Catalytic Deoxygenation of Sulfoxides by Molecular Hydrogen and its Application to the Homologation of Aromatic Aldehydes

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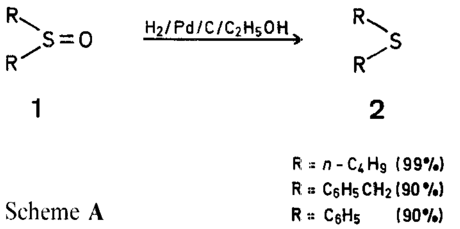
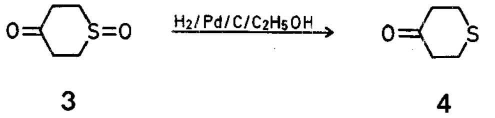
For deoxygenation of sulfoxides to the corresponding sulfides, a variety of methods have been developed[1]. To our knowledge, however, there has not been described catalytic deoxygenation[2] of a sulfinyl group by molecular hydrogen, which has the following distinct features: (i) the reaction can be carried out under neutral conditions; (ii) the reduced product is easily isolated by filtrating off an insoluble catalyst; (iii) the sulfoxide moiety is selectively reduced without affecting a reducible carbonyl group; (iv) the sulfoxide containing a carbon-carbon double bond can be converted into the corresponding saturated sulfide, with the concomitant reduction of the carbon-carbon double bond. Hence, a catalyst which is able to accelerate the reduction of sulfoxides by molecular hydrogen has been sought in our laboratory, and we now wish to report the deoxygenation of sulfoxides with molecular hydrogen under the action of palladium-on-charcoal catalyst and its application to the homologation of aromatic aldehydes as shown in Scheme **C**.

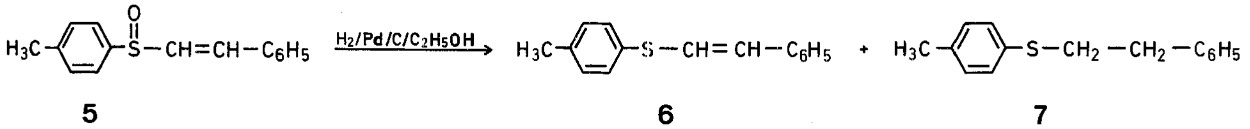
The catalytic deoxygenation of a sulfoxide (**1**) was carried out in a steel autoclave (50 ml capacity). A mixture containing a sulfoxide (**1**) (15 mmol) and 5% palladium-on-charcoal (0.6 g) in ethanol (40 ml) was shaken at temperature of 80–90° under an atmosphere of hydrogen, until uptake of hydrogen had ceased (1–4 days). The pressure of hydrogen was 70–90 atm at the initial stage and decreased with the progress of the reaction to be finally 30–50 atm. The yields of **2** are given in Scheme **A** and these results demonstrate that the present reaction can reduce both an alkyl sulfoxide and an aryl sulfoxide.



Scheme **A**

In a similar manner, 4-oxothiane 1-oxide (**3**) was transformed into 4-oxothiane (**4**) in 59% yield (the conversion yield: 69%), leaving the carbonyl group intact. It should be noted that, under the condition mentioned above, *trans*-β-styryl *p*-tolyl sulfoxide (**5**) gave *trans*-β-styryl *p*-tolyl sulfide (**6**) as a major product (66% yield), along with the formation of β-phenethyl *p*-tolyl sulfide (**7**, 16%). Interestingly, the latter product (**7**) was mainly formed (60%) when an excess amount of 5% palladium-on-charcoal was used with the further addition of active charcoal (see experimental procedures).





Scheme **B**

The present reaction was also applied to the reduction of 1-methylsulfinyl-1-methylthio-2-arylethylene (**9**), which was easily obtained by the Knoevenagel-type condensation of an aromatic aldehyde (**8**) with methyl methylthiomethyl sulfoxide as previously reported[3]. As depicted in Scheme **C**, the combination of this reaction with the following process leading to the corresponding arylacetaldehyde provides a new method for the homologation of an aromatic aldehyde.

The latter process could be achieved by the route via the arylacetaldehyde dimethyl dithioacetal *S*-oxide derivative (**11**), i.e., the oxidation of the reduced product (**10**)[4] with hydrogen peroxide in acetic acid to give **11**, followed by the acid-hydrolysis reported already[5]. The results are summarized in the Table. Thus, phenylacetaldehyde, *p*-methoxyphenylacetaldehyde, and (3,4-dimethoxyphenyl)acetaldehyde were derived from benzaldehyde, *p*-anisaldehyde, and veratraldehyde in overall yields of 50%, 46%, and 36%, respectively.

