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A Facile Synthesis of Sulfones by the Oxidation of Various Sulfides with Oxone in Aprotic Solvent in the Presence of "Wet-Montmorillonite"

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Oxidation of sulfide with Oxone in dichloromethane in the presence of wet-montmorillonite clay gave sulfones in excellent yields under mild conditions.

Oxone (1) is a stable ternary composite of $KHSO_5$, $KHSO_4$, and K_2SO_4 in 2:1:1 molar ratio.1) The oxidative property of 1 is closely related to a conventional peracid,2) and thus 1 has been conveniently used for such oxygen-transfer-type reactions as epoxidation of olefins,3) and oxidation of sulfides to sulfoxides4) and/or sulfones5) in the mixed solvents with water, because of negligible solubility of 1 in organic solvents. In the previous work, we have reported a novel Baeyer-Villiger-type lactonization of alicyclic ketones by a Oxone-"wet-alumina" system.6) We present here a novel and convenient synthesis of sulfones by using the title oxidation.

The following procedures are representative. "Wet-montmorillonite" (2) was prepared by adding distilled water (4 g) in eight portions to a commercial montmorillonite clay (20 g) and by vigorous shaking of the mixture on the every addition untill a free-flowing powder was obtained (It should be done in a few min). To a cloudy slurry of 1 (2.5 moles of a sulfide) and 2 (1.2 g) in dichloromethane (DM; 6 cm^3) in a round-bottomed flask was added 3 (1 mmol) in one portion. The flask was flushed with dry argon to exclude any influence of autoxidation and then capped tightly with a glass stopper. After magnetic stirring for 2 h at ambient temperature, the whole mixture was transferred onto a sintered glass disk and the product was thoroughly eluted with DM (required ca. 100 cm^3). Removing the solvent *in vacuo* left 4, which had adequate purity (100% by GLC).

$$\text{Ph-S-Me}\ \ \underline{3}\ \xrightarrow[\text{Ambient/CH}_2\text{Cl}_2]{\text{Oxone-"wet-Montmorillonite"}}\ \text{Ph-SO}_2\text{-Me}\ \ \underline{4}$$

Table 1 summarizes the results obtained under comparable conditions; suitable choice of the eluents, as remarked in the fifth column in Table 1, is necessary to get high yields of the sulfones. Some differences in reaction times and temperatures were ascribed to the differences in reactivity of the sulfides. GLC as well as NMR analyses showed that the sulfones so obtained were of high purities (over 98%).

Table 1. Oxidation of Sulfides with Oxone in Dichloromethane[a)]

Entry No.	Sulfides	Time/h	Temp	Eluents	Sulfones Isolated yield/%
1	PhSMe	2	Ambient	DM	98
2	p-$MeOC_6H_4SMe$	1.5	Ambient	AcOEt	97
3	p-MeC_6H_4SMe	2	Ambient	AcOEt	98
4	p-BrC_6H_4SMe	3	Ambient	DM	98
5	p-$NO_2C_6H_4SMe$	3	Ambient	AcOEt	96
6	PhSPh	5	Reflux	AcOEt	90
7	$PhCH_2SPhCH_2$	3	Reflux	AcOEt	98
8	$(CH_2{=}CHCH_2)_2S$	2	Ambient	DM	92
9	$(Octyl)_2S$	6	Reflux	DM	97
10	(Octyl)SMe	2	Reflux	DM	96
11	$(Hexyl)_2S$	4	Reflux	DM	96
12	$(Butyl)_2S$	2	Ambient	DM	94
13	(s-Butyl)$_2$S	3	Ambient	DM	93
14	(t-Butyl)$_2$S	2	Ambient	DM	92
15	$(Propyl)_2S$	2	Ambient	DM	97
16	$(Isopropyl)_2S$	2	Ambient	DM	95
17	Tetrahydro- thiophene	1	Ambient	$CHCl_3$	96

a) Under argon; 1 mmol of sulfide, 1.2 g of 2, and 6 cm^3 of DM were used in every run; [1]/[Sulfide]= 2.5 (mole ratio).

Thus, oxidation of sulfides with a Oxone-"wet-montmorillonite" system efficiently afforded almost quantitative yields of the sulfones in DM in a reasonable period of times under mild conditions.

References

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