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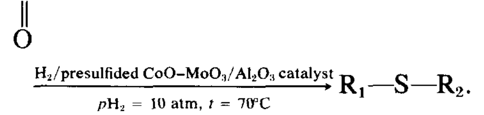
An Efficient and Selective Deoxygenation of Sulfoxides over $CoO–MoO_3/Al_2O_3$ Hydrodesulfurization Catalyst

Sulfoxides are important intermediates in various synthetic transformations but the successful application of these procedures generally requires the removal of the residual sulfoxide moiety. For the reduction of sulfoxides to sulfides numerous methods have been used and recently reported (*1*). Most of them employ laboratory reagents and homogeneous processes. Catalytic reductions by molecular hydrogen have been carried out using rhodium (III) complexes (*2*) or 5% palladium on charcoal (*3*) as catalysts. Yields in sulfides were better than 90% but both procedures require a very long time (1–4 days) for completion.

In the course of our studies on the hydrodesulfurization of sulfoxides and sulfones in the benzo[*b*]thiophene and dibenzothiophene series on $CoO–MoO_3/Al_2O_3$ we noticed in the case of the sulfoxides that the first step on the entire pathway leading to ethylbenzene derivatives or biphenyl was deoxygenation prior to any hydrogenation or desulfurization step (*4*). The transformation from the sulfoxides to the sulfides can be achieved in a very simple way by using an inexpensive common industrial hydrodesulfurization catalyst according to the scheme



$$R_1-\underset{\underset{O}{\|}}{S}-R_2 \xrightarrow[pH_2\,=\,10\ \text{atm},\ t\,=\,70^\circ C]{H_2/\text{presulfided } CoO–MoO_3/Al_2O_3 \text{ catalyst}} R_1-S-R_2.$$

The experimental conditions used in hydrodesulfurization processes (usually 50 atm, 250°C) can be reduced to very mild conditions, namely, 10 atm, 70°C, and applied to various sulfoxides (dialkyl, arylalkyl, diaryl, benzo[*b*]thiophene derivatives, dibenzothiophene) as reported in this note.

The catalyst is a desulfurization catalyst used industrially [HR 103 from Procatalyse (RP)] which has the following composition (wt%) : CoO, 2.8; MoO_3, 13.5; NiO, <0.03; SiO_2, 2.8; and Al_2O_3, 80.9. This catalyst was sulfurized using a fluidized bed technique with a gas mixture composed of 15% H_2S and 85% H_2 by volume; the operational pressure was 1 atm, the rate of gas flow was 4 liters/h per 100 g of catalyst, and the initial temperature was 100°C. It was increased from 100 to 400°C during 24 h and then held at 400°C for 24 h.

The sulfoxide and the catalyst were introduced into the reactor in a dodecane or benzene solution. The apparatus used was an agitated autoclave of 0.5-liter capacity. This autoclave was equipped with sample inlets, heated by an external oven, and could be agitated at different speeds. The characteristics of this batch operation have been given by Barret (*5*). Air was removed by purging with nitrogen at 5 atm pressure. Hydrogen was introduced at 10 to 15°C below the working temperature. Throughout the experiments the sulfur content of the sulfoxides was kept at 0.3 wt% of the charge.

All products were analyzed by vapor-phase chromatography on an OV-17 or SE-30 column and identified by comparison of infrared, ^{1}H-NMR, and ^{13}C-NMR spectra with those of authentic specimens (*4*).

The results are presented in Table 1. For all compounds, the duration of the reaction can be shortened by warming to 100°C and increasing the pressure to 30 atm. In these conditions, for example, diphenyl sulfoxide

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TABLE I

Reduction of Sulfoxides 1 to Sulfides 2 over CoO–MoO_3/Al_2O_3 Hydrodesulfurization Catalyst[a]

No.	Product		Yield in sulfide %	Time (h)	Remarks
	R_1	R_2			
1a	C_2H_5	C_2H_5	98	3	2% Hydrogenolysis
1b	CH_3	C_6H_5	100	6	No hydrogenolysis No hydrogenation
1c	C_6H_5	C_6H_5	100	4	
1d	C_6H_5–CH_2	C_6H_5–CH_2	100	8	
1e	2-Methylbenzo[*b*]thiophene sulfoxide		100	4	
1f	3-Methylbenzo[*b*]thiophene sulfoxide		100	4	
1g	2,3-Dimethylbenzo[*b*]thiophene sulfoxide		100	5	
1h	2-Phenylbenzo[*b*]thiophene sulfoxide		100	4	
1i	3-Phenylbenzo[*b*]thiophene sulfoxide		100	4	
1j	Dibenzothiophene sulfoxide		100	4	

[a] pH_2 = 10 atm; t = 70°C; wt% of S based on charge = 0.3 in dodecane or benzene.

is totally deoxygenated to diphenyl sulfide within 20 min with no trace of hydrogenolysis of the C–S bond or hydrogenation of the phenyl ring.

The kinetic studies undertaken in the case of the methylbenzo[*b*]thiophene sulfoxides, dibenzothiophene sulfoxide, and diphenyl sulfoxide reveal that the order in reactant is unity for temperatures varying from 50 to 100°C and for pressures between 10 and 30 atm. The individual rate constants give the following apparent activation energies of the deoxygenation reaction (kcal/mole): 3-methylbenzo[*b*]thiophene sulfoxide, 8; 2,3-dimethylbenzo[*b*]thiophene sulfoxide, 13; dibenzothiophene sulfoxide, 8; and diphenyl sulfoxide, 12. These values are lower than the values previously found (*4*) for the first step of the overall hydrodesulfurization process, i.e., the hydrogenation of the sulfides in the benzo[*b*]thiophene series (kcal/mole): benzo[*b*]thiophene, 25; 3-methylbenzo[*b*]thiophene, 32; 2,3-dimethylbenzo[*b*]thiophene, 37; or the hydrogenolysis of the C–S bond for dibenzothiophene, 28. This is indicative of the facility of the deoxygenation reaction.

Under these defined experimental conditions, the corresponding sulfones remain totally unaffected. This behavior has been observed under other conditions (*6*) and is probably due to the greater stability of these derivatives.

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