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TAPC-Promoted Oxidation of Sulfides and Deoxygenation of Sulfoxides

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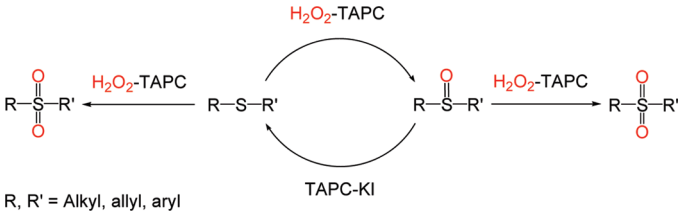


1,3,5-Triazo-2,4,6-triphosphorine-2,2,4,4,6,6-tetrachloride (TAPC) was found to be an efficient promoter for the oxidation of sulfides and deoxygenation of sulfoxides. Excellent yields, short reaction time, easy and quick isolation of the products, solvent-free process, and excellent chemoselectivity are the main advantages of this procedure.

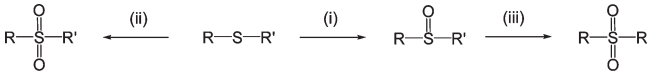
Introduction

During the last few decades, a central objective in synthetic organic chemistry has been to develop greener and more economically competitive processes for the efficient synthesis of biologically active compounds with potential application in the pharmaceutical or agrochemical industries. Organic reactions under solvent-free conditions have gained in popularity in recent years.[1] The solvent-free approach is simple with amazing versatility. It reduces the use of organic solvents and minimizes the formation of other waste. The reactions occur under mild conditions and usually require easier workup procedures and simpler equipment. Moreover, solvent-free processes often exhibit significant rate enhancements due to increased reactant concentrations.[2]

Sulfoxide reactions have significant importance in organic chemistry, medicinal chemistry, and drug metabolism.[3] Sulfones are useful reagents in organic synthesis, and they are also valuable synthetic intermediates for the construction of chemically and biologically important molecules.[4] The increasing interest and applications of sulfoxides and sulfones have stimulated investigations on new methodologies for the preparation of these compounds.

Despite a number of alternative methods available for the synthesis of sulfoxides and sulfones, oxidation of sulfides to the corresponding sulfoxides or sulfones is the most favored method. The popularity of this method is due to the availability

SCHEME 1[a]



[a]Reagents and conditions: (i) H_2O_2 (1 mmol), TAPC (0.1 mmol), solvent-free, 25 °C; (ii) H_2O_2 (2 mmol), TAPC (0.1 mmol), solvent-free, 25 °C; (iii) H_2O_2 (1 mmol), TAPC (0.1 mmol), solvent-free, 25 °C.

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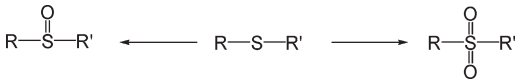
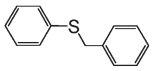
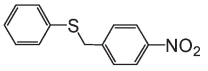
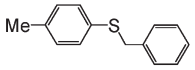
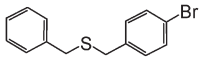
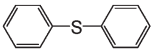
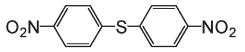
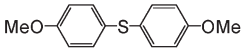
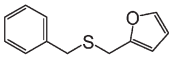
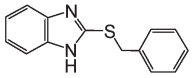
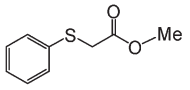
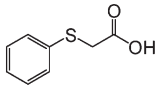
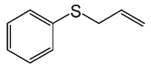
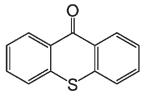
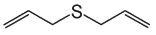
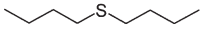
TABLE 1. Selective Oxidation of Sulfides to Sulfoxides or Sulfones[a]