Table. Yields (%) of the Homologation Reaction of Aromatic Aldehydes (**8**)

Substituents X	 Y	$8 \rightarrow 9$	$9 \rightarrow 11$	$11 \rightarrow 12$
H	H	91[3]	62[a] (43)[c]	88[5]
H	OCH_3	99[3]	59[b] (43)[b,c]	79[5]
OCH_3	OCH_3	87[3]	57[b] (57)[b,c]	73

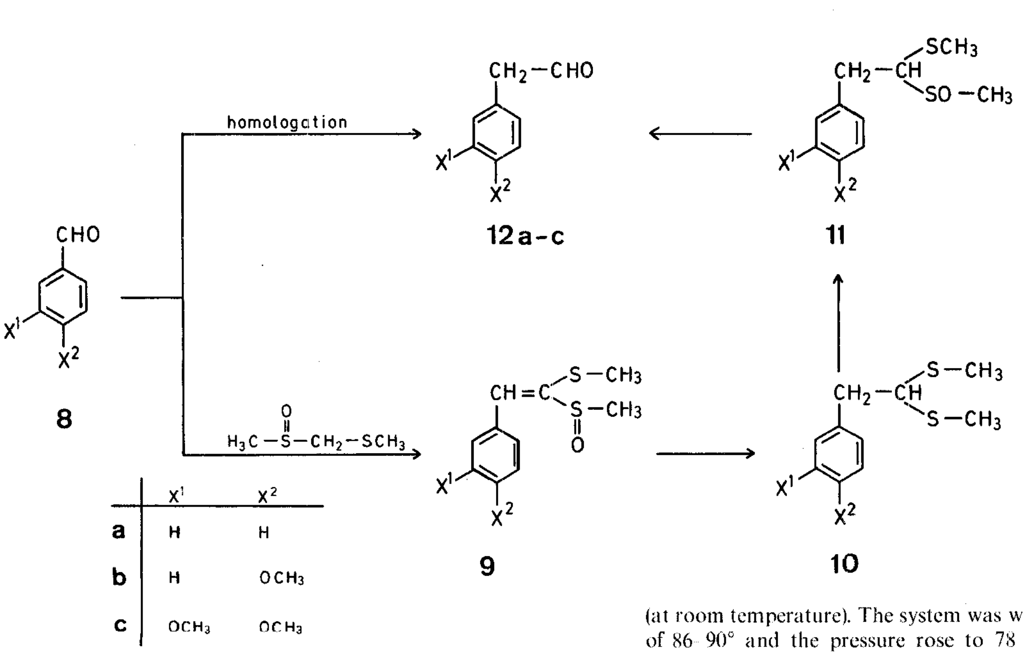
[a] The yields of **9** → **10** and **10** → **11** were 80% and 77%, respectively.

[b] The crude reduced product (**10**), without purification, was subjected to the subsequent oxidation reaction.

[c] The yield for the reduction of **9** with lithium aluminium hydride, followed by the oxidation with hydrogen peroxide.

Deoxygenation of Dibenzyl Sulfoxide: Typical Procedure:

In an autoclave (50 ml-capacity), ethanol (40 ml) and 5% palladium-on-charcoal (0.6 g) were shaken under an atmosphere of hydrogen (79 atm) at room temperature in order to activate the catalyst. Then, dibenzyl sulfoxide (3.50 g, 15.2 mmol) was added and hydrogen was introduced again to make the pressure 65 atm (at room temperature). The system was warmed at a temperature of 86–90° and the pressure rose to 78 atm. The shaking was continued for 4 days until the pressure had become constant (53 atm). The catalyst was filtered off and the filtrate was evapor-



Scheme **C**

ated under reduced pressure. The residue was chromatographed (silica gel-column, eluted with benzene and ethyl acetate) to afford 0.23 g of the starting sulfoxide and 2.94 g of colorless crystals (m.p. 48–49°) which were identified as dibenzyl sulfide by the comparison of their N.M.R. and I.R. spectra with those of an authentic sample and mixture melting point. The yield was 90% (the conversion yield: 97%).

