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$P(MeNCH_2CH_2)_3N$: An Efficient Desulfurizing Reagent

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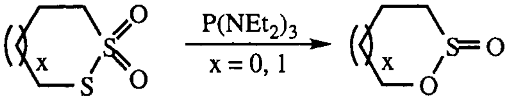
ABSTRACT: *The nonionic superbase $P(MeNCH_2CH_2)_3N$ (**A**) efficiently desulfurizes trisulfides to disulfides and monosulfides, disulfides to monosulfides, and propylene sulfide to propene. $S{=}P(MeNCH_2CH_2)_3N$ (**B**) was formed as the sulfur acceptor. $P(NMe_2)_3$ was a much poorer desulfurizing agent than **A** under the same reaction conditions. Thiocyanates and triphenylphosphine sulfide were also desulfurized with **A**, but N-(phenylthio)phthalimide formed [**A**-SPh]$^+$ phthalimide in quantitative yield.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10:544–547, 1999

INTRODUCTION

The desulfurization of organosulfur compounds with trivalent organophosphorus reagents has been studied for more than four decades. For example, one or more of the reagents triphenylphosphine [1–5], trisdimethylaminophosphine [4,6–8], trisdiethylaminophosphine [7–10], triethylphosphite [1], trimorpholinophosphine [4,7] and tributylphosphine [11,12] have been employed to convert trisulfides to the corresponding disulfides or monosulfides, *β*-keto sulfides to ketones, and sulfenimides to amines in moderate yields. Trisdiethylylaminophosphine usually removes sulfur more efficiently than trisdimethylaminophosphine from disulfides to form monosulfides under refluxing conditions (e.g., ≥ 80°C) [10]. Trialkyl phosphines can be used to remove sulfur from thioethers [13], thiols [14], and organometallic dithiocarboxylates [15], trisdiethylaminophosphine effects reaction 1; triphenylphosphite effects reaction 2 [16], and very recently thiol groups were reductively eliminated photochemically from L-cysteine derivatives in the presence of triethylphosphite and triethylboron [17]. Polymeric aminophosphines have also shown moderate to good efficiencies in the desulfurization of organic sulfides [18].



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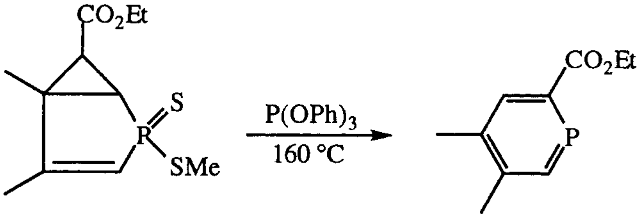

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In the course of our ongoing investigations on new synthetic applications of the exceedingly strong nonionic base and catalyst **A** first reported from our laboratories [19–21], we found that **B** could be formed from **A** in the presence of sulfur [22]. Recently, we found

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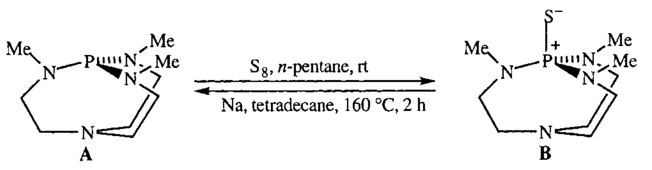
Dedicated to Alfred Schmidpeter on the occasion of his 70th birthday.



(3)

that **B** could be desulfurized with excess sodium in refluxing toluene or in tetradecane at 160°C. These results suggested a potential application of **A** in desulfurizing organosulfur compounds in a cyclic process, since **A** can be recycled as shown in Equation 3. Here we report desulfurizations with **A** under mild conditions.

Using 1.0 equiv of **A,** trisulfides were desulfurized primarily to disulfides with monosulfides as minor products at room temperature, and **B** was formed as the only other product (entries 1–3, Table 1). With more than 2.0 equiv of **A,** benzyl trisulfide was desulfurized to benzyl monosulfide via benzyl disulfide (entry 5, Table 1). Disulfides such as propyl, butyl, methyl benzyl, and benzyl disulfides were efficiently desulfurized to monosulfides at room temperature or at 40°C (entries 7, 12, 16, and 17, Table 1). Increasing the steric hindrance of the disulfide decidedly decreased the desulfurization rate (entries 8 and 14, Table 1). Although (Et$_2$N)$_3$P was effective for desulfurizing trisulfides to disulfides, disulfides to monosulfides, and some activated monosulfides to sulfur-free compounds [7–10], it showed poorer desulfurizing efficiency than **A** (Table 1, entries 4, 9, 15, and 17). Under the same reaction conditions (entries 6, 10, 11, and 13, Table 1), (Me$_2$N)$_3$P showed much poorer desulfurization efficiency. Using excess (Me$_2$N)$_3$P, benzyl trisulfide was desulfurized to benzyl disulfide (39.6%) and benzyl monosulfide (42.9%) in THF at room temperature within 25.5 hours, but at the same temperature it was quantitatively desulfurized by **A** to benzyl monosulfide within 3 hours (entries 5 and 6, Table 1). For disulfides, (Me$_2$N)$_3$P led to poor desulfurization efficiencies (entries 10, 11, and 13, Table 1). Phenyl disulfide could not be efficiently desulfurized at room temperature by **A,** and raising the temperature led to the formation of **C** (entry 19, Table 1). Analogs of **C** have