Entry	Substrate	Sulfoxide[a]		Sulfone[a]	
		Yield%[b] (t/min)	Mp (°C)[Ref.]	Yield%[b] (t/min)	Mp (°C)[Ref.]
1		99 (5)	121-122[8a]	99 (13)	146-147[12a]
2		95 (9)	162[5f]	96 (15)	204-205[5f]
3		95 (5)	122-123[8b]	97 (9)	143-145[5g]
4		94 (7)	138-139[5f]	93 (17)	177-178[5f]
5		93 (13)	69-70[8c]	95 (17)	125-126[12a]
6		90 (20)	179-181[7f]	91 (35)	275-277[11f]
7		94 (8)	92-93[7f]	97 (15)	128-130[11g]
8		95 (7)	72-74	96 (12)	84-85[12b]
9		92 (12)	171-172[5i]	93 (15)	215
10		91 (10)	Oil[5i]	92 (18)	Oil[12c]
11		98 (7)	109-111[8d]	92 (16)	111[8d]
12		97 (5)	Oil[8b]	98 (9)	Oil[5g]
13		97 (7)	199-201[8e]	97 (10)	186-188[12d]
14		92 (6)	Oil[5i]	95 (15)	Oil[12e]
15		92 (9)	29-30[5h]	91 (18)	44-45[12a]

[a]The products were characterized by comparison of their spectroscopic and physical data with authentic samples synthesized by reported procedures. [b]Isolated yields.

of a wide variety of sulfides that can be utilized in the oxidation of sulfides to the corresponding sulfoxides or sulfones. Several procedures for the synthesis of sulfoxides[5−8] and sulfones[9−12] have been developed. However, only a few

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reports are available where a given oxidant is suitable for the controlled synthesis of sulfoxides and sulfones.[13]

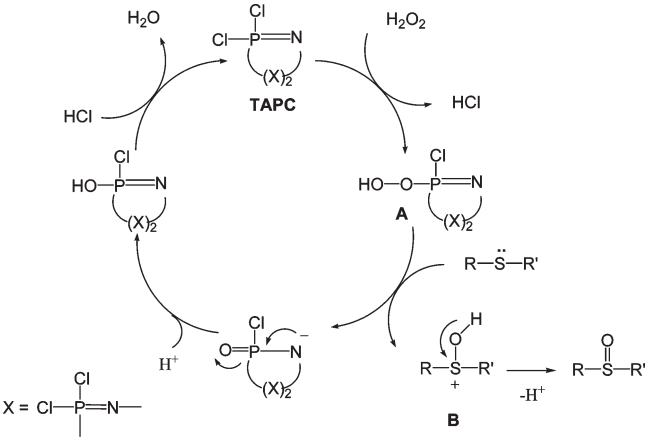
It is often noticed that sulfide oxidation is accompanied by several disadvantages such as long reaction times, low yields, inconvenient reaction conditions, expensive oxidants, undesired side reactions at other functionalities, and the use of organic solvents.

Hydrogen peroxide, in contrast to other oxidizing agents, is the most attractive from an environmental viewpoint. It is an ideal waste-avoiding oxidant since water is the only theoretical byproduct and is very attractive as an oxidant for liquid-phase reactions because of its solubility in water and many organic solvents.[14,15] Moreover, aqueous hydrogen peroxide solution shows safety in storage, operation, and transportation, is easily available on the market, and is relatively cheap.[16,17]

1,3,5-Triazo-2,4,6-triphosphorine-2,2,4,4,6,6-tetrachloride, commonly called hexaclorocyclo(triphos-phazene) or trimeric phosphonitrilic chloride, has been widely used in organic reactions;[18] however, it has not been studied as a promoter in the oxidation of sulfides and the deoxygenation of sulfoxides until now.

Recently, we reported several new synthetic methods for environmentally benign reactions using aqueous 30% hydrogen peroxide.[19,5f–i] Herein, we wish to report an efficient protocol in which H_2O_2 has been used as the oxidizing agent in the presence of TAPC for the chemoselective oxidation of sulfides to their sulfoxides in excellent yields and short reaction times (Scheme 1).

SCHEME 2. Proposed Mechanism for the Oxidation of Sulfides



Results and Discussion

In the first step, we carried out a set of initial experiments on benzyl phenyl sulfide (1 mmol) as a model substrate using 30% H_2O_2 (1 mmol) in the presence of 0.05, 0.075, and 0.1 mmol of TAPC under solvent-free conditions at room temperature. The best result (99% yield) was obtained by carrying out the reaction with 1:1:0.1 mol ratios of sulfide, H_2O_2, and TAPC for 5 min.

It is noteworthy that in a blank experiment, no significant oxidation was observed under similar reaction conditions in the absence of TAPC, and only a low yield (35%) was obtained in the presence of 1 mmol of H_2O_2 after 6 h.

