

SODIUM SULFIDE AS A SELECTIVE REDUCING REAGENT FOR ALDEHYDES TO ALCOHOLS.
USE OF ALUMINA AS AN EFFECTIVE CATALYST

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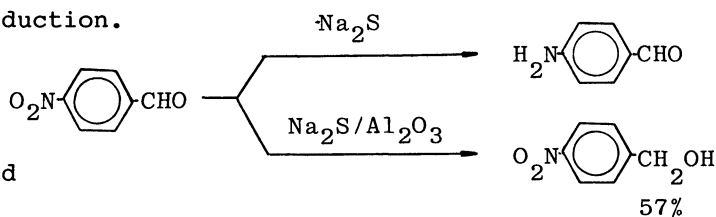
Intrinsic reactivity of sodium sulfide is well controlled by impregnating it on alumina, so that aldehydes can be readily reduced to the corresponding alcohols, while ketones, esters and even nitro compounds are all inert toward this reagent.

Sodium sulfide has long been known as a specific reagent for reduction of aromatic nitro compounds to the corresponding amino derivatives.¹⁾ This reagent also reduces quinones to hydroquinones,¹⁾ but carbonyl compounds in general are resistant to this reagent.²⁾ In fact, p-nitrobenzaldehyde is easily reduced to p-aminobenzaldehyde by sodium sulfide under usual conditions.³⁾ Sodium sulfide supported on alumina ($\text{Na}_2\text{S}/\text{Al}_2\text{O}_3$), however, has been found to reduce only the formyl group to hydroxymethyl group without any reduction of the nitro group. For example, p-nitrobenzaldehyde was successfully converted to p-nitrobenzyl alcohol with the use of this reagent, $\text{Na}_2\text{S}/\text{Al}_2\text{O}_3$, and none of the species derived by the reduction of the nitro group was detected even by careful inspection of the raw product by $^1\text{H-NMR}$. We now wish to communicate this striking effect of alumina on the Na_2S reduction.

Typical procedure for this reduction is as follows.

To a solution of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (2 g) in 10 ml of water was added 10 g of acidic alumina (Alumina

Woelm acid TLC)⁴⁾ and the mixture was stirred for 0.5 h. Alumina was filtered off, washed with two 20 ml portions of ether, and dried overnight in a vacuum desiccator. The reagent ($\text{Na}_2\text{S}/\text{Al}_2\text{O}_3$) thus prepared is powdery and slightly grayish in color. To a mixture of 2-phenylpropanal (134 mg, 1 mmol) and $\text{Na}_2\text{S}/\text{Al}_2\text{O}_3$ (2.0 g of that prepared by above procedure) was added 7 ml of heptane under atmosphere of nitrogen. After the mixture was stirred for 20 h at the refluxing temperature, alumina was filtered off and washed thoroughly with ether containing a small amount (ca. 10%) of methanol. Filtrate and washings were combined and the solvent was removed to give 95 mg (yield 70%) of 2-phenylpropanol. Without further purification the product was proved essentially pure by $^1\text{H-NMR}$. As is shown in Table 1, reduction of several aldehydes 1a-1f by $\text{Na}_2\text{S}/\text{Al}_2\text{O}_3$ proceeded successfully and aliphatic as well as aromatic aldehydes were converted



to the corresponding alcohols. Although the yields are not so high,⁵⁾ the work-up process is very simple and the present reaction may be used as an alternative method for reducing aldehydes.

Under these reaction conditions nitro compounds, ketones and carboxy esters were all inert toward this reagent; attempted reduction of nitrobenzene, acetophenone, methyl styryl ketone and even relatively sensitive ketone such as 4-t-butyl-cyclohexanone resulted in complete recovery of the starting materials. The work was extended to check for chemoselectivity of this reaction. Only aldehydes were reduced to corresponding alcohols when equimolar mixtures (1 mmol/1 mmol)

of benzaldehyde and benzophenone, benzaldehyde and nitrobenzene, and 2-phenylpropanal and methyl benzoate were treated with Na₂S/Al₂O₃ (69%, 73%, and 100% yield respectively). In the case of bifunctional substrates too, only the formyl groups of p-butyrylbenzaldehyde **1g**, methyl p-formylbenzoate **1h** and m-nitrobenzaldehyde **1i** were reduced to the hydroxymethyl groups by this reagent (Table 1). All these results indicate that reactivity of sodium sulfide can be well controlled in the presence of alumina. Of particular interest is that a reducing agent specific to nitro group can be changed completely to another specific reagent for formyl group by merely supporting it on alumina.

References

- 1) Y. Ogata, "Yuki-Kagobutsu No Sanka To Kangen," Nankodo, Tokyo (1963), pp. 879-908, and the references cited therein.
- 2) As a special case reduction of aldehydes by Na₂S has been reported but it is in liquid NH₃ and yields are not so high. See, Y. Takigawa, T. Minami, K. Shimada, and S. Takazawa, 45th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1982, Abstr., No. 2I25.
- 3) H. G. Beard and H. H. Hodgson, J. Chem. Soc., 1944, 4.
- 4) When basic alumina (Alumina Woelm basic TLC) or neutral alumina (Alumina activated 300/ Nakarai Chemical Co.) was used instead of acidic alumina, conversion of aldehyde to alcohol decreased to 0-20%.
- 5) Probably, some Cannizzaro reaction occurs during the present reaction. However, in many cases yields of the alcohols exceed 50%. The resulting carboxylic acids are bound firmly to the alumina and can be collected only by treating this alumina (after reaction) with concd. HCl (for instance in the case of **1b**). Therefore, the product in the extract is essentially pure alcohol.
- 6) Satisfactory elemental analysis was given for this compound; Found: C, 73.86; H, 8.01%. Calcd for C₁₁H₁₄O₂: C, 74.13; H, 7.92%.

Table 1. Reduction of RCHO by Na₂S/Al₂O₃

	RCHO <u>1</u> R	Yield of RCH ₂ OH ^{a, b)} / %
1a	Ph(CH ₃)CH-	70
1b	CH ₃ (CH ₂) ₃ CH- CH ₃ CH ₂	50
1c	Ph-	56
1d	o-ClC ₆ H ₄ -	67
1e	p-CH ₃ C ₆ H ₄ -	58
1f	p-CH ₃ OC ₆ H ₄ -	48
1g	p-(i-PrC)C ₆ H ₄ - O	41 ⁶⁾
1h	p-(CH ₃ OC)C ₆ H ₄ - O	42
1i	m-O ₂ NC ₆ H ₄ -	42

a) ¹H-NMR and IR spectra are in good accordance with those of authentic samples.

b) Isolated yield.

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