

## 보란-붕산트리페닐(1 : 0.1)계에 의한 술폭시화물의 신속한 탈산소화반응에 관한 연구

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## Fast Deoxygenation of Sulfoxides with Borane- Triphenyl Borate (1 : 0.1) System

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**요 약.** 술폭시화물을 보란으로 환원할때 붕산트리페닐을 촉매량 (10몰 퍼센트) 가하면 대응하는 황화물로 환원이 현저히 촉진됨이 관찰되어 이 환원계에 의해 구조적으로 서로 다른 몇가지 술폭시화물의 환원반응이 조사되었다. 술폭시화 테트라메틸렌은 5분 이내(보란만으로는 24시간 걸림) 술폭시화 디에틸, 술폭시화 디벤질, 술폭시화 벤질페닐은 1시간내에 정량적으로 환원이 완결되었으며 술폭시화 디페닐은 반응이 느려서 24시간에 90% 수율(보란만으로는 24시간에 18% 수율)로 환원되었다. 삼플루오르화붕소 에틸에테르 및 붕산트리에틸의 촉매효과는 붕산트리페닐보다 덜하였다.

**ABSTRACT.** The presence of 10 mole percent triphenyl borate accelerated dramatically the rate of reduction of structurally different sulfoxides with borane in tetrahydrofuran at room temperature, compared to the slow reduction with borane itself. Tetramethylene sulfoxide underwent complete reduction in 5 min and diethyl sulfoxide, dibenzyl sulfoxide and benzylphenyl sulfoxide were reduced quantitatively within 1 h, whereas the reduction of diphenyl sulfoxide was rather slow, giving diphenyl sulfide in 90% yield in 24 h. Boron trifluoride etherate and triethyl borate were less effective than triphenyl borate. A possible mechanism is presented.

### INTRODUCTION

Reduction of sulfoxides to sulfides has recently been the subject of extensive research. In reviewing the literatures<sup>1</sup>, it appeared that sulfoxides were reduced by organosilicon compounds<sup>2</sup>, by trivalent phosphorus compounds<sup>3</sup>, by metal halides<sup>4</sup>, by acylating<sup>5</sup>, or alkylating agents<sup>6</sup>, by iron pentacarbonyl<sup>7</sup>, by hydroiodic acid<sup>8</sup> and by dichlorocarbene with phase transfer catalysts.<sup>9</sup> However, these procedures mostly

required elevated temperature or excess reagents to give moderate yields and only few methods could accomplish the reduction rapidly in high yields under mild conditions with common, inexpensive laboratory reagents.<sup>3b, 5b, 6a</sup>

In the reaction of sulfoxides with metal hydrides, it was found that sulfoxide was essentially inert to sodium borohydride,<sup>10</sup> lithium borohydride,<sup>11</sup> zinc borohydride<sup>12</sup> or lithium triethylborohydride,<sup>13</sup> and was reduced slowly with lithium aluminum hydride<sup>14</sup> and catechol-

borane.<sup>15</sup> And it was reported that a large excess of sodium borohydride-cobalt chloride mixture reduced readily aromatic sulfoxides, although little or no sulfides were obtained from dibenzyl sulfoxide and tetramethylene sulfoxide with this reagent.<sup>16</sup> On the other hand, Brown and Ravindran<sup>17</sup> reported that dichloroborane reduced rapidly aliphatic sulfoxides to the corresponding sulfides, in contrast to the slow reduction with borane<sup>18</sup> or alkyboranes.<sup>19</sup>

Recently, we have carried out a systematic study on the effect of triphenyl borate on the reduction of representative organic functional groups with borane.<sup>20</sup> In this study, we observed that the rate of reduction of sulfoxides with borane increased dramatically in the presence of triphenyl borate in tetrahydrofuran at room temperature. This report describes the scope and synthetic usefulness of this procedure for the reduction of sulfoxides to sulfides.

## EXPERIMENTAL

**General.** All glasswares were thoroughly dried in a drying oven and cooled down under a stream of dry nitrogen just prior to use.