In order to study the generality of this procedure, a series of sulfides having varied R and R′ groups containing aromatic, allylic, and aliphatic groups attached to the sulfur atom was reacted according to optimized reaction conditions, and the results are presented in Table 1. As shown, dialkyl, diallyl, diaryl, and aryl−allyl sulfides were oxygenated, and most of the reactions proceeded nearly quantitatively. All of the reactions occurred with complete selectivity for sulfoxide formation in excellent yield without any noticeable overoxidation to sulfones. These substrates selectively underwent oxidation at the sulfur atom without undergoing further structural changes in their functional groups as suggested by NMR analyses of the products. For example, in the case of allylic sulfides, no over oxidation to the sulfones or hydrochlorination of the double bond was observed, and only the corresponding sulfoxides were obtained in excellent yields (Table 1, entries **12** and **14**). Acid sensitive sulfides such as 2-[(benzylthio)methyl] furan worked well without the formation of any side products, which are normally observed either in the presence of protic or Lewis acids (Table 1, entry **8**). Interestingly, the presence of ester and carboxyl groups did not interfere with the oxidation process of the sulfide, and desired sulfoxides were obtained in excellent yields (Table 1, entries **10** and **11**). The protocol worked efficiently in oxidizing 2-(benzylthio)benzimidazole to afford the corresponding sulfoxide (Table 1, entry **9**). This procedure can also be applied to the oxidation of cyclic sulfides (Table 1, entry **13**).

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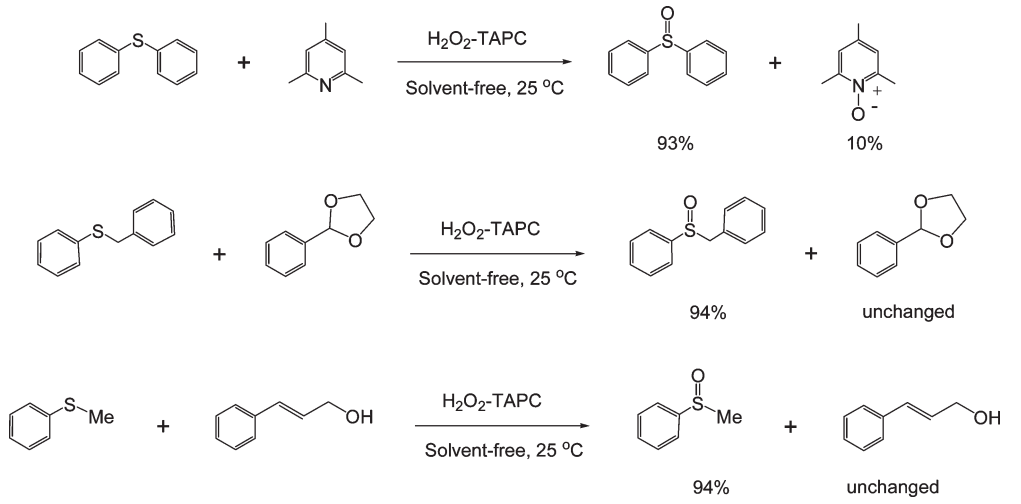
SCHEME 3[a]



[a]Reagents and conditions: molar ratio of substrates to H_2O_2 to TAPC (1:1:1:0.1), solvent-free, 25 °C.

To investigate the reaction mechanism, a competition oxidation of bis(4-methoxyphenyl), bis(4-nitrophenyl), and diphenyl sulfides was carried out under the same reaction conditions described above for 13 min to give 47%, 14%, and 28% yields of the corresponding sulfoxides, respectively. The results indicate that the sulfur atom of these sulfides bearing an electron-donating group of 4-methoxy is oxidized more rapidly than that bearing an electron-withdrawing group of 4-nitro due to its more nucleophilic character.

A plausible reaction mechanism is shown in Scheme 2. The nucleophilic attack of H_2O_2 on TAPC leads to the intermediate **A** in which oxygen atom is more electrophilic. Then, the nucleophilic attack of sulfide derivative on this intermediate gives the intermediate **B** followed by the abstraction of hydrogen to yield the corresponding sulfoxide.

