sulfate) organic phase gave *tert*-butyl azidoformate as a pale amber liquid in quantitative yield.[15]

*tert*-Amyl azidoformate[9a] was prepared in 84% yield[10] from *tert*-amyl chloroformate. Similarly phenyl azidoformate was prepared in better than 97% yield using chloroform as the sole solvent; in this case, tetramethylguanidinium chloride (87% yield) crystallized out of solution.

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(15) Neutralization of the aqueous layer followed by extraction with ether allows recovery of tetramethylguanidine.

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## Dimethyl Sulfide–Borane. A Convenient Hydroborating Agent

Linda M. Braun, Raymond A. Braun, H. Ray Crissman,
Myles Opperman, and Roy M. Adams*

*Geneva College, Beaver Falls, Pennsylvania 15010*

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The utility of hydroboration as a tool in reducing and synthetic reactions has received extensive study since the extent of the reaction was first indicated by Brown and Subba Rao.[1,2] However, the application of this tool has been limited by certain properties of the reagent diborane and its solutions. These properties follow: (1) diborane itself is not stable at room temperature and hence it must normally be generated *in situ* in the glycol ethers, (2) it may be purchased as a quite dilute (1.5 wt %) solution in tetrahydrofuran,[3] but this solvent and the glycol ethers are slowly cleaved by borane at room temperature, (3) both these solvents are relatively expensive and hazardous to store and purify. They are also miscible with both polar and nonpolar solvents and hence difficult to separate from desired products.

It seemed to us that dimethyl sulfide–borane (I), which was first reported by Burg and Wagner[4] and studied by Stone, *et al.*,[5,6] might have certain advantages as a storable hydroboration agent. Chief among these is that I is a stable liquid at room temperature. Samples stored in a nitrogen atmosphere have retained their hydridic activity after several months at room temperature. The density was found to be 0.80 g/ml at room temperature (23°). Since the formula weight is 76 g/mol, 1.0 mmol is conveniently 0.10 ml. Tetrahydrofuran–borane solution has a millimolar volume tenfold greater and gaseous diborane in the dilutions which can be shipped at ambient temperatures has a millimolar volume $10^5$ greater. I is also miscible with inexpensive, unreactive volatile solvents such as petroleum ether, benzene, diethyl ether, and methylene chloride.

Chart I

aldehydes → alcohol
ketones → alcohol
acid chloride → no reaction
lactone → glycol
epoxide → alcohol
ester → alcohol (slow)
carboxylic acid → alcohol (fast)
nitrile → amine
nitro → no reaction
olefin → organoborane (fast)

Brown and Subba Rao[1,2] listed reduction products (Chart I) from hydroboration (after hydrolysis) for some of the common functional groups. They initially studied the reactivity of borane in ethers toward these groups on a millimolar scale. The results were evaluated by measuring the residual hydridic hydrogen after reaction between stoichiometric quantities of the borane and the reducible moiety. Hence we studied the reactivity of I as a hydroborating agent on a millimolar scale by a procedure parallel to that of Brown and Subba Rao. I (2.0 mmol, measured in a glove bag as 0.20 ml with a hypodermic syringe) was injected into 5 ml of benzene in a 25-ml two-necked flask, one neck of which was fitted with a serum cap and the other with a gas delivery tube leading through a mercury bubbler to a gas measuring tube over water. The reducible organic compound (6 mmol) was then added. The benzene was generally necessary as a heat diluent to avoid uncontrolled reactions. After the mixture was stirred for 30 to 45 min, 5 ml of methanol was added to consume any unreacted borane. The gas evolved was measured over water and assumed to be hydrogen. Results with

$$(CH_3)_2SBH_3 + 3CH_3OH \longrightarrow B(OCH_3)_3 + 3H_2 + (CH_3)_2S$$

typical organic functional groups are presented in Table I. The data represents averages of at least three determinations. In the last column comparable results by Brown and Subba Rao[1] with diborane in ethers are tabulated.

Coyle, Kaesz, and Stone[6] reported that tetrahydrothiophene, another readily available sulfide, is a weaker base toward borane than dimethyl sulfide. This should make tetrahydrothiophene–borane (II) a better hydroborating agent. We found that tetrahydrothiophene absorbed diborane quite slowly at room temperature and required very vigorous stirring to completely absorb 1 equiv of borane. II also proved to dissolve slowly in benzene, requiring about 15 min to form a homogeneous solution with moderate magnetic stirring. The density was measured to be 0.94 g/ml. Its reaction with several substrates was tested. These are summarized in Table II and again compared with the results of Brown and coworkers.

### Discussion

In general the reactivity of dimethyl sulfide–borane parallels that of the ether–boranes. Table I indicates significantly less reaction with acids, nitriles, epoxides, and lactones. With epoxides the ether–boranes have been reported to react very slowly except in the presence of traces of borohydride.[7] Traces of boron trifluoride catalyze the reduction of lactones.[8] These substances are generally present in diborane generated *in situ* by the following reaction in the dimethyl ether of dieth-

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(1) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1135 (1957).

(2) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

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(5) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 1964 (1956).

(6) T. D. Coyle, H. D. Kaesz, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **81**, 2989 (1959).

(7) H. C. Brown and N. M. Yoon, *ibid.*, **90**, 2686 (1968).

