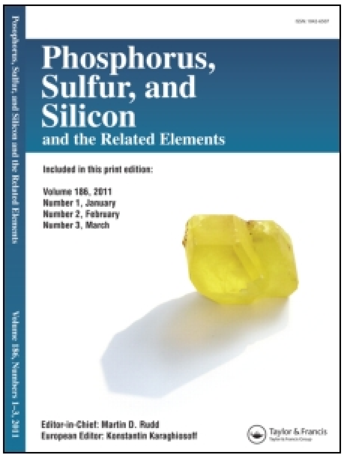

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A NOVEL METHOD OF SULFIDE SYNTHESIS FROM SULFOXIDES WITH *N,N*-DIMETHYLTHIOFORMAMIDE

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To cite this Article Kamijo, Haruo , Takido, Toshio , Nakazawa, Toshikatsu , Itabashi, Kunio and Seno, Manabu(1993) 'A NOVEL METHOD OF SULFIDE SYNTHESIS FROM SULFOXIDES WITH *N,N*-DIMETHYLTHIOFORMAMIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 82: 1, 207 — 210

To link to this Article: DOI: 10.1080/10426509308047423

URL: http://dx.doi.org/10.1080/10426509308047423

Phosphorus, Sulfur, and Silicon, 1993, Vol. 82, pp. 207–210
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Communication

A NOVEL METHOD OF SULFIDE SYNTHESIS FROM SULFOXIDES WITH *N*,*N*-DIMETHYLTHIOFORMAMIDE

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(Received March 15, 1993; in final form May 14, 1993)

Sulfoxides were deoxygenated by *N*,*N*-dimethylthioformamide (DMTF) to give quantitatively the corresponding sulfides in the presence of the catalytic amount of sulfuric acid under mild conditions. DMTF changes into dimethylformamide (DMF) by this reaction and it may be used in a recycling way, since DMF is converted into DMTF by diphosphorus pentasulfide in a good yield.

Key words: *N*,*N*-Dimethylthioformamide; reduction, sulfide synthesis.

INTRODUCTION

Sulfoxides are reduced to the corresponding sulfides with a reducing agent such as lithium aluminum hydride[1] and sodium borohydride.[2] It was found that diphosphorus tetraiodide,[3] diphosphorus pentasulfide,[4] phosphorus sulfide[5] and Lawesson reagent[6] convert sulfoxides into sulfides and thiourea also is effective in this reaction with the presence of iodine at 80°C.[7] We have investigated synthetic applications of *N*,*N*-dimethylthioformamide (DMTF) based on the nucleophilicity of the thiocarbonyl sulfur.[8] Previous papers deal with syntheses of thiols from alkyl halides[9] and of thioacides from acyl halides[10] with DMTF.

In this paper, we wish to report a novel route of synthesis of sulfides from the corresponding sulfoxide with DMTF. This reaction proceeds nearly quantitatively in the presence of a catalytic amount of sulfuric acid under the mild conditions. DMTF changes into dimethylformamide (DMF) by this reaction. It may be used in a recycling way, because DMF is converted into DMTF by diphosphorus pentasulfide in a good yield.

RESULTS AND DISCUSSION

Sulfide Synthesis from Sulfoxides with DMTF

It was found that diphenylsulfoxide (**1a**) reacts with DMTF (**2**) at a molar ratio of 1:2 to give nearly quantitatively diphenylsulfide (**3a**) in the presence of a catalytic amount (0.1 mol equivalent) of sulfuric acid at 80°C. During this reaction DMTF is converted to DMF (**4**) and elemental sulfur. If sulfuric acid is not added, the reaction does not proceed even at 150°C. As a catalyst, sulfuric acid is most effective among the acids tested including trifluoroacetic acid and *p*-toluenesulfonic acid. If the molar ratio of DMTF to sulfoxide is reduced from 2.0 to 1.2, the reaction proceeds to give sulfide in the yield of 80%. The result suggests that this reaction is essentially an equimolar reaction of sulfoxides with **2**. The reaction is found to proceed nearly quantitatively in acetone at 50°C under the conditions similar to the reaction without the solvent.

This synthetic method is useful as a general method of sulfide synthesis. As shown in Table I, not only symmetrical sulfoxides but also asymmetrical and cyclic sulfoxides are converted to the corresponding sulfides in good yields. A relatively low yield was found in the case of diphenylsulfoxide (**1a**) and *p,p'*-dichlorodiphenylsulfoxide (**1h**) at 30°C, but the reaction proceed nearly quantitatively at 80°C.

