

**NOVEL DESULFURIZATION OF THIOCARBONYL COMPOUNDS INTO THEIR
CORRESPONDING OXO-DERIVATIVES USING A PEROXY-SULFUR INTERMEDIATE
GENERATED FROM 2-NITROBENZENESULFONYL CHLORIDE AND SUPEROXIDE ANION.**

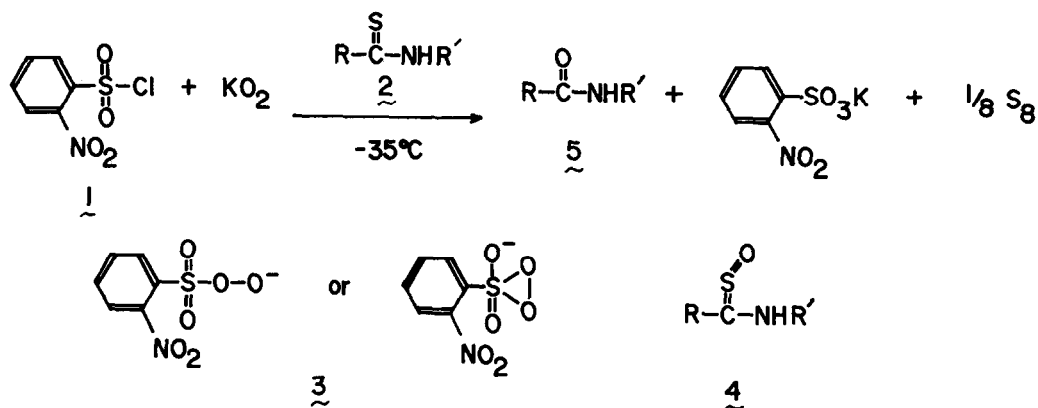
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Summary. Thiocarbonyl compounds such as substituted-thioureas, -thioamides, and -thiocarbamates were found to react with a peroxysulfur intermediate (3) which is generated by the treatment of 2-nitrobenzenesulfonyl chloride with potassium superoxide to convert into the corresponding carbonyl compounds in quantitative yield at -30°C in acetonitrile.

Considerable interest has recently been focused on the desulfurizations of thiourea derivatives using superoxide anion¹⁻³ and a related system of alkaline autoxidation⁴ since oxidative desulfurizations of cyclic thioureas of thiouracil, ethionamide and thiobarbital are known to occur in vivo metabolism to form the corresponding carbonyl compounds though there is no direct evidence for involving any activated oxygen like superoxide which is distributed widely in living cells.^{5,6} We recently reported that a peroxysulfur intermediate (3) is an excellent oxidizing reagent for the facile and regioselective epoxidation of olefins.⁷ We have now found that various thiocarbonyl derivatives such as thioureas, thioamides, and thiocarbamates were readily desulfurized into their carbonyl compounds quantitatively by addition of 2-nitrobenzene sulfonyl chloride to the reaction mixture of the substrates and potassium superoxide ($\text{O}_2^{\cdot-}$) at -35°C in acetonitrile. The work up is simple: after monitoring the complete reaction by t.l.c. on silica gel, filtration and concentration give a highly pure product.

In a general procedure, a solution of 2-nitrobenzene sulfonyl chloride (0.151g, 0.68 mmol) and 4-(p-nitrothiobenzoyl)-morpholine (0.09g, 0.47 mmol; CH_3CN , 1.5 ml) was added to a heterogeneous solution of potassium superoxide (0.15g, 2.045 mmol; CH_3CN , 1.0 ml) at ca. -35°C under dry argon atmosphere. After being stirred for ca. 5.0h at -35°C with good stirring, the reaction mixture was filtered, and washed with CH_3CN : concentration of CH_3CN layer gave the highly pure amide (0.088g, 98%) and sulfur (S_8 , 0.014g, 88%) without accompanying other side products. Further purification by recrystallization from hot-water afforded pure amide (0.082g, 91%). The products obtained were identified by comparing their i.r. and ^1H n.m.r., and mp. with those of authentic samples. Results obtained are summarized in Table I.







