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Deoxygenation of Sulfoxides to Sulfides in an Iodine–Pyridine–Sulfur Dioxide System

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Synopsis. Sulfoxides were deoxygenated quantitatively in an iodine–pyridine–sulfur dioxide system under mild reaction conditions. The same reaction also occurred with bromine.

An iodine–pyridine–sulfur dioxide system was found to be effective for the dehydration reaction between carboxylic acid and amine.[1] Deoxygenation of sulfoxides to sulfides was examined in this system in order to find a convenient and selective reduction method for sulfoxides.[2]

Sulfoxides were allowed to react with 1 equiv. mole of iodine in the presence of excess pyridine–sulfur dioxide complex (1 : 1 molar ratio) using acetonitrile as a solvent at 80 °C for 2 hr. The products were isolated and characterized by comparing the physical data with those of authentic samples.

$$\mathrm{RS(O)R}\ (1) \xrightarrow[\text{in acetonitrile, 80°C, 2 hr.}]{\mathrm{I_2}\ (1),\ \mathrm{SO_2}\text{-Pyridine}\ (10)} \mathrm{RSR}$$

The results obtained are summarized in Table 1. All the sulfoxides were selectively deoxygenated to give the corresponding sulfides in excellent yields. Although diphenyl sulfoxide was reduced slowly, diphenyl sulfide was obtained quantitatively when the reaction was continued for 18 hr.

TABLE 1. REDUCTION OF SULFOXIDES

Sulfoxide	Yield of Sulfide (%)	
	Reaction with Iodine[a]	Reaction with Bromine[b]
Diphenyl	20 95[c]	38
Dibenzyl	93	95
Di-*n*-butyl	84	73
Dimethyl	96	85
Tetramethylene	95	19

a) A solution of 1×10^{-3} mol of sulfoxide, 1×10^{-3} mol of iodine, 1×10^{-2} mol of sulfur dioxide–pyridine complex in 50 ml of acetonitrile was allowed to react at 80 °C for 2 hr. b) The reaction was carried out by keeping a mixture of 1×10^{-3} mol of sulfoxide, 1×10^{-3} mol of bromine and 1×10^{-2} mol of sulfur dioxide in 50 ml of acetonitrile at 80 °C for 2 hr. c) The reaction was carried out for 18 hr.

The reaction with bromine was carried out in the absence of pyridine, since in its presence α-bromination of the sulfoxide[3] competes with reduction. The reaction proceeded well, but in the case of tetramethylene sulfoxide a complex side-reaction took place.

In order to investigate the behavior of iodine we examined the UV spectra of iodine and tetraethylammonium iodide in the pyridine–sulfur dioxide–acetonitrile system.[4] No absorption of iodine was detected. An absorption considered to be that of iodosulfinate ion[5] was observed at 362 nm (ε, 7400 $\mathrm{l\cdot mol^{-1}\,cm^{-1}}$). The value is consistent with that of iodosulfinate ion in this system (ε, 8900 $\mathrm{l\cdot mol^{-1}\,cm^{-1}}$). It is reasonable to consider that iodine is dissociated into iodonium ion and iodosulfinate ion quantitatively. In the system of bromine–pyridine–sulfur dioxide, the absorption of bromosulfinate ion was also observed at 322 nm.[5]

In order to clarify the mechanism of the reaction, the following reactions were examined. When *N*-iodosuccinimide[6] or tetraethylammonium iodide was used instead of iodine, no reaction occurred suggesting the necessity of both iodonium and iodide ions for the reduction of sulfoxides. The reaction did not proceed either in the absence of sulfur dioxide. By the reaction of di-*n*-butyl sulfoxide with one third molar equiv. of iodine sulfide was obtained in 54% yield indicating that iodine works as a catalyst. No reversible reaction seems to occur in this system, since diphenyl sulfoxide was not obtained by the reaction of diphenyl sulfide with iodine in the presence of sulfur trioxide–pyridine complex.

The following scheme is considered to be the most plausible one for this novel deoxygenation reaction.

$$\mathrm{I_2} \xrightarrow{\mathrm{SO_2}} \mathrm{I^+} + {}^-\mathrm{SO_2I}$$

$$\mathrm{RS(O)R} \xrightarrow{\mathrm{I^+}} \mathrm{RS^+(I)(O)R} \xrightarrow{-\mathrm{SO_2I}} \mathrm{RS^{\delta+}(I)R}\ \ (\mathrm{OSO_2I^{\delta-}})$$

A

$$\mathrm{A} \longrightarrow \mathrm{RS^+(I)R} + {}^-\mathrm{SO_3I}$$

$$-\mathrm{SO_3I} + \mathrm{SO_2\cdot Py} \longrightarrow {}^-\mathrm{SO_2I} + \mathrm{SO_3\cdot Py}$$

Iodine ionizes to iodonium ion and iodosulfinate ion. Iodonium ion attacks sulfoxide first,[7] and then iodosulfinate ion may add to form intermediate A. Elimination of iodosulfonate ion and iodonium ion probably occurs from A to produce sulfide. Iodosulfonate ion formed would react with sulfur dioxide–pyridine complex generating again iodosulfinate ion with sulfur trioxide–pyridine complex.

Experimental

Reaction of Diphenyl Sulfoxide in the Iodine–Pyridine–Sulfur Dioxide System. In a round-bottomed flask fitted with a dry ice condenser was placed 2.52 g (0.01 mol) of iodine and 10 ml of pyridine–sulfur dioxide complex in 30 ml of acetonitrile. To this was added diphenyl sulfoxide (2.02 g,

0.01 mol) in 20 ml of acetonitrile over a period of 10 min at room temperature. The reaction mixture was kept at 80 °C for 2 hr, and then treated in the usual way. The product was analyzed with a Hitachi K-53 vpc apparatus equipped with a flame ionization detector.

Reaction of Diphenyl Sulfoxide in the Bromine-Sulfur Dioxide System. To a mixture of diphenyl sulfoxide (2.52 g, 0.01 mol) and bromine (1.6 g, 0.01 mol) in 50 ml of acetonitrile was added 5.0 ml of sulfur dioxide. The reaction mixture was kept at 80 °C for 2 hr and then extracted with ether and dried over anhydrous sodium sulfate. After removal of the solvent the product was analyzed by vpc. Diphenyl sulfide was obtained as the sole product.

References

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