TABLE I

Reactions of sulfoxides (**1**) with DMTF (**2**)[a]

Entry	(1)		Yield(%)		b.p.[°C/760 torr] or m.p.(°C) of (3)
	R^1	R^2	(3)	(4)	
a	Ph	Ph	85	87	[42 - 43]
b	Bz	Bz	99	95	[49 - 50]
c	n-Bu	n-Bu	99	100	78 - 80
d	iso-Bu	iso-Bu	98	95	71 - 73
e	$-(CH_2)_4-$		100	97	118 - 119
f	Ph	Me	100	98	185 - 187
g	Ph	Bz	98	100	[48 - 49]
h	*p*-ClPh	*p*-ClPh	80	82	94 - 95

a) All the reactions were carried out in acetone at 30°C for 3h at the molar ratio 1 : 1.2 : 0.1 of sulfoxide, DMTF, and sulfuric acid.

TABLE II

Solvent effect on reactions of diphenylsulfide (**1a**) with DMTF (**2**)[a]

Entry	Mol. ratio		Solvent [ε]	React. Temp. (°C)	Products(%)		Recovered(%)	
	(1a)	:(2)			(3)	(4)	(1a)	(2)
1	1	2	-	80	96	78	+	58
2	1	2	C_6H_6 [2.3]	50	+	+	99	195
3	1	2	CH_2Cl_2 [8.7]	50	57	49	40	138
4	1	2	MeCN [37.5]	50	65	44	30	132
5	1	2	Me_2CO [20.8]	50	97	95	+	83
6	1	2	Me_2CO	30	78	71	10	98
7	1	1.2	Me_2CO	30	86	87	13	34

a) H_2SO_4 was used as a catalyst and its molar ratio is 0.1 against (1a). Yields were calculated based on (1a).

Solvent Effect

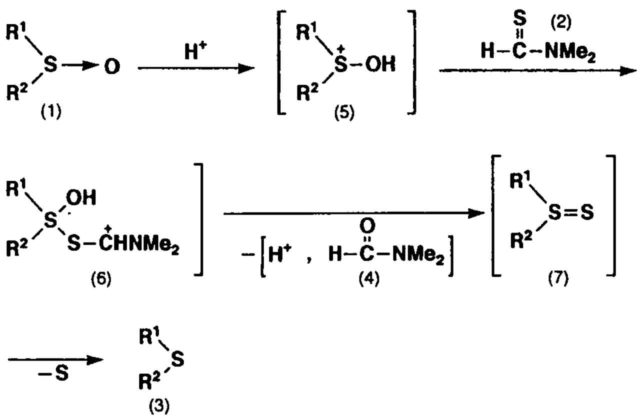
In Table II are shown the results of the reaction of diphenylsulfoxide carried out in various solvents. Clearly, the yield of sulfide decreases with a decrease in dielectric constant of solvent. The reaction hardly proceeds in a nonpolar solvent such as benzene. This suggests that the reaction is of ionic nature.

Reaction Mechanism

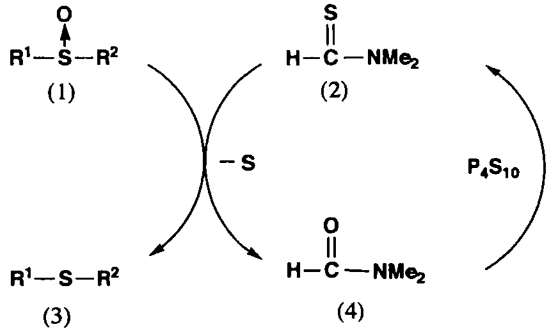
It could be supposed that the reaction precedes as shown in Scheme I. The protonation[11] of sulfoxide gives the intermediate (**5**) having a positively charged sulfur atom, which was confirmed by observation with NMR.[12] The nucleophilic attack of the thiocarbonyl sulfur of **2** affords thiosulfoxide (**7**)[13] by the elimination of **4** from Wittig-like four membered transition state (**6**)[4] and **7** is degraded to sulfide (**3**) and elemental sulfur.

Recycling of DMF

DMF (**4**) produced by the reaction could be converted to **2** by the treatment with phosphorus pentasulfide. Since this recovering reaction proceeds in a good yield, this synthetic method can be carried out in a recycling way as shown in Scheme II.



SCHEME I



SCHEME II

It is considered from this diagram that the method of sulfide synthesis developed in this study is the conversion of sulfoxide into the corresponding sulfide which is derived by the oxidation of diphosphorus pentasulfide into elemental sulfur via a cyclic reaction between **2** and **4**. Owing to this feature, this method will be useful for many practical applications.

EXPERIMENTAL

N,N-Dimethylthioformamide (DMTF, **2**) was obtained by the treatment of DMF with diphosphorus pentasulfide and was distilled at 68°C–69°C/l mmHg.[14]

A general method for the sulfide synthesis. A mixture of sulfoxide (**1**, 10 mmol), **2** (12 mmol) and sulfuric acid (1 mmol) in acetone (30 ml) was stirred at 30°C for 3 hours under nitrogen atmosphere. The precipitated yellow-greenish elmental sulfur was filtered off and sulfide (**3**) was obtained by removing the solvent and **4**.

Crude sulfide was recrystallized or distilled in vacuo for purification. The products were identified by the mixed mp test with the authentic samples.

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