TABLE 1 Desulfurization of Trisulfides, Disulfides, and Monosulfides using **A**[a]

Entry	*Sulfide*	*Equiv of A*[b]	*Solvent*	*Temp/Time (°C/h)*	*Product(s)*[c] *(% yield)*
1	PrS$_3$Pr	1.0	THF	rt/4	PrS$_2$Pr (95.0), PrSPr (2.2)
2	BuS$_3$Bu	1.0	THF	rt/4	BuS$_2$Bu (95.0), BuSBu (2.0)
3	BnS$_3$Bn	1.0	THF	rt/3	BnS$_2$Bn (74.0), BnSBn (12.4)
4	BnS$_3$Bn	~1.1[d]	C$_6$H$_6$	rt/3	BnS$_2$Bn (94.0) [7]
5	BnS$_3$Bn	2.2	THF	rt/1.5	BnS$_2$Bn (94.0), BnSBn (2.8)
				rt/3	BnSBn (>99.0)
6	BnS$_3$Bn	2.2[e]	THF	rt/3	BnS$_2$Bn (7.7), BnSBn (36.7)
				rt/25	BnS$_2$Bn (39.6), BnSBn (42.9)
7	PrS$_2$Pr	1.1	C$_6$H$_6$	40/26	PrSPr (100)
8	^{i}PrS$_2$ ^{i}Pr	1.1	toluene	110/17	^{i}PrS^{i}Pr (30.0)
				110/64	^{i}PrS^{i}Pr (100)
9	^{i}PrS$_2$ ^{i}Pr	1.2[d]	C$_6$H$_6$	80/48	^{i}PrS^{i}Pr (<50) [10]
10	PrS$_2$Pr	1.1[e]	C$_6$H$_6$	40/26	PrSPr (11.0)
11	PrS$_2$Pr	2.2[e]	C$_6$H$_6$	40/26	PrSPr (38.8)
12	BuS$_2$Bu	1.1	C$_6$H$_6$	40/26	BuSBu (100)
13	BuS$_2$Bu	1.1[e]	C$_6$H$_6$	40/26	BuSBu (10.4)
14	^{t}BuS$_2$ ^{t}Bu	1.1	toluene	110/17	^{t}BuS^{t}Bu (10.7)
				110/65	^{t}BuS^{t}Bu (45.0)
15	^{t}BuS$_2$ ^{t}Bu	>100[d]	–	80/48	^{t}BuS^{t}Bu (1.0) [10]
16	BnS$_2$Me	1.0	THF	rt/19	BnSMe (97.0)
17	BnS$_2$Bn	1.0	THF	rt/1	BnSBn (98.0)
18	BnS$_2$Bn	1.2[d]	C$_6$H$_6$	80/4	BnSBn (92.0) [10]
19	PhS$_2$Ph	1.0	THF	rt/48	PhSPh (<5.0)
		1.2	tetradecane	160/18	PhSPh (7.0), C (90.0)[f]
20	propylene sulfide	1.0	C$_6$H$_6$	rt/19[g]	propylene (>95.0)

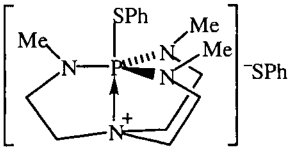
[a] Reaction conditions: 0.1 MPa, sulfide (1.0 mmol), solvent (5 mL).
[b] **A** was used in all cases except where indicated.
[c] The products were analyzed by GC.
[d] P(NEt$_2$)$_3$ used as the base instead of A.
[e] P(NMe$_2$)$_3$ used as the base instead of A.
[f] Determined by ^{31}P NMR spectroscopy.
[g] The reaction time was not optimized.