In order to show the chemoselectivity of the described method, we have also performed several competitive reactions (Scheme 3). The experimental results show that the reaction tolerates sensitive functional groups such as pyridine, acetal, and alcohol and that only the sulfur atom is selectively oxidized. These selectivities are practical achievements in organic synthesis.

In order to demonstrate the efficiency and applicability of the H_2O_2−TAPC system further, the chemoselective oxidation of sulfides to sulfones was also investigated (Scheme 1). The same reaction conditions were applied for the preparation of sulfones via the oxidation of sulfide (1 mmol), H_2O_2 (2 mmol), and TAPC (0.1 mmol). A series of structurally diverse sulfides was then reacted with this remarkably simple procedure, and the results of these studies are collected in Table 1. As can be seen, all substrates including aliphatic, aromatic, allylic, benzylic, and heterocyclic sulfides were oxygenated, and most of the reactions proceeded nearly quantitatively. All of the reactions occurred with complete selectivity for sulfone formation, no products such as sulfoxides were detected in the reaction mixtures. The selectivity of the present method is fairly wide, as several functionalities remain unaffected under these reaction conditions.

In continuation of this work, we also investigated the reaction of a wide variety of structurally diverse sulfoxides with the H_2O_2−TAPC system (Scheme 1). When sulfoxides were reacted under similar reaction conditions, by using 1 equiv of 30% H_2O_2, sulfones were obtained in almost quantitative yields as the sole oxidation products. However, as can be seen from the data in Table 2, the chemoselectivity of this process is similar to that of the synthesis of sulfoxides.

Since the oxidation of sulfides proved the potential of TAPC as an effective and mild promoter agent, deoxygenation of sulfoxides to the corresponding sulfides was studied.

The deoxygenation of sulfoxides to sulfides is a valuable transformation in the application of organosulfur compounds in organic synthesis. Accordingly, several methods have been developed to reduce sulfoxides.[20−22] However, since many of these transformations are limited by side reactions, low yields, lack of chemoselectivity, unavailable reagents, or harsh conditions, a search for new improved methods based on easily accessible reagents and operationally simple procedures remains justifiable.

In continuation of our recent works on the deoxygenation of sulfoxides,[23] we describe the successful use of the TAPC−KI

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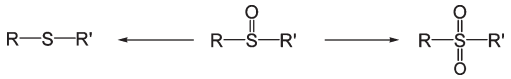
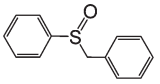
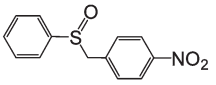
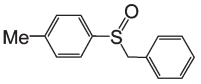
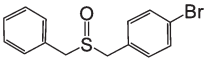
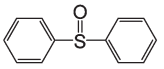
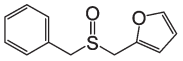
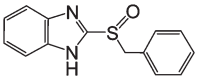
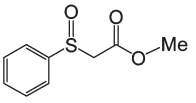
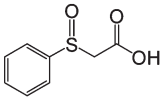
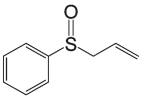
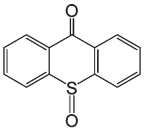
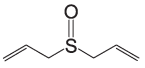
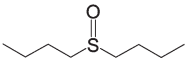
TABLE 2. Selective Oxidation and Deoxygenation of Sulfoxides



Entry	Substrate	Sulfone[a]	Sulfide[a]	
		Yield%[b] (t/min)	Yield%[b] (t/min)	Mp (°C)[Ref.]
1		99 (10)	98 (1)	45-46[24a]
2		95 (14)	92 (3)	73-74[24b]
3		96 (5)	94 (2)	44-45[24b]
4		94 (11)	96 (2)	Oil[24c]
5		97 (16)	91 (2)	Oil[24d]
6		93 (11)	97 (2)	Oil[24e]
7		94 (13)	95 (3)	184-185
8		95 (13)	92 (3)	Oil[24f]
9		97 (12)	98 (5)	60-61[24g]
10		95 (8)	92 (4)	Oil[24h]
11		98 (7)	94 (2)	207-208[24i]
12		99 (11)	93 (2)	Oil[24j]
13		92 (13)	91 (2)	Oil[24d]

[a]The products were characterized by comparison of their spectroscopic and physical data with authentic samples synthesized by reported procedures. [b]Isolated yields.

system as an efficient method to deoxygenate sulfoxides to the corresponding sulfides (Scheme 4).

