

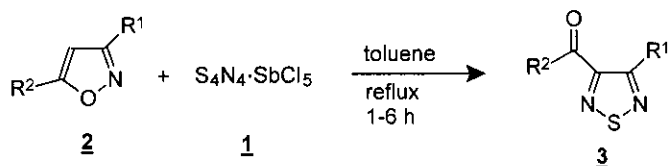
REACTIONS OF ALKYL METHYL KETOXIMES WITH TETRASULFUR
TETRANITRIDE ANTIMONY PENTACHLORIDE COMPLEX ($S_4N_4 \cdot SbCl_5$): A
REGIOSELECTIVE FORMATION OF 3-ALKYL-4-METHYL-1,2,5-THIA-
DIAZOLES AND THEIR MECHANISM OF FORMATION

Kil Joong Kim and Kyongtae Kim*

Department of Chemistry, Seoul National University, Seoul 151-742, Korea

Abstract – Treatment of alkyl methyl ketoximes with tetrasulfur tetranitride antimony pentachloride complex ($S_4N_4 \cdot SbCl_5$) in aromatic solvents such as benzene and toluene at 60 °C led to the regioselective formation of 3-alkyl-4-methyl-1,2,5-thiadiazoles in low yields, whereas the reactions of alkyl aryl ketoximes under the same conditions gave exclusively *N*-arylalkanamides in good yields. A mechanism is proposed for the formation of 3-alkyl-4-methyl-1,2,5-thiadiazoles.

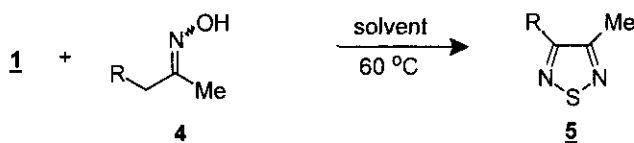
Previous work in our group has demonstrated that tetrasulfur tetranitride antimony pentachloride complex ($S_4N_4 \cdot SbCl_5$) (**1**) is a useful reagent for the synthesis of α -chloro ketones from either α -bromo- and α -iodo ketones¹ and for the complete regioselective synthesis of 4-substituted 3-acyl- and 3-aryl-1,2,5-thiadiazoles (**3**) from 3-substituted 5-alkyl- and 5-arylisoxazoles (**2**) (Scheme 1).²



Scheme 1

Although 1,2,5-thiadiazoles possessing a variety of substituents at C-3 and C-4 have been synthesized,³ synthesis of 3,4-dialkyl-1,2,5-thiadiazoles has received little attention. There appears to be only one paper dealing with the synthesis of 3,4-dimethyl-1,2,5-thiadiazole by the reaction of dimethylglyoxime with sulfur monochloride in DMF at room temperature.⁴ In a continuation of our study on the development of

the potential synthetic utilities of **1**, we have found that **1** reacts with alkyl methyl ketoximes (**4**) in either benzene or toluene at 60 °C to give 3-alkyl-4-methyl-1,2,5-thiadiazoles (**5**) (Scheme 2).



Scheme 2

RESULTS AND DISCUSSION

(A) Reactions of Alkyl Methyl Ketoximes (**4**) with **1**

The reactions of methyl ketoximes (**4**) with **1** in toluene were sensitive to the reaction temperature. After some trial, the optimum temperatures yielding **5** in better yields were found to be 60 to 70 °C. When a mixture of ketoximes (**4**) and **1** in toluene was heated at 60 °C, the color of the solution slowly turned dark red and an unknown spot began to appear at the origin on TLC (*n*-hexane : EtOAc = 4 : 1). The unknown spot, which is thought to be an intermediate, showed a blue color when visualized with a mineral UV lamp and was gradually intensified. At the same time, the color of the spot corresponding to the starting ketoximes (**4**) faded on TLC. After about 30 min, a new spot corresponding to 1,2,5-thiadiazole (**5**) appeared with the disappearance of the spot at the origin. The reaction mixture was worked up in 1 to 4 h. Reaction conditions and yields of **5** are summarized in Table 1 and the spectroscopic data of **5** are in Table 2. Compounds (**5**) are all volatile liquids. Therefore, loss of considerable amounts of **5** occurred while toluene was removed *in vacuo*. By changing the solvent with a lower boiling benzene, yields of **5** increased somewhat. In order to know how much amounts of **5** is removed from the reaction mixture when the solvent was evaporated *in vacuo*, **4** (R = *n*-Pr, 1.82 mmol) was treated with **1** (1.83 mmol) in toluene (30 mL) and in benzene (30 mL), respectively at 60 °C for 1 h. Each reaction mixture was filtered and each filtrate was concentrated *in vacuo*. The contents of **5b** in the filtrate and in toluene removed *in vacuo* were analyzed by a GC-MS spectrometer, respectively. It has been found that 49% of **5b** was removed from the reaction mixture when toluene was evaporated *in vacuo*, whereas only 1% of **5b** was removed from the reaction mixture in benzene. The results suggest that the