In contrast to the previous results^{2,3} obtained from the desulfurization of thioureas with $\text{O}_2^{\cdot-}$ in the absence of 1 at 25°C , our new method takes an advantage to result in a clean and quantitative conversion of the thiocarbonyl compounds into their corresponding oxygen analogues without the side or intermediate products formation at -35°C . The desulfurization appears to be initiated via the oxidation with a peroxysulfur intermediate, 3 which is formed by a nucleophilic attack of $\text{O}_2^{\cdot-}$ on the sulfonyl sulfur of 1 and may have an oxidizing ability to oxidize 2 to 4 though 3 has neither been isolated nor confirmed.⁸ The sulfine intermediate, 4 may quickly convert to the products, 5 by an intramolecular desulfurization like the case of the oxidation of thiones to the ketones through the sulfine intermediates.⁹

The reaction mechanism is apparently different from that of the direct desulfurization of thioureas by $\text{O}_2^{\cdot-}$ ^{2,3} in the absence of 1, where potassium sulfate was obtained together with ureas and guanidines at 25°C , but desulfurization did not occur at -35°C : namely starting material for instance, diphenylthiourea was recovered quantitatively.

However our new reaction results in elementary sulfur (88%) and only carbonyl compounds quantitatively. It is noteworthy that though the usual desulfurization of 1,3-diphenyl-1-ethylthiourea gave a poor yield of the urea analogue probably due to the steric hindrance of the bulky groups of diphenyl and ethyl ones, the new reaction yielded excellent yield of the urea (run 9 88%) under mild conditions. There have been quite intensive studies on the transformation of the thiocarbonyl groups into their corresponding oxo-analogues using various reagents such as nitric acid,¹⁰ mercuric acetate,¹¹ selenium dioxide,¹² potassium permanganate,¹³ manganese dioxide,¹⁴ alkyl nitrites,¹⁹ benzeneselenic anhydride,²⁰ and *m*-chloroperbenzoic acid²¹ with some degree of success. The work described herein may be more advantageous for synthetic use in view of the scope and chemical yield and sheds further light on the mechanism of oxidation by $O_2^{\cdot-}$.

Table 1. Desulfurization of Thiocarbonyl Compounds at -35°C in Acetonitrile

Run	Substrates	Reaction Time (h)	1:K ₂ O ₂ :2	Product 5(%) ^a	Reference ^b
1	$4\text{-NO}_2\text{-C}_6\text{H}_4\text{-C(=S)-N}$ 	5.0	1:3:0.6	91(98) ^c	22
2	"	6.5	1:1.5:0.6	90(98) ^c	
3	$\text{C}_6\text{H}_5\text{-C(=S)-NHCH}_3$	5.0	1:3:0.6	86	23
4	$\text{C}_6\text{H}_5\text{-C(=S)-NH-nPr}$	5.5	1:3:0.6	92	24
5	$\text{C}_6\text{H}_5\text{-C(=S)-NH-C}_6\text{H}_5$	6.5	1:3:0.6	91	25
6	$4\text{-Cl-C}_6\text{H}_4\text{-C(=S)-NHCH}_3$	4.5	1:3:0.6	86	26
7	$\text{CH}_3\text{-C(=S)-NH-C}_6\text{H}_4\text{-NO}_2\text{-4}$	5.0	1:3:0.6	95	26
8	$\text{C}_6\text{H}_5\text{NH-C(=S)-NHEt}$	5.5	1:3:0.6	91	27
9	$\text{Ph(Et)N-C(=S)-NHPh}$	6.5	1:3:0.6	88	28
10	PhNH-C(=S)-NH 	6.0	1:3:0.6	89	29
11	Ph-S-C(=S)-N 	5.0	1:3:0.6	93	30
12	Ph-S-C(=S)-N 	8.5	1:1.5:0.6	87	
13	$\text{Ph-CH}_2\text{NH-C(=S)-C(=O)-NHCH}_2\text{Ph}$	7.0	1:3:0.6	92	

a) Isolated yields (purified by crystallization)

b) The data of all the products are identical with those from known compounds

c) Crude yields without crystallization

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References and Notes

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8. Though the conceivable peroxy-sulfur intermediate that seems to have potential oxidizing abilities has neither been isolated nor detected, it can be demonstrated to be structure **3** like a persulfoxide ($\begin{array}{c} \text{R} \diagup \text{S} \text{O} \text{O}^- \\ \text{R} \diagdown \end{array}$, $\begin{array}{c} \text{R} \diagup \text{S} \text{O} \\ \text{R} \diagdown \text{O} \end{array}$) suggested by Burgess, et al. E.M. Burgess, U. Zoller, and R.L. Burger, Jr., *J. Am. Chem. Soc.*, **106**, 1128 (1984).
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