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TABLE I

RESULTS OF REACTION OF DIMETHYL SULFIDE–BORANE[a] WITH ORGANIC COMPOUNDS

| Compd | Compound used, mmol | $H_2$ after addition of compound, mmol | $H_2$ evolved after MeOH addition, mmol | $H^-$ involved in reduction of organic compd, mmol | mmol of $H^-$ from I consumed/mmol of organic function | Brown[b] results with ether boranes for same functional group |
|---|---|---|---|---|---|---|
| Blank | | 0 | 6.0 | 0 | 0 | 0 |
| Pentene | 6.0 | 0 | 0 | 6.0 | 1.0 | 1.0 |
| Propargyl bromide | 3.0 | 0 | 0.4 | 5.6 | 1.87 | 1.57 to 1.85 |
| 3-Hexyne | 3.0 | 0 | 0.55 | 5.45 | 1.78 | 1.57 to 1.85 |
| Benzaldehyde | 6.0 | 0 | 0 | 6.0 | 1.0 | 1.0 |
| Acetone | 6.0 | 0 | 0 | 6.0 | 1.0 | 1.0 |
| Acetic acid | 2.0 | 2.7 | 0.41 | 2.9 | 1.45 | 2.8 |
| Formic acid | 2.0 | 0.0 to 5.0[c,d] | 0 | 6.0 to 1.0 | 3.0 to 0.5 | 2.8 |
| Benzoyl chloride | 3.0 | 0 | 4.59 | 1.41 | 0.47 | 0.4 |
| *N*,*N*-Dimethylacetamide | 6.0 | 0 | 0.39 | 5.61 | 0.94 | |
| Ethyl acetate | 6.0 | 0 | 0 to 4.0[d] | 6.0 to 2.0 | 1.0 to 0.3 | 0.4 |
| Ethyl formate | 6.0 | 0.82 | 1.0 | 4.18 | 0.7 | 0.4 |
| Acetonitrile | 3.0 | 0 | 3.6 | 2.4 | 0.8 | 2.0 |
| Benzonitrile | 3.0 | 0 | 0 to 4.0[d] | 6.0 to 2.0 | 2.0 to 0.7 | 2.0 |
| Butyrolactone | 6.0 | 0 | 4.06 | 1.94 | 0.32 | 2.0 |
| 1,2-Butylene oxide | 6.0 | 0 | 2.59 | 3.41 | 0.57 | 1.2 |
| Nitroethane | 2.0 | 0 | 5.47 | 0.53 | 0.26 | 0.1 |
| Sulfolane | 3.0 | 0 | 3.62 | 2.38 | 0.79 | |

[a] Two millimoles. [b] References 1 and 2. [c] Solid insoluble in benzene formed. [d] Unexplained erratic behavior.

TABLE II

| Organic compd | II, mmol | Organic compd, mmol | $H_2$ released on addition of organic compd, mmol | $H_2$ released after addition of methanol, mmol | mmol of $H^-$ involved in reduction/mol of organic compd | Brown[a] results with ether boranes for same functional group |
|---|---|---|---|---|---|---|
| Benzaldehyde | 2.0 | 6.0 | 2.0 | 0.4 | 0.6 | 1.0 |
| Acetophenone | 4.0 | 4.0 | 0 | 9 | 0.75 | 1.0 |
| | 4.0 | 12.0 | 2.4 | 3.7 | 0.56 | 1.0 |
| Cyclohexene | 4.0 | 12.0 | 1.0 | 0 | 1.0 | 1.0 |
| Acetyl chloride | 2.0 | 6.0 | 0 | 6.0 | 0 | 0.4 |
| Formic acid | 2.0 | 6.0 | 2.9[b] | 0.0 | 1.0 | 2.8 |

[a] References 1 and 2. [b] White solid formed and gas evolution ceased after addition of 2.7 mmol of formic acid.

ylene glycol (diglyme). We have studied the effect of

$$3NaBH_4 + 4BF_3\cdot OEt_2 \xrightarrow{\text{diglyme}} 2B_2H_6 + 3NaBF_4 + 4Et_2O$$

adding 1 drop of boron trifluoride–ethyl etherate (III) to the reductions of lactones and epoxides with I and found that it does indeed give results equivalent to those with ether–boranes.

The mechanism and products of hydroboration of nitriles have been shown to be quite complex;[9] nevertheless we corroborated Brown and Subba Rao's data with tetrahydrofuran–borane. Addition of III did not appreciably catalyze their reduction by I. We attribute the difference in reactivity of I to the fact that nitriles are weaker donors than alkyl sulfides, but stronger than ethers toward soft Lewis acids.[10]

We have no explanation for the erratic results with formic acid. Brown has postulated the formation of triacylboranes as intermediates in the reduction of acids by borane. These should also be soft acids which would

$$3RCOOH + BH_3 \longrightarrow (RCOO)_3B + 3H_2$$

coordinate dimethyl sulfide more strongly than ethers. This may hinder further reduction. Brown and coworkers[11] have recently reported that disiamylborane $\{[(CH_3)_2CHCHCH_3]_2BH\}$ also does not reduce acids and reacts very sluggishly with nitriles. They attribute these differences to steric hindrance.

## Conclusions

Dimethyl sulfide–borane (I) provides a means of handling diborane as a storable liquid with most of its hazardous nature tamed, yet retaining sufficient reactivity for most hydroboration and reduction applications. Contrary to expectations tetrahydrothiophene–borane is less reactive than dimethyl sulfide–borane and hence less useful for general hydroborations and reductions.

**Registry No.**—I, 13292-87-0.

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