difference in yields of **5b** obtained in two different solvents, i.e., toluene and benzene (Entries 3, 4), is primarily due to the volatility of **5b**, not to the intrinsic solvent properties. Similarly, the difference in yields of **5a** in two different solvents can be rationalized (Entries 1, 2). On the other hand, in the case of the reaction of 4-phenyl-2-butanone oxime (**4**, R = C₆H₅CH₂), a small difference in yields of **5d** (Entries 6, 7) was observed. The result may be attributable to the lower volatility of **5d** compared with **5a** and **5b**. Despite low yields of **5**, it is noteworthy that only regioselective single isomers, i.e., 3-alkyl-4-methyl-1,2,5-thiadiazoles (**5**) rather than 3-alkyl-1,2,5-thiadiazoles (**5'**), were obtained. On the other hand, when 3-heptanone oxime (**6**) was subjected under the same conditions as for compounds (**4**), a mixture of 3-*n*-butyl-4-methyl- (**5f**) (R = *n*-Bu) and 3-ethyl-4-*n*-propyl-1,2,5-thiadiazoles (**7**) was isolated in 26% yield (Scheme 3).

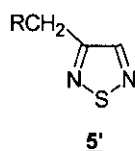


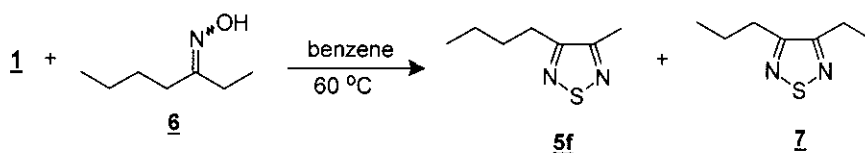
Table 1. Reaction Conditions and Yields of 3-Alkyl-4-methyl-1,2,5-thiadiazoles (**5a-5e**)

Entry	Oxime (4)	1	Solvent	Temp	Time	Yield		
	R	(mmol)	(mmol)	(°C)	(h)	(%)		
1	Et	1.61	1.53	<i>a</i>	60	1	5a	8
2		1.48	1.51	<i>b</i>	60	1	5a	16
3	<i>n</i> -Pr	2.08	2.07	<i>a</i>	60	1	5b	10
4		1.04	1.04	<i>b</i>	60	2	5b	24
5	<i>i</i> -Pr	1.50	1.50	<i>b</i>	60	2	5c	3
6	C ₆ H ₅ CH ₂	1.63	1.63	<i>a</i>	60	1	5d	32
7		1.63	1.63	<i>b</i>	50	4	5d	37
8		1.63	1.63	<i>b</i>	rt	24	5d	0
9	C ₆ H ₅	1.41	1.41	<i>a</i>	80	2	5e	21 ⁵
10		0.938	0.938	<i>b</i>	c	d	5e	28

^a Toluene. ^b Benzene. ^{c, d} The reaction was carried out at 60 °C for 2 h, followed by heating at reflux for 1 h.

Table 2. Analytical, IR, and ^1H NMR Data of 3-Alkyl-4-methyl-1,2,5-thiadiazoles (**5a-5d**)

