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OXIDATION OF SULFIDES TO SULFOXIDES WITH N-CHLORO NYLON-66

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Sulfides are almost quantitatively converted into the corresponding sulfoxides by N-chloro nylon-66 in the presence of water or alcohol.

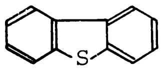
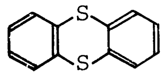
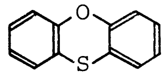
Several methods have been developed for the oxidation of sulfides to the corresponding sulfoxides using N-halogen compounds, such as N-chloro-[1)] and N-bromo-succinimide,[2)] 1-chlorobenzotriazole,[3)] chloramine-B,[4)] and bromine complex of diazabicyclo[2,2,2]-octane,[5)] as oxidizer. In this communication, we wish to report the oxidation of several sulfides with N-chloro nylon-66(NCN-66) which has similarly active halogen atoms in polyamide molecule.

As was expected from its structure, we have found that NCN-66 can also cause the oxidation of sulfides specifically to the corresponding sulfoxides in the presence of water or alcohol. This oxidation is clean and very convenient, and proceeds almost quantitatively. Recently, R.C.Schulz et al.[6,7)] have reported that NCN-66 is also a good oxidizer of alcohols to the corresponding aldehydes or ketones. NCN-66 used here was prepared by the chlorination of nylon-66 with tert-butyl hypochlorite.[8)]

In a typical reaction, a sulfide(1 mmol) and NCN-66(1 mg-atom-Cl) were dissolved in 6 ml of benzene or dioxane, and then alcohol or water(in the case of dioxane solvent) was added quickly. The mole ratio of alcohol or water to the sulfide was 5-10 : 1. The mixture was stirred at 35-40°C. When the reaction mixture became muddy by the precipitation of nylon-66, it was poured into a large amount of ether, and nylon-66 precipitated was filtered off. The product was obtained from the ethereal filtrate, and its mp, IR and glc data were identical with those of the corresponding sulfoxide. The results of the oxidation are summarized in Table 1.

Table 1

Oxidation of Sulfides with NCN-66 at 35°C[a)]

Sulfide	Solvent[b)]	Reaction Time(hr)	Yield of Sulfoxide(%)
$C_6H_5SCH_3$	Benzene-MeOH	0.5	97
$C_6H_5CH_2SCH_2C_6H_5$	Benzene-MeOH	0.5	100
$C_6H_5CH_2SC_6H_5$	Benzene-MeOH	0.5	100
	Dioxane-H_2O	0.5	100
$C_6H_5SC_6H_5$	Benzene-MeOH	15	97
	Dioxane-H_2O	0.5	92
	Benzene-MeOH[c)]	20	Sulfone only
	Benzene-MeOH	21	100
	Benzene-MeOH	22	99
	Benzene-MeOH	24	99

a) NCN-66(g-atom-Cl)/Sulfide(mol) = 1.

b) Mole ratio of sulfide to alcohol or water is 1 : 10.

c) NCN-66(g-atom-Cl)/Sulfide(mol) = 3.

The reaction proceeds almost completely not only in benzene—methanol but also in dioxane—water without side reaction, while the reaction is faster in the latter. When the reaction was carried out in the same procedure described above, but using more than two equivalents of NCN-66, the only product obtained was the corresponding sulfone.

The possibility of ^{18}O-incorporation was then examined for the oxidation of diphenyl sulfide and benzyl phenyl sulfide to the corresponding sulfoxides using $H_2{}^{18}O$(1.46 atom%-^{18}O) in dioxane. As shown in Table 2, the oxygen of water was found to be incorporated almost quantitatively in the sulfoxides obtained. When the oxidation was carried out in a mixture of $H_2{}^{18}O$ and ordinary methanol(ca. 1 : 1 M/M), the degree of the ^{18}O-incorporation was found to be slightly lower.

For the oxidation in benzene-alcohol, a remarkable retardation of oxidation was observed in the case of the reaction in benzene—iso-propyl alcohol or benzene—tert-butyl alcohol, as shown in Table 3, which clearly indicates the importance of

Table 2

Oxidation in the Presence of $H_2{}^{18}O$ a)

Sulfide	Solvent	^{18}O-atom% of Sulfoxide
$C_6H_5SC_6H_5$	Dioxane-$H_2{}^{18}O$	1.41
	Dioxane-$H_2{}^{18}O$-MeOH b)	1.35
$C_6H_5CH_2SC_6H_5$	Dioxane-$H_2{}^{18}O$	1.43

a) Mass-spectrometric analysis was carried out with CO_2 gas method and atom%-^{18}O was calculated from the mass peak heights 44 and 46. $H_2{}^{18}O$ used is 1.46 atom%-^{18}O, natural CO_2 is 0.206 atom%-^{18}O. Sulfide = 1 mmol, NCN-66 = 1 mg-atom-Cl, $H_2{}^{18}O$ = 0.18 ml, dioxane = 6 ml; 30°C, 12 hr.

b) Methanol(0.4ml) was added to the system.

the steric effect in this reaction. This steric requirement with alcohols is closely similar to that observed in the oxidation of sulfides with tert-butyl hypochlorite in alcohols.[9)]

However, further investigation is necessary before we can obtain any clear understanding of the NCN-oxidation. The detailed studies of ^{18}O-experiments and kinetics now in progress will shed further light on this reaction.

Table 3

Yields of Diphenyl Sulfoxide with the Change of Alcohols Added (in benzene) a)

Alcohol	Yield of Sulfoxide (%)
Methanol	96.9
Ethanol	96.7
iso-Propyl alcohol	67.6
tert-Butyl alcohol	68.1

a) Diphenyl sulfide = 2 mmol, alcohol = 10 mmol, NCN-66 = 2 mg-atom-Cl, benzene = 10 ml; 35°C. 12 hr.

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7) More recently, at 164th National Meeting of ACS, Aug. 27- Sept. 1, New York, (1972), R.C. Schulz et al. have spoken on the subject of "N-Chloro-nylons as polymer reagents", and have reported that sulfides are also oxidized to the corresponding sulfoxides with N-chloro nylon by the similar procedure described in this communication.

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