The optimum molar ratio of sulfoxide to TAPC to KI (1:1:2.5) is found to be ideal for the complete conversion of sulfoxide into sulfide under solvent-free conditions, while with lesser amounts, the reaction remains incomplete (Figure 1).

Under these optimized reaction conditions, the generality and scope of this new protocol was then explored. A range of structurally diverse sulfoxides were subjected under solvent-free conditions to produce the corresponding sulfides. The results are presented in Table 2. Both aromatic and aliphatic, cyclic and acyclic, sulfoxides can be reduced to sulfides in excellent yields. This reaction is also compatible with other functional groups such as halo, ester, acid, alkene, and ketone (Table 2, entries **4** and **8**−**11**).

Attempts to convert aryl or alkyl sulfones into the corresponding sulfides with the TAPC−KI system were unsuccessful, and only low to moderate yields of the desired products

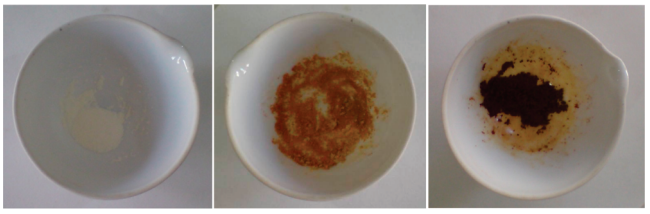
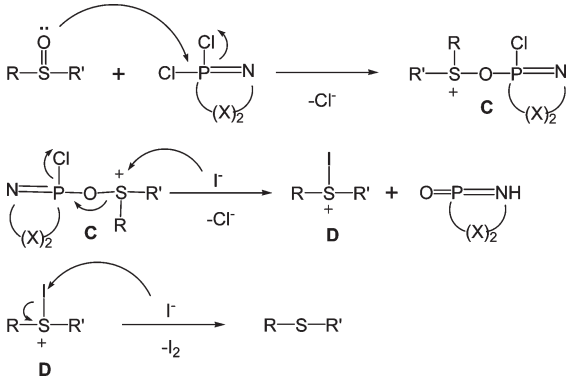


FIGURE 1. Illustration of the reaction of benzyl phenyl sulfoxide in the presence of TAPC (1 mmol) and KI (2.5 m mol) at (a) the beginning of the reaction time, (b) the middle of the reaction time, and (c) the end of the reaction time.

SCHEME 4[a]

[a]Reagents and conditions: TAPC (1 mmol), KI (2.5 mmol), solvent-free, 25 °C.

SCHEME 5. Proposed Mechanism for the Deoxygenation of Sulfoxides to the Corresponding Sulfides with the TAPC−KI System



were obtained even when the reaction was lengthened up to 2 h.

The possible mechanism for this reaction is outlined in Scheme 5. First, coordination of TAPC to the oxygen atom of the sulfoxide makes the sulfur atom more electrophilic. After that, the nucleophilic attack of the iodide anion on the sulfur atom in the intermediate **C** produces intermediate **D**. The resultant iodinated species (**D**) is in turn attacked by another iodide anion to give the deoxygenated sulfide and concomitantly I_2 (Figure 1).

Conclusions

In summary, H_2O_2−TAPC is an extremely efficient reagent system for selective oxidation of a variety of sulfides. Furthermore, we have shown the versatility of the TAPC−KI system as an excellent and convenient deoxygenation reagent for a series of sulfoxides. The advantages are the excellent yields, inexpensive nature and availability of the reagents, easy and clean workup process, safe nature for sensitive functional groups, the fact that it is a solvent-free process, and the ability to be operated at room temperature. This methodology also overcomes the formation of unwanted byproducts; thus, we believe that the present methodology opens new possibilities for medicinal chemistry and material sciences and could be an important addition to the existing methodologies.

Experimental Section

General Procedure for the Preparation of Sulfoxides. To the mixture of sulfide (1 mmol) and TAPC (0.1 mmol, 0.035 g), 30% H_2O_2 (1 mmol, 0.1 mL) was added at room temperature with continuous stirring for the desired time as indicated in Table 1. The progress of the reaction was monitored by TLC. After the completion of the reaction, H_2O (10 mL) was added to the reaction mixture. The residue was then extracted with EtOAc (4 × 5 mL), and the combined extracts were dried ($MgSO_4$). The filtrate was evaporated, and the corresponding sulfoxide was obtained as the only product.