Compound	IR (neat) (ν , cm^{-1})	^1H NMR (CDCl_3) (δ , ppm)	Molecular Formula	Calcd/Found %			
				C	H	N	S
5a	2960, 2912, 1449, 1408, 1369, 1283, 1260, 1049, 928, 822, 780, 729	1.34 (3H, t, $J = 6$ Hz, CH_2Me), 2.51 (3H, s, Me), 2.87 (2H, q, $J = 6$ Hz, MeCH_2)	$\text{C}_5\text{H}_8\text{N}_2\text{S}$	46.85	6.29	21.85	25.01
				46.81	6.28	21.79	25.05
5b	2944, 1446, 1404, 1366, 1139, 1030, 992, 816, 790	0.98 (3H, t, $J = 8$ Hz, CH_2Me), 1.80 (2H, sextet, $J = 8$ Hz, CH_2Me), 2.53 (3H, s, Me), 2.83 (2H, t, $J = 8$ Hz, $\text{CH}_2\text{CH}_2\text{Me}$)	$\text{C}_6\text{H}_{10}\text{N}_2\text{S}$	50.67	7.09	19.70	22.54
				50.62	7.11	19.74	22.50
5c	2960, 2912, 1456, 1404, 1372, 1267, 1075, 924, 822, 730	1.31 (6H, d, $J = 8$ Hz, 2Me), 2.54 (3H, s, Me), 3.00-3.60 (1H, m, CHMe_2)	$\text{C}_6\text{H}_{10}\text{N}_2\text{S}$	50.67	7.09	19.70	22.54
				50.69	7.10	19.64	22.59
5d	3024, 2912, 1596, 1484, 1440, 1401, 1190, 1049, 1024, 812, 780, 739, 716, 691	2.44 (3H, s, Me), 4.20 (2H, s, CH_2), 7.10-7.49 (5H, m, ArH)	$\text{C}_{10}\text{H}_{10}\text{N}_2\text{S}$	63.13	5.30	14.72	16.85
				63.10	5.32	14.74	16.80

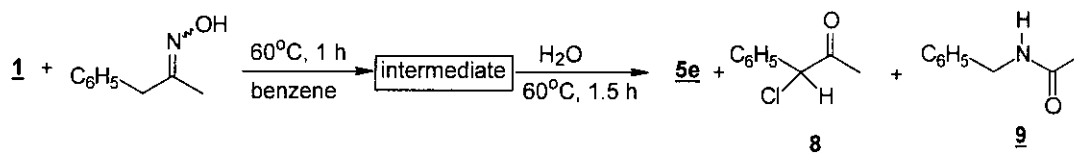


Scheme 3

The attempted separation of two compounds (**5f**) and (**7**) by chromatography (column and TLC) and HPLC (μ Bondapak, acetonitrile, flow rate 0.5 mL/min, retention time 11.400 min) was unsuccessful. However, GC-MS analysis indicated the ratio of two compounds, (**5f**, retention time, 4.628 min) and (**7**, retention time, 4.417 min) in a mixture to be 64 : 100. The fragments m/z 114($\text{M}^+ - \text{CH}_3\text{CHN}$) and 73(CH_3CHN) for **5f** and m/z 101($\text{M}^+ - \text{CH}_3\text{CH}_2\text{CN}$) and 87($\text{CH}_3\text{CH}_2\text{CNS}$) for **7** indicate clearly the existence of **5f** and **7** in the mixture.

Since compounds (**5**) were envisaged to be formed *via* an intermediate which has a relatively long life-time, attempts were made to investigate its chemical properties. The reaction of benzyl methyl ketoxime (**4**) ($\text{R} = \text{C}_6\text{H}_5$) with **1** gave a reaction mixture which showed a spot at the origin on TLC, to which water was added, and then heating for 1.5 h resulted in a deep red solution with yellow solids stuck on the

surface of the reaction flask. From a chromatographic separation of the reaction mixture were isolated a small amount of a mixture of **5e**, 1-chloro-1-phenylpropanone (**8**), and *N*-benzylacetamide (**9**) (Scheme 4). It was too small an amount to be separated by chromatography, but the ratio of three compounds (**5e** : **8** : **9**) in a mixture was determined to be 100 : 11 : 9 based on GC-MS analysis.



Scheme 4

The structure of **8** was determined on the basis of GC-MS as well as ¹H NMR and IR spectroscopic data of the mixture isolated. The possibility for the formation of **8** from benzyl methyl ketone, which may be formed by hydrolysis of **4** (R = C₆H₅), and **1** was ruled out on the basis of the absence of the spots corresponding to **5e**, **8**, and **9** when the reaction mixture was quenched with water, despite the presence of a spot at the origin on TLC (*n*-hexane : EtOAc = 4 : 1). In order to observe the effects by external chloride ions on the yields of **5** and **8**, various ammonium halides were added to the reaction mixture with and without water as a quencher after ketoxime (**4**) had disappeared. After being stirred for 2 h at reflux, the mixture was worked up. The results are summarized in Table 3.