Transformation of *trans*-β-Styryl *p*-Tolyl Sulfoxide (5) into β-Phenethyl *p*-Tolyl Sulfide (7):

The suspension of 5% palladium-on-charcoal (0.5 g) and active charcoal (1 g) in ethanol (40 ml) was shaken under an atmosphere of hydrogen, and *trans*-β-styryl *p*-tolyl sulfoxide (**5**; 1.00 g, 4.13 mmol) was added. Then, the shaking of the system was continued at 80–90° under an atmosphere of hydrogen (initial pressure: 75 atm) for 3 days. The solid phase was filtered off and the filtrate was evaporated under reduced pressure. The residue was chromatographed (silica gel-column, eluted with benzene and ethyl acetate) to give β-phenethyl *p*-tolyl sulfide (**7**; 0.56 g, 60%), along with *trans*-β-styryl *p*-tolyl sulfide (**6**; 0.07 g) and *p*-thiocresol (0.03 g). The structure of **7** was confirmed by its spectral data and elemental analysis.

$C_{15}H_{16}S$	calc.	C 78.90	H 7.06	S 14.04
(228.4)	found	78.63	6.79	14.15

I.R. (Film): $\nu_{max} = 3020, 2915, 1496, 1456, 1090, 804, 699\ cm^{-1}$.

^1H-N.M.R. ($CDCl_3$): $\delta = 2.33$ (s, 3H), 3.00 (m, 4H), 7.23 ppm (m, 9H).

Derivation of Phenylacetaldehyde from Benzaldehyde; Typical Procedure:

1-Methylsulfinyl-1-methylthio-2-phenylethylene (**9**, X=Y=H; 2.58 g, 12.2 mmol), obtained by the condensation of benzaldehyde with methyl methylthiomethyl sulfoxide in the presence of Triton B[3], was reduced in the similar manner described above, using 5% palladium-on-charcoal (1 g), to give phenylacetaldehyde dimethyl dithioacetal (**10**, X=Y=H); yield: 1.92 g (80%); which was identified by comparison with an authentic specimen prepared by the reaction of phenylacetaldehyde with methyl mercaptan in the presence of concentrated hydrochloric acid; b.p. 105–106°/4 torr.

$C_{10}H_{14}S_2$	calc.	C 60.55	H 7.12
(198.3)	found	60.50	7.12

To a solution containing **10** (X=Y=H; 6.21 g) in acetic acid (10 ml), was added an aqueous solution (30% concentration) of hydrogen peroxide (3.9 ml) under cooling with ice, and then the resulting mixture was stirred for 1 h at room temperature. After dichloromethane (100 ml) had been added, the acetic acid was neutralized with potassium carbonate (12 g). The mixture was filtered, and the filtrate was dried with anhydrous sodium sulfate. After the evaporation of the solvent, the residue was column-chromatographed on silica gel (eluted with dichloromethane) to give **11** (X=Y=H); yield: 5.18 g (77%); as a colorless oil, which appeared, by N.M.R. analysis, to consist of two diastereomers (7:3).

$C_{10}H_{14}OS_2$	calc.	C 56.03	H 6.58	S 29.92
(214.3)	found	55.91	6.47	30.00

A solution of **11** (X=Y=H, 270 mg), ethyl orthoformate (390 mg), and 3 drops of concentrated sulfuric acid in ethanol (4 ml) was heated at 54° for 1.5 h. After addition of sodium hydrogen carbonate (500 mg), the mixture was stirred for 30 min and the solvent was evaporated under reduced pressure. Dichloromethane (10 ml) was added to the residue, and the mixture was filtered. The filtrate was concentrated under reduced pressure to give a light yellow liquid; yield: 225 mg. By a short-path distillation (oil bath temperature 100°/14 torr), a colorless liquid was obtained; yield: 198 mg; which was identified as phenylacetaldehyde diethyl acetal by the comparison of its infrared spectrum with that of the authentic specimen; yield: 88%.

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[2] Catalytic reduction of sulfoxides with bromine-hydrobromic acid system was also reported, but the yields were relatively low: T. Aida, N. Furukawa, S. Oae, *Tetrahedron Lett.* **1973**, 3853.

[3] K. Ogura, G. Tsuchihashi, *Tetrahedron Lett.* **1972**, 1383.

[4] The reduction of **9** into **10** was also possible by treatment with an excess of lithium aluminum hydride in tetrahydrofuran. The yields were given in the Table.

[5] K. Ogura, G. Tsuchihashi, *Tetrahedron Lett.* **1971**, 3151.