General Procedure for the Preparation of Sulfones. To the mixture of sulfide (1 mmol) and TAPC (0.1 mmol, 0.035 g) was added 30% H_2O_2 (2 mmol, 0.2 mL). The mixture was stirred at room temperature for the appropriate period of time until the complete consumption of starting material as observed by TLC. After the completion of the reaction, H_2O (10 mL) was added to the reaction mixture. The residue was then extracted with EtOAc (4 × 5 mL), and the combined extracts were dried ($MgSO_4$). The filtrate was evaporated and the corresponding sulfone was obtained as the only product (Table 1). An identical procedure was employed using sulfoxide (1 mmol) 30% H_2O_2 (1 mmol, 0.1 mL) and TAPC (0.1 mmol, 0.035 g), for the oxidation of sulfoxides to sulfones (Table 2).

General Procedure for the Deoxygenation of Sulfoxides. A mixture of sulfoxide (1 mmol), KI (2.5 mmol, 0.42 g), and TAPC (1 mmol, 0.35 g) in a mortar was prepared. The mixture was ground with a pestle for the length of time provided in Table 2. The progress of the reaction was monitored by TLC. When the starting sulfoxide had completely disappeared, the mixture was quenched by adding H_2O (10 mL). The product was extracted with EtOAc (4 × 5 mL), and the combined extracts were dried ($MgSO_4$). The filtrate was evaporated, and the corresponding sulfide was obtained as the sole product. Spectral and analytical data for new compounds follow.

2-[(Benzylsulfinyl)methyl]furan. (Table 1, Entry **8**). Mp 72−74 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.91 (d, 2 H, J = 14 Hz), 4.03 (d, 2 H, J = 14 Hz), 6.41−6.44 (m, 2 H), 7.31−7.46 (m, 5 H), 7.48 (dd, 1 H, J = 1.24, 2.49 Hz). ^{13}C NMR (50 MHz $CDCl_3$) δ: 48.8, 57.1, 111.2, 111.6, 128.4, 128.9, 129.6, 130.3, 143.5, 143.9. Anal. Calcd for $C_{12}H_{12}O_2S$: C, 65.43; H, 5.49; S, 14.56. Found: C, 64.82; H, 5.49; S, 13.94.

2-(Benzylsulfonyl)-1*H*-benzo[*d*]imidazole. (Table 1, Entry **9**). Mp 215 °C. ^{1}H NMR (DMSO, 200 MHz): δ 4.96 (s, 2 H), 7.21−7.40 (m, 8 H), 7.68 (br, 2 H). ^{13}C NMR (50 MHz, DMSO) δ: 60.4, 121.1, 125.1, 127.5, 129.0, 129.2, 131.5, 135.5, 148.0. Anal. Calcd for $C_{14}H_{12}N_2O_2S$: C, 61.75; H, 4.44; N, 10.29; S, 11.77. Found: C, 61.47; H, 4.52; N, 9.73; S, 11.09.

2-[(Benzylthio)-1*H*-benzo[*d*]imidazole. (Table 2, Entry **7**). Mp 184−185 °C. ^{1}H NMR (200 MHz, DMSO) δ: 4.59 (s, 2 H), 7.11−7.16 (m, 2 H), 7.25−7.36 (m, 3 H), 7.45−7.50 (m, 4 H). ^{13}C NMR (50 MHz, DMSO) δ: 35.6, 114.4, 121.8, 127.8, 129.0, 129.3, 138.2, 140.1, 150.3. Anal. Calcd for $C_{14}H_{12}N_2S$: C, 69.97; H, 5.03; N, 11.66; S, 13.34. Found: C, 69.12; H, 5.01; N, 10.96; S, 12.96.

Acknowledgment. We are thankful to the Razi University Research Council for partial support of this work.

Supporting Information Available: Complete experimental procedures and relevant spectra (^{1}H NMR and ^{13}C NMR spectra) for some compounds. This material is available free of charge via the Internet at http://pubs.acs.org.