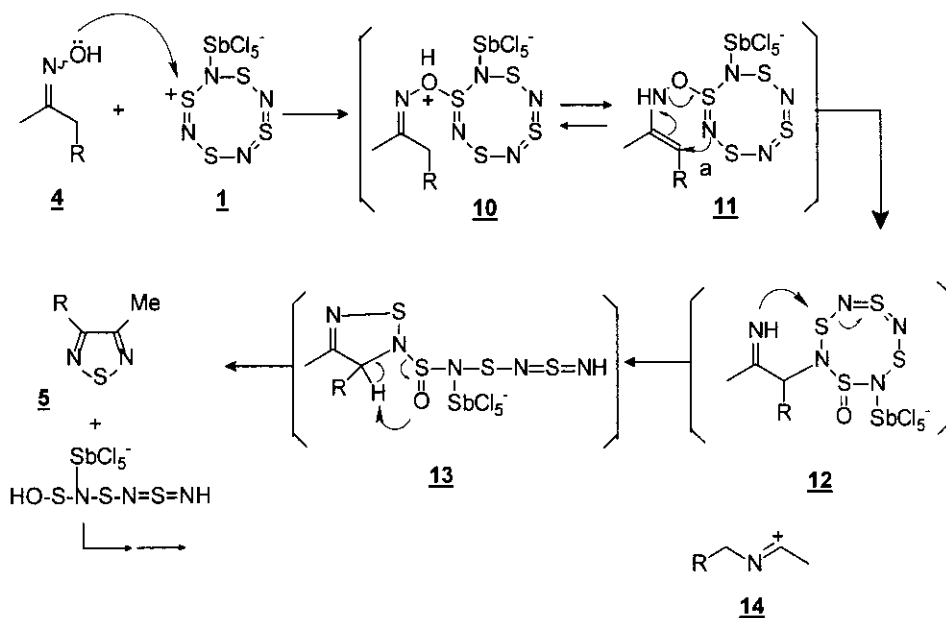
Table 3. Quenching Conditions, and Yields of 1,2,5-Thiadiazole (**5e**), Chloro Ketone (**8**), and Amide (**9**)

Entry	Oxime (4) (R = C ₆ H ₅) mmol	1 mmol	solvent ^a	H ₂ O ^b	Ammonium Halide	Time h	Yield (ratio) ^c 5e : 8 : 9
1	1.00	1.00	benzene	No	Bz(Et) ₃ NCl	2	(31%)
2	0.718	0.745	benzene	Yes	Bz(Et) ₃ NCl	2	33 mg (100 : 18 : 49)
3	0.659	0.724	benzene	Yes	Et ₄ NBr	2	24 mg (100 : 18 : 16)
4	0.650	0.724	benzene	Yes	(<i>n</i> -Bu) ₄ NF	2	32 mg (100 : 10 : 63)
5	0.637	0.724	acetone	Yes	Et ₄ NBr	2	11 mg (100 : 5 : 24)
6	0.671	0	benzene	Yes or No	Bz(Et) ₃ NCl		^d

^a Volume of the solvent: 10 mL. ^b Volume of water: 1 mL. ^c The ratio of products was determined based on ¹H NMR spectroscopic data. ^d The starting oxime was recovered in 92% yield.

