# A Facile Reduction of Sulfones to Sulfides

J. N. GARDNER AND S. KAISER
*Technical Development Department, Hoffmann-La Roche Inc., Nutley, New Jersey 07110*
AND
A. KRUBINER AND H. LUCAS
*Chemical Research Department, Hoffmann-La Roche Inc., Nutley, New Jersey 07110*

Received October 11, 1972

Diisobutylaluminum hydride is shown to be an effective reagent for the reduction of sulfones to sulfides. Yields as high as 70% are obtained in this normally difficult reduction. A technique for the easy isolation from the reaction mixture of volatile sulfides is described.

---

Il est montré que l'hydrure de di-iso-butylaluminium est un réactif permettant la réduction facile des sulfones en sulfures. Des rendements aussi hauts que 70% ont été obtenus pour cette réduction qui est normalement difficile. On décrit une technique permettant la récupération facile des sulfures volatiles des mélanges réactionnels. [Traduit par le journal]

Can. J. Chem., 51, 1419 (1973)

We wish to report that diisobutylaluminum hydride (Dibal-H) is an effective and convenient reagent for the reduction of sulfones to sulfides. Over the past 20 years, only one major paper dealing with conversion of sulfones to sulfides (1) has appeared and, indeed, it is widely recognized that this reduction is a difficult operation. This is unfortunate because sulfones are compounds of potential synthetic utility as a result of the ability of the sulfone moiety to stabilize a negative charge on the carbon atom α to sulfur.

In their paper, Bordwell and McKellin (1) describe the reduction of sulfones with lithium aluminum hydride (LAH) using in most cases 3–9 mol of this reagent per mol of sulfone, which is equivalent to 6–18 times the theoretical amount of active hydrogen. Only in cases of sulfones related to benzothiophene and dibenzothiophene were high yields of the corresponding sulfides obtained when using smaller excesses of the reagent. Furthermore, those sulfides which are relatively volatile (*e.g.*, tetramethylene sulfide) were isolated only as their mercuric chloride complexes.

Our results are presented in Table 1. As may be seen, aliphatic, alicyclic, and aromatic sulfones were reduced using between 2.2 and 5.0 mol of Dibal-H per mol of sulfone. The fact that 2.2 mol of Dibal-H effected almost complete reduction of 1 mol of benzyl methyl sulfone strongly suggests that the stoichiometry of the reaction is as indicated in the equation:

$$R_2SO_2 + 2(C_4H_9)_2AlH \rightarrow R_2S + 2(C_4H_9)_2AlOH$$

This equation implies that the sulfide is formed in a free state and does not require water to liberate it from a complex with the aluminum salts. In agreement with this, we have found that volatile sulfides are conveniently made by reduction of sulfones with Dibal-H in mineral oil, the sulfide being distilled directly from the reaction mixture.

The reactivity of the sulfones with Dibal-H follows a similar order to their reactivity with LAH. Thus, in both cases the alicyclic sulfones with five-membered rings are the most easily reduced, and it is noteworthy that the reaction of Dibal-H with tetramethylene sulfone is quite exothermic. The aliphatic sulfones are the most resistant to reduction, while other compounds listed in Table 1 fall between these two extremes.

None of the reductions reported in Table 1 has been optimized, and in three reactions the products were not isolated. The reduction of 2,5-dihydrothiophene sulfone to 2,5-dihydrothiophene is not a simple reaction as several attempts to improve the yield resulted in none of the desired product. It may be that interaction of the Dibal-H with the double bond occurs under all except carefully defined conditions, and it is interesting to note that Bordwell and McKellin obtained only polymeric material when they attempted to carry out this reduction with LAH. Preparation of 2,5-dihydrothiophene in

TABLE 1. Reduction of sulfones to the corresponding sulfides

| Sulfone | Reaction time (h) | Solvent | Reaction temperature (°C) | Dibal-H mol/mol sulfone | Yield (%) | Footnote |
|---|---|---|---|---|---|---|
| Di-*n*-propyl | 72 | Toluene | 110 | 4 | 77 | *a, b* |
| Di-*n*-butyl | 72 | Toluene | 110 | 3 | 68 | *a, c, d* |
| Tetramethylene | 72 | Mineral oil | 20–25 | 3 | 73 | *a, c, e* |
| 2,5-Dihydrothiophene | 1.5 | Mineral oil | 20–25 | 3 | 12 | *e, f* |
| Benzyl methyl | 18 | Toluene | 110 | 2.2 | — | *a* |
|  | 18 | Hexane–Toluene | 103 | 5 | 61 | *a, d, g* |
| Diphenyl | 48 | Hexane–Toluene | 103 | 5 | 57 | *a, d, h* |
| Methyl phenyl | 20 | Toluene | 110 | 5 | 61 | *a, b* |

