical, IR, and ^{1}H NMR data in Table 11.

X-Ray structure analysis of compound 7f

Crystal data: $C_8H_6Cl_3NO$, $M = 238.49$, Triclinic, $a = 6.467$ (3), $b = 7.218$ (2), $c = 11.038$ (5) Å, $\alpha = 85.79$ (3), $\beta = 74.33$ (4), $\gamma = 76.13$ (3)°, $V = 481.6$ (3) Å^3 [by least-squares refinement on diffractometer angles for 25 automatically centred reflections with $23 \leqslant 2\theta \leqslant 30°$, $\lambda = 0.710\,96$ Å, $T = 293$ (2) K], space group $P\bar{1}$ $Z = 2$, $D_x = 1.645$ g cm^{-3}, colourless crystals were grown from $CHCl_3$, $F(000) = 240.00$, μ(Mo-Kα) = 9.1 cm^{-1}.

Data collection and processing. An Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo-Kα radiation, $\omega/2\theta$ scans with ω scan width (0.65 + 0.35 tan θ)°; 1536 reflections measured ($1.8 \leqslant \theta \leqslant 25°$, $0 \leqslant h \leqslant 7$, $-8 \leqslant k \leqslant 8$, $-12 \leqslant l \leqslant 13$), giving 1404 with $I \geqslant 2\sigma(I)$.

Structure solution and refinement. Automatic direct methods[21] (all non-H atoms). Full-matrix least-squares refinement[22] on F^2 with all non-H atoms anisotropic; hydrogen atoms were located from the successive electron density maps and their positions and isotropic thermal parameters were refined with no constraint. Final R_1 [$I \geqslant 2\sigma(I)$] = 0.0345; wR_2 [all data] = 0.1225, $S[F^2] = 0$ for 119 refined parameters (R indices defined in ref. 21). The final ΔF synthesis showed no peaks outside the range −0.417→+0.528 e Å^{-3}. Fig. 1 was produced using SHELXTL/PC.[23] Atomic coordinates and equivalent isotropic and anisotropic displacement parameters, and bond distances and angles, have been deposited at the Cambridge Crystallographic Data Centre and are available on request. Any such request should be accompanied by a full bibliographic citation for this work together with the reference number 207/156.†

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† For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans 1*, available *via* the RSC web pages (http://www.rsc.org/authors).

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