TABLE 2 Desulfurization of other Sulfur Containing Substrates using **A**[a]

Entry	*Substrate*	*Equiv of* **A**	*Solvent*	*Temp/Time (°C/h)*	*Product(s)*[b] *(% yield)*
1	EtSCN	1.0	THF	40/10	EtCN (95.0)
2	$PhCH_2SCN$	1.0	CH_3CN	35/14	$PhCH_2CN$ (95.0)
3	*N*-(phenylthio)phthalimide	1.0	pentane	rt/14	**E** (99.0)[c]
4	$Ph_3P=S$	1.1	toluene	110/20	Ph_3P (60.0)[d]
5	$Bu_3P=S$	1.1	toluene	110/20	Bu_3P (<5.0)
6	$(Me_2N)_3P=S$	1.1	toluene	110/20	$(Me_2N)_3P$ (<5.0)[d]

[a] Reaction conditions: 0.1 MPa, substrate (1.0 mmol), solvent (5 mL).
[b] The products were analyzed by GC.
[c] Product **E** was characterized by ^1H, ^{13}C, and ^{31}P NMR and elemental analysis.
[d] The yield was obtained by ^{31}P NMR integrations.

been observed in desulfurizations using trialkylaminophosphines [10]. The ^{31}P NMR spectrum of the reaction mixture of phenyl disulfide with **A** in tetradecane at 160°C revealed a major peak at 45.1 ppm in addition to a small peak at 76.3 ppm (assigned to **B**). Acidifying the same reaction mixture with 1N HCl led to the formation of phenylthiol, which was detected by GC–MS analysis. Interestingly, propylene sulfide in the presence of **A** lost sulfur to give propene in high yield at room temperature (entry 20, Table 1).



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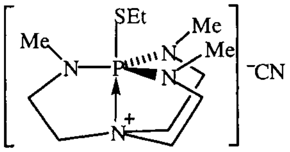
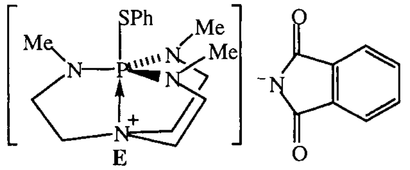


D



E

(4)

Thiocyanates were desulfurized by **A** to their corresponding cyanides (entries 1, 2, Table 2). In the reaction of ethyl thiocyanate with **A** at room temperature, **D** ($\delta^{31}P = 50.7$ ppm) and **B** were formed in roughly equivalent amounts according to ^{31}P NMR integration, but raising the temperature decomposed **D** to ethyl cyanide and **B** presumably via nucleophilic attack of cyanide anion at the Et-S bond. **A** and N-(phenylthio)phtahalimide reacted cleanly at room temperature forming **E** quantitatively [23]. Analogs of **E** wherein the cation is $ArSP(NMe_2)_3^+$ (Ar = Ph or *p*-MeC_6H_4) were reported (on the basis of transient ^{31}P chemical shifts at ca. −60 ppm) in the desulfurization of the corresponding thioaryl phthalimides [24]. Triphenylphosphine sulfide was desulfurized in moderate yield by **A** (60%, entry 4, Table 2) indicating that **A** is the stronger desulfurizing reagent. However, neither $Bu_3P=S$ nor $(Me_2N)_3P=S$ was desulfurized by **A** under conditions employed herein.

General Procedure for Desulfurization with **A**

Under argon, 1.0 mmol of substrate was added to a solution of **A** in the solvent and the reaction was carried out under the conditions stated in Tables 1 and 2. The reaction mixtures were subjected to GC, GC–MS, or ^{31}P NMR analyses.

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[23] Compound **E,** a yellow crystalline solid, was obtained by evaporating the solvent from the reaction mixture. ^{1}H NMR (CDCl$_3$): δ7.83, 7.67, 7.62, 7.43, 7.34, and 7.23 (1:1:2:3:1:1 H, m each, 9C*H* aromatic protons), 2.98 and 2.94 (6H, t each, 3CH$_2$), 2.76 (6H, t, 3CH$_2$), 2.73 (9H, d, 3CH$_3$). ^{13}C NMR (CD$_3$CN): δ174.9 (C = O), 135.8, 135.7, 131.4, 131.2, 131.1, 130.8, 130.7, 130.7, 129.6, 127.3, 51.78, 50.54(d), 37.65(d). ^{31}P NMR: δ44.3 ppm. Anal. calcd. for C$_{14}$H$_9$NO$_2$SP (255.3): C, 65.87; H, 3.55; N, 5.49. Found: C, 65.42; H, 3.40; N, 5.30.

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