Table 3 shows that compounds (**8**) and (**9**) are not produced in the absence of water and the yield of **5e** (31%) (Entry 1) is close to the yield (28%) (Table 1, Entry 10) obtained without the external source of chloride ion. The result suggests that the formation of compound (**5e**) is independent of the presence of external ammonium chloride. Hydrolysis of an intermediate, followed by addition of either ammonium bromide (Table 3, Entries 3, 5) or ammonium fluoride (Table 3, Entry 4) does not lead to the formation of the corresponding halo ketones. The results indicate that the chloride ions that participated in the reaction leading to **8** come intramolecularly from an intermediate complexed with SbCl_5 or from other source, possibly the solvated chloride ions. Since the solubilities of ammonium halides in benzene are relatively poor, benzene was substituted for acetone (Table 3, Entry 5). However, total yield of the products decreased without giving any other isolable products except for **5e**, **8**, and **9**. Nevertheless, the ratio of the three compounds, i.e., **5e**, **8**, and **9** varies somewhat with the ammonium halides employed. In the mean time, treatment of benzyl methyl ketoxime (**4**) with SbCl_5 under the same conditions as for the reaction with **1** gave **8**, **9**, and benzyl methyl ketone, whose ratio was found to be 46 : 33 : 100 based on GC-MS analysis. The results suggest that compounds (**8**) and (**9**) can be formed in wet benzene by the reaction of the ketoxime (**4**) with either SbCl_5 or unknown species, whose identity is uncertain. This reaction is worth studying further to delineate this uncertainty. Recovery of ketoxime (**4**) in 92% yield when the ketoxime was treated with only benzyltriethylammonium chloride in benzene regardless of the presence and absence of water (Table 3, Entry 6) implies that complex (**1**) is needed for the formation of **5e**, **8**, and **9**. The formation of compounds (**5**) can be explained by a nucleophilic attack of ketoxime (**4**) to the electron deficient sulfur of **1** to give an intermediate (**10**) (Scheme 5). Deprotonation, followed by tautomerization, yields exclusively a more stabilized enamine type of an intermediate (**11**), which undergoes an intramolecular cyclization to give an intermediate (**12**). The intramolecular nucleophilic attack of an imino nitrogen of **12** to sulfur concomitant with a S-N bond cleavage would lead to a new intermediate (**13**), which undergoes aromatization to give **5**. Aromatization leading to **5** may be a driving force for a bond cleavage between sulfinyl and the ring nitrogen of **13**. Stability of an enamine (**11**) having more substituents at the olefinic carbons compared with the other form may be responsible for the regioselective formation of **5**. However, the reaction of 3-heptanone oxime (**6**) gave a mixture of **5f** and **7**, in which the latter was a major compound. Less steric interaction between S_4N_4 moiety and propyl group ($\text{R} = n\text{-Pr}$ for **7**) rather than n -butyl group ($\text{R} = n\text{-Bu}$ for **5f**) in an intermediate (**11**) may be attributable to compound (**7**) being a major compound. The observations in which the addition of benzyltriethylammonium chloride does not affect the yield of **5e** (Table 3, Entry 1) is consistent with the proposed mechanism. On the other hand, the fact that no bromo- and fluoro ketones analogous to **8** were detected from the reactions in the presence of tetraethylammonium bromide (Table 3, Entry 3) and tetrabutylammonium fluoride (Table 3, Entry 4), respectively, in wet benzene suggest alternative

pathway(s) leading to **8** and **9**, which is uncertain. The formation of *N*-alkylacetamide (**9**) can be explained by assuming the involvement of imminium ion (**14**), which would be expected to be formed *via* either intermediate (**10**) or ketoxime (**4**) in the presence of Lewis acids including SbCl_5 by a mechanism analogous to the Beckmann rearrangement.⁶



Scheme 5

(B) Reactions of Alkyl Aryl Ketoximes (**15**) with **1**

In contrast with the reactions of methyl ketoximes (**4**), a Beckmann type of rearrangement occurred when alkyl aryl ketoximes (**15**) were treated with **1** under the same conditions as for methyl ketoximes (**4**). Consequently, *N*-arylalkanamides (**16**) were obtained in good yields. Reaction conditions, yields, and melting points of **16** are summarized in Table 4.

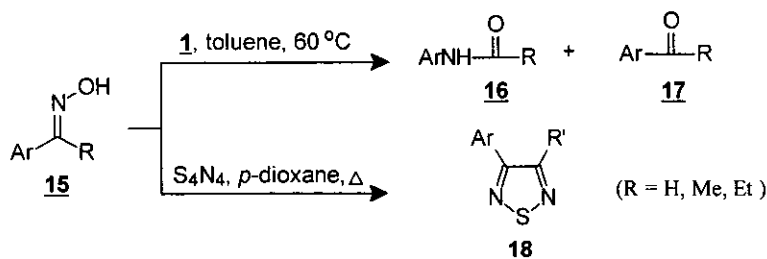


Table 4. Reaction Conditions, Yields, and Melting Points of *N*-Aryl-alkanamides (**16**)