Most of the organic compounds utilized in this study were commercial products of the highest purity. They were further purified by distillation or recrystallization when necessary. Sodium borohydride (Alrich Chem. Co) was used without further purification, but dried out in a heating vacuum oven at 120° for 12 h.

All of the solvents used were dried with excess lithium aluminum hydride, distilled under nitrogen, and stored in a flask equipped with a rubber septum inlet and a connection to a mercury bubbler, over 4Å molecular sieve.

All reduction experiments were carried out under a dry nitrogen atmosphere. Hypodermic syringes were used to transfer the solution.

Glp analysis was performed on Hewlett

Packard Model 5840A instrument equipped with flame ionization detector. All of the yields of products were determined by utilizing suitable internal standards and authentic mixtures. The following columns were used: 10% OV-17 on chromosorb WHP, 6ft, 0.125 inch(Column A) and 10% OV-1 on chromosorb WHP, 6ft, 0.125 inch. (Column B)

**Preparation of Sulfoxides.** The preparation of benzylphenyl sulfoxide from benzylphenyl sulfide<sup>21</sup> is representative. Benzylphenyl sulfide (54 g, 0.25 mol) was dissolved in 250 ml of acetone. The solution was filtered to remove undissolved substances. Then 30% hydrogen peroxide (41 g) was added, the solution was stirred for 8 h at 10~15° and allowed to stand at room temperature for 72 h. The acetone was evaporated. The crude sulfoxide was recrystallized from 60% ethyl alcohol. Yield: 38 g, mp 119~120° (*lit.*,<sup>21a</sup> mp 122~123°). Diethyl sulfoxide was prepared by the similar procedure. Yield, 65%, bp, 78~80°/10mmHg (*lit.*,<sup>21b</sup> 83°/12mmHg).

**Borane-Tetrahydrofuran Solution.** Predried hot sodium borohydride (97%, 11.7 g, 300 mmol) was introduced into a 500 ml, oven-dried flask, equipped with a side arm, fitted with a rubber cap, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler. After the flask was cooled down to room temperature under a stream of dry nitrogen, 240 ml of freshly distilled tetrahydrofuran was introduced. To this slurry, dimethyl sulfate (36.6 g, 290 mmol) was added dropwise with stirring in an ice-water bath. Stirring was continued for 10~12 hours until gas evolution was stopped. Then the reaction mixture was cooled down to 0°, allowed to stand to settle down the precipitate and stored in a refrigerator under slight positive pressure of nitrogen. The hydride concentration was determined by hydrolyzing

aliquots from the clear supernatant with 2 *N* sulfuric acid-tetrahydrofuran (1 : 1) mixture and measuring the hydrogen evolution. It was found to be 3.1 *M* in hydride, 1.03 *M* in borane.

**Triphenyl Borate Solution in Tetrahydrofuran.** Phenol (244 g 2.6 mmol) and boric acid (31 g, 0.5 mol) were placed in a dry 500 ml flask with a magnetic stirring bar and heated until water-phenol azeotrope was distilled off at 98~99°. The remaining phenol was removed at low pressure (62°, 1~2 mmHg) and the triphenyl borate was distilled under reduced pressure. (192~210°, 1~2 mmHg). The crude yield was 80% (116 g). The pure triphenyl borate was obtained by a fractional vacuum distillation (210°, 1 mmHg). (*lit.*<sup>22</sup> 177~178°, 0.5 mmHg). Overall yield: 72% (104 g). The triphenyl borate (104 g) was dissolved in THF to give 200 ml of 1.8 *M* solution.