[a] Identified by g.c. comparison with an authentic sample.
[b] The yield was determined gas chromatographically. A solution containing the authentic product at a concentration similar to its concentration in the reaction product was used as a standard.
[c] Identified by comparison of i.r. spectra.
[d] Product isolated by conventional aqueous procedures.
[e] Product isolated by distillation from the reaction mixture.
[f] See Experimental.
[g] The yield given allows for recovery of 10% of the starting sulfone.
[h] The yield given allows for recovery of 14% of the starting sulfone.

this way may have some synthetic merit if the reaction can be controlled as the normal preparation, by sodium-in-ammonia reduction of thiophene (2), involves the separation of 2,5- and 2,3-dihydrothiophenes.

In contrast to Dibal-H, sodium diethyl aluminum dihydride (OMH-1), which has recently become commercially available, was ineffective in reducing di-*n*-butyl and tetramethylene sulfones under conditions comparable with those under which Dibal-H brought about reduction.

## Experimental

Dibal-H was purchased from the Stauffer Chemical Company as an approximately 20% solution in either toluene or hexane. OMH-1 (25% in toluene) was a gift from the Ethyl Corporation, and the attempted reductions with it were carried out in toluene. All the sulfones were commercial materials and were used as received.

### *Use of Mineral Oil as the Solvent. Tetramethylene Sulfide*

Light mineral oil (500 ml) was added to 500 ml of a 23.5% solution of Dibal-H (0.75 mol) in toluene. The mixture was distilled to a residue temperature of 100° at 0.5 mm and then, while this vacuum and temperature were held, nitrogen was passed through the solution for 2 h to remove the last traces of toluene. The mixture was cooled to 20–25° and tetramethylene sulfide 1,1-dioxide (30 g, 0.25 mol) was added slowly while cooling to hold 20–25°. The mixture was stirred for 1.5 h and then distilled to a residue temperature of 125° at 3 mm. The distillate weighed 11.5 g. The reaction mixture was cooled to ambient temperature and again stirred for 72 h.[1] It was then distilled as before to yield a further 10 g of distillate. The combined distillates were redistilled at atmospheric pressure via a 4 in. × 0.5 in. Goodloe column to yield tetramethylene sulfide (16 g, 0.18 mol; 73%); b.p. 121°.

### *Use of Toluene as the Solvent. Dibutyl Sulfide*

A solution of di-*n*-butyl sulfone (44.5 g, 0.25 mol) in toluene (50 ml) was added to 500 ml of a 23.5% solution of Dibal-H (0.75 mol) in toluene. The mixture was heated under reflux for 72 h and cooled to room temperature, and ethanol (50 ml) was cautiously added, followed by water (200 ml), and concentrated hydrochloric acid (100 ml). The organic layer was separated and washed with water (2 × 50 ml). The solvent was distilled off at atmospheric pressure and the residue was distilled through a Vigreux column to yield the sulfide (18 g); b.p. 69°/11 mm. G.c. evaluation of the residue from fractionation of the recovered solvent detected another 6.8 g of sulfide, giving a total yield of 24.8 g (0.17 mol; 68%).

### *2,5-Dihydrothiophene*

A solution of Dibal-H (0.75 mol) in mineral oil (500 ml) was prepared as in the preparation of tetramethylene sulfide. To this at 20° was added slowly 2,5-dihydrothiophene 1,1-dioxide (30 g, 0.25 mol), the mixture being cooled as required. When the addition was

---

[1] This time was determined purely on the basis of convenience.

complete, the reaction mixture was stirred for 1.5 h and then distilled to a residue temperature of 150° at 4 mm. The distillate weighed 10 g. Stirring for another 18 h and distillation gave no additional distillate. The distillate was redistilled at atmospheric pressure through a 4 in. × 0.5 in. Goodloe column to yield 2,5-dihydrothiophene (2.7 g, 0.03 mol; 12%) assaying 92.4% by g.c.; b.p. 122°; $n_D^{20}$ 1.5279; n.m.r. ($CDCl_3$) δ 3.73 (s, 4, C*H*$_2$) and 5.83 p.p.m. (s, 2, C*H*=); Raman (neat liquid) 1630 cm$^{-1}$ (C=C); i.r. ($CHCl_3$) 1638 cm$^{-1}$ (C=C) (lit. (2), b.p. 122.3°; $n_D^{20}$ 1.5306).

Anal. Calcd. for $C_4H_6S$: C, 55.77; H, 7.02; S, 37.22. Found: C, 55.63; H, 7.15; S, 36.92.

1. F. G. Bordwell and W. H. McKellin. J. Am. Chem. Soc. **73**, 2251 (1951).
2. S. F. Birch and D. T. McAllan. Nature, **165**, 899 (1950).