Ar	R	15 (mmol)	1 (mmol)	Time (h)	Comp- ound	Yield (%)	mp (°C)	Comp- ound	Yield (%)
C ₆ H ₅	Me	2.63	0.621	1	16a	67	86-90 (lit., ⁷ 87-93)		
4-MeC ₆ H ₄	Me	2.43	0.559	1	16b	72	138-142 (lit., ⁷ 144-148)		
4-ClC ₆ H ₄	Me	2.50	0.559	1	16c	61	177-178 (lit., ⁸ 179)	17a	5
C ₆ H ₅	Et	2.50	0.518	1	16d	64	102-105 (lit., ⁷ 99-103)	17b	25
C ₆ H ₅	<i>n</i> -Pr	2.50	0.621	1	16e	64	95-96 (lit., ⁸ 97)	17c	20

It is rather interesting to note that alkyl aryl ketoximes (**15**) undergo exclusively a Beckmann type of rearrangement to give amides (**16**), although **15** have an alkyl group capable of an enolization yielding a species like an intermediate (**11**) (Scheme 5). Furthermore, the fact that treatment of **15** with S₄N₄ in *p*-dioxane at reflux gives 3-alkyl-4-aryl-1,2,5-thiadiazoles (**18**)⁹ clearly shows the differences in the reactivities between S₄N₄·SbCl₅ (**1**) and S₄N₄.

In summary, the reactions of alkyl methyl ketoximes (**4**) with S₄N₄·SbCl₅ (**1**) in aromatic solvents such as benzene and toluene give regioselective products, i.e., 3-alkyl-4-methyl-1,2,5-thiadiazoles (**5**), albeit in low yields, whereas the reactions of alkyl aryl ketoximes (**15**) under the same reaction conditions give exclusively *N*-arylalkanamides (**16**). The stability of an enamine type of the intermediate (**11**) is thought to be responsible for the regioselective formation of **5**.

EXPERIMENTAL

Tetrasulfur tetranitride (S₄N₄)¹⁰ and tetrasulfur tetranitride antimony pentachloride complex¹¹ were prepared by the literature procedures. Alkyl and aryl ketoximes were prepared from the corresponding ketones and hydroxylamine hydrochloride in methanol.¹² IR spectra were obtained on a Shimadzu 470 spectrophotometer. ¹H NMR spectra were measured on a Bruker AC 80 spectrometer using tetramethylsilane as an internal standard. MS spectra were obtained by electron impact at 70 eV using a VG 12-250 mass spectrometer. Elemental analyses were determined by the Korea Basic Science Center. Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected. Column chromatography was performed on a silica gel (Merck 70-230 mesh, ASTM).

General Procedure for the Reaction of Ketoximes (**4**) with $S_4N_4 \cdot SbCl_5$ (**1**)

A mixture of an oxime (**4**) and **1** in an aromatic solvent was heated for an appropriate time at 60 °C to 80 °C. The color of the solution gradually turned dark red. After the oxime had disappeared completely, the reaction mixture was cooled and filtered to remove the undissolved solids. After removal of the solvent *in vacuo*, the residue was chromatographed on a silica gel column (1.5 × 6 cm), eluting with *n*-hexane to elute a small amount of sulfur (< 10 mg). Elution with a mixture of carbon tetrachloride and chloroform (2 : 1) gave S_4N_4 (< 10 mg). Elution with the same solvent mixture (1 : 2) gave 3-alkyl-4-methyl-1,2,5-thiadiazoles (**5**). In each case, consult Table 1 for quantities of reactants, reaction times, and yields, and Table 2 for analytical and spectroscopic data of **5**.