**Reaction of Sulfoxides with Borane in Tetrahydrofuran at Room Temperature.** Reduction of tetramethylene sulfoxide is described as a representative. A 50 ml, oven-dried flask, equipped with a side arm, fitted with a rubber septum, a magnetic stirring bar, and a reflux condenser connected to a gas buret, was cooled down under a stream of dry nitrogen. The flask was immersed in a water bath (*ca* 20°). Then 3.3 ml of tetrahydrofuran was introduced into the reaction flask by a hypodermic syringe, followed by 6.7 ml (6.7 mmol) of a 1.0 *M* solution of borane in THF and 2.5 mmol of toluene (5 ml in THF) to serve as the internal standard. Finally, 5 mmol (5 ml in THF) of tetramethylene sulfoxide was added to the reaction mixture. The mixture was stirred well. The mixture became cloudy to evolve hydrogen (5 mmol) rapidly. At different intervals of time, the mixture was quenched with dilute sulfuric acid, made alkaline with dilute sodium hydroxide, extracted with ether, and the organic layers

were analyzed by glpc using column A. The analysis indicated the formation of tetramethylene sulfide in the yields of 70% (0.25 h), 88% (0.5 h), 95% (1 h) and 100% (2 h). The same procedure was performed for the other sulfoxides. The results were summarized in *Table 2*.

**Reaction of Diphenyl Sulfoxide with Borane in the Presence of Different Molar Equivalents of Triphenyl Borate in Tetrahydrofuran at Room Temperature.** The experimental set-up and work-up procedure for analysis of product were the same as in the previous experiments. The reduction with borane-triphenyl borate (1 : 1) system is described as a representative. Into a 50 ml flask were introduced THF (2.1 ml), borane (6.7 mmol, 20 mmol in hydride, 6.7 ml in THF), diphenyl ether (0.5 mmol, 2.5 ml in THF) to serve as an internal standard and triphenyl borate (6.7 mmol, 3.7 ml in THF) in a water bath (*ca* 20°). Finally, diphenyl sulfoxide (5 mmol, 5 ml) was added to the reaction mixture. The mixture was maintained at room temperature. After 24 h, glpc analysis using column A indicated the presence of 96% diphenyl sulfide. The same procedure was also performed in the presence of 0.67 mmol, 1.675 mmol, 3.35 mmol and 13.4 mmol of triphenyl borate under the same condition. The results were summarized in *Table 1* and *Fig. 1*.

**Reaction of Diphenyl Sulfoxide with Various Molar Equivalents of Borane in the Presence of 10 Mole Percent Triphenyl Borate in Tetrahydrofuran at Room Temperature.** The reduction with 1 molar equivalent of borane is described as a representative. A clean 50 ml, oven-dried flask with a side arm, fitted with a rubber cap, a magnetic stirring bar, and a reflux condenser connected to a gas buret, was cooled down to room temperature in a water bath under a stream of dry nitrogen. Then,

THF (7.2 ml) was introduced into the flask by a hypodermic syringe, followed by borane (5 mmol, 5 ml) in THF, diphenyl ether (0.5 mmol, 2.5 ml in THF) to serve as an internal standard and triphenyl borate (0.5 mmol, 0.28 ml in THF). Finally, diphenyl sulfoxide (5 mmol, 5 ml) in THF was introduced. The reaction mixture was both 0.25 M in the sulfoxide and borane. The reaction mixture was maintained at room temperature. At appropriate intervals of time, 1 ml of the mixture was withdrawn by a hypodermic syringe, quenched with dilute sulfuric acid, made alkaline with dilute sodium hydroxide, extracted with ether, and the organic layers were analyzed by glpc using column A. The analysis revealed the presence of diphenyl sulfide in the yields of 28% (3 h), 45% (6 h) and 73% (24 h). The same procedure was performed with 6.7 molar equivalent of borane in the presence of 0.67 molar equivalent of triphenyl borate in THF at room temperature. The results were illustrated in Fig. 2.

**Reaction of Sulfoxides with Borane in the Presence of 10 Mole Percent Triphenyl Borate in Tetrahydrofuran at Room Temperature.**