Reaction of Benzyl Methyl Ketoxime with **1:** (i) A mixture of ketoxime (140 mg, 0.983 mmol) and **1** (453 mg, 0.938 mmol) in benzene (15 mL) was heated at 60 °C for 1 h. By the time no spot corresponding to 3-methyl-4-phenyl-1,2,5-thiadiazole (**5e**) was observed on TLC, in spite of the absence of the spot corresponding to the ketoxime. After additional heating at reflux for 1 h, the reaction mixture was worked up as described in the general procedure for compounds (**5**) to give **5e** in 28% yield. (ii) A mixture of ketoxime (110 mg, 0.737 mmol) and **1** (0.745 mmol) in benzene (15 mL) was heated at 60 °C for 1 h and then water (1 mL) was added to the reaction mixture, which was additionally heated for 1.5 h. The color of the solution turned gradually from dark red to deep red, and pale yellow solids were stuck on the surface of the reaction flask. The mixture was cooled and then dried over $MgSO_4$. The solvent was removed *in vacuo*. Chromatography (1.5 × 7 cm) of the residue using a mixture of *n*-hexane and EtOAc (10 : 1) gave a mixture of **5e**, 1-chloro-1-phenylpropanone (**8**), and *N*-benzylacetamide (**9**) which was analyzed by GC-MS: **5e**: MS (*m/z*) 176 (M^+ , 100), 135 ($M^+ - CH_3CN$, 97.11), 103 (22.00), 73 (34.86). **8**: 170 ($M^+ + 2$, 5.98), 168 (M^+ , 18.52), 133 ($M^+ - Cl$, 11.84), 127 (32.27), 125 (100), 105 (15.46), 89 (42.40), 77 (9.49); 1H NMR (300 MHz, $CDCl_3$, δ , ppm) 2.22 (3H, s, Me), 5.35 (1H, s, CHCl), 7.46-7.52 (5H, m, ArH); IR (neat) (ν , cm^{-1}) for a mixture of **5e**, **8**, and **9**: 1705 (CHClC(=O)), 1664 (NHC(=O)), 1590, 1440, 1398, 1152, 1068, 1004, 828, 774, 694. **9**: MS (*m/z*) 149 (M^+ , 0.40), 148 ($M^+ - 1$, 2.26), 105 (100), 77 (63.82); 1H NMR (300 MHz, $CDCl_3$, δ , ppm) 2.17 (3H, s, Me), 2.53 (2H, s, CH_2), 7.40-7.53 (6H, m, ArH, NH). (iii) Quenching Studies: As described in (ii), water (1 mL) was added to the reaction mixture and then ammonium halides were subsequently added. The mixture was worked up as usual. In each case, consult Table 3 for quantities of reactants, i.e., **4** and **1**, solvents, and ammonium halides, and yields of **5e**, **8**, and **9**.

General Procedure for the Reaction of Alkyl Aryl Ketoximes (14**) with **1**:** A mixture of **14** and **1** in toluene (20 mL) was heated at 60 °C for the appropriate time. The color of the solution immediately turned dark. The reaction mixture was worked up as described for the general procedure for the

reactions of **4**. Chromatography (2.5 × 5.0 cm) of the residue using *n*-hexane as an eluent gave a minute amount of sulfur. Elution with a mixture of *n*-hexane and benzene (3 : 1) gave S₄N₄. Subsequent elution with dichloromethane, followed by EtOAc gave alkyl aryl ketone (**17**) and *N*-arylalkanamide (**16**), respectively. In each case, consult Table 4 for quantities of reactants, reaction times, and yields of **16** and **17**.

Reaction of **1 with 3-Heptanone Oxime (**6**):** A mixture of **6** (250 mg, 1.94 mmol) and **1** (950 mg, 1.97 mmol) in benzene (30 mL) was heated at 60 °C for 2 h and the reaction mixture was worked up as described in the general procedure for the reactions of **4** with **1**. Elution with *n*-hexane, followed by a mixture of carbon tetrachloride and chloroform (1 : 1) as eluents gave a mixture of 3-ethyl-4-*n*-propyl-1,2,5-thiadiazole (**7**) and 3-*n*-butyl-4-methyl-1,2,5-thiadiazole (**5f**) (80 mg, 26%). TLC (R_f = 0.70, CCl₄ : CHCl₃ = 2 : 1) of which showed one spot and HPLC analysis (μ Bondapak, acetonitrile, flow rate 0.5 mL/min, retention time 11.400) failed. The mixture was resolved by GC-MS:

Compound	MS (m/z) (rel. int.)
5f	156 (M ⁺ , 7.82), 141 (M ⁺ - Me, 8.40), 127 (M ⁺ - Et, 23.10), 114 (M ⁺ - CH ₃ CHN, 100), 73 (CH ₃ CNS, 18.02)
7	156 (M ⁺ , 27.36), 141 (M ⁺ - Me, 46.86), 128 (M ⁺ - CH ₃ CH, 100), 113 (M ⁺ - <i>n</i> -Pr, 2.08), 101 (M ⁺ - CH ₃ CH ₂ CN, 5.58), 87 (CH ₃ CH ₂ CNS, 13.84)

ACKNOWLEDGMENT

The authors are grateful for financial support by the Basic Science Research Institute Program (BSRI-97-3414) and the Research Institute of Molecular Science.

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Received, 12th June, 1998