Reduction of diethyl sulfoxide is described as a representative. A clean 50 ml, oven-dried, flask equipped with a side arm, fitted with a rubber cap, a magnetic stirring bar, and a reflux condenser connected to a gas buret, was cooled down to room temperature in a water bath (ca 20°) under a stream of dry nitrogen. 2.93 ml of THF was introduced into the flask by a hypodermic syringe, followed by borane (6.7 mmol, 6.7 ml) in THF, toluene (2.5 mmol, 5 ml) in THF to serve as the internal standard and triphenyl borate (0.67 mmol, 0.37 ml) in THF. Finally, diethyl sulfoxide (5 mmol, 5 ml) in THF was added to the reaction mixture. The mixture was stirred at room temperature. The mixture gradually became cloudy to evolve

hydrogen (5 mmol). At appropriate intervals of time, 1 ml of the reaction mixture was withdrawn by a hypodermic syringe, quenched with 1 ml of 1 M sulfuric acid, made alkaline with 1 ml of 6 N sodium hydroxide, extracted with 4 ml of ether and the organic layers were analyzed by glpc using column B. The analysis indicated the presence of diethyl sulfide in the yield of 83% (5 min), 95% (15 min) and 100% (30 min). The same procedure was performed for the other sulfoxides. The results were summarized in Table 2. In the case of dibenzyl sulfoxide, the sulfoxide was also reduced with boron methyl sulfide (BMS) following the exactly same procedure. Dibenzyl sulfide was obtained in the yields of 62% at 1h, 87% at 3h, and 100% at 6h. The results were illustrated in Fig. 3.

**Reaction of Sulfoxides with Borane in the Presence of 10 Mole Percent Various Catalysts in Tetrahydrofuran at Room Temperature.** Reduction of diethyl sulfoxide with borane in the presence of 10 mole percent boron trifluoride etherate is described as a representative. The experimental set-up and work-up procedure for analysis of product were the same as in the previous experiments. Into the flask were introduced THF (2.3 ml), borane (6.7 mmol, 6.7 ml) in THF, toluene (2.5 mmol, 5 ml) in THF to serve as the internal standard and boron trifluoride etherate (0.67 mmol, 1 ml) in THF. Finally, diethyl sulfoxide (5 mmol, 5 ml) in THF was added to the reaction mixture. The reaction mixture was stirred at room temperature. Hydrogen was evolved slowly. Glpc examination revealed the formation of diethyl sulfide in the yield of 30% (5 min), 47% (15 min), 62% (30 min) 82% (1h) and 97% (3h). Reactions were also carried out in the presence of triethyl borate. The results were summarized in Table 3 and Fig. 4.

## RESULTS AND DISCUSSION

**Catalytic Effect of Triphenyl Borate.** In our preliminary study, we found that the reduction of diphenylsulfoxide with borane was greatly accelerated by the presence of equimolar triphenyl borate. Thus, borane-triphenyl borate (1:1) system reduced the sulfoxide in 96% yield, whereas only 18% yield with borane itself, both at room temperature in 24 h (Table 1 and Fig. 1). In order to study the effect of triphenyl borate on the borane reduction of sulfoxides more in detail, diphenyl sulfoxide was treated with borane in the presence of 0.1, 0.25, 0.5, 1 and 2 molar equivalents of triphenyl borate in tetrahydrofuran at room temperature. As shown in Table 1, we found that the presence of only 10 mole percent triphenyl borate enhanced the rate of reduction dramatically, showing that triphenyl borate played a role as a catalyst.

**Optimum Requirement of Hydride.** In order to investigate the optimum requirement of hydride in achieving such reduction satisfactorily, 2 (stoichiometric amount), 3 (50% excess), and 4 (100% excess) molar equivalents of hy-

Table 1. Effect of triphenyl borate on the reduction of diphenyl sulfoxide with borane in THF at room temperature.<sup>a</sup>

Triphenyl Borate <sup>b</sup>	Product <sup>c</sup>		
	3 h	6 h	24 h
None	6	9	18
0.1	34	48	90
0.25	41	62	94
0.5	40	68	98
1.0	40	65	96
2.0	36	67	94

<sup>a</sup>Reaction mixtures were 0.25 M in diphenyl sulfoxide and 1.0 M in hydride. <sup>b</sup>The molar ratio to borane. <sup>c</sup>Percent yields of diphenyl sulfide estimated by glpc analysis.

dride were reacted with the sulfoxide in the presence of 10 mole percent triphenyl borate in tetrahydrofuran at room temperature. The reduction of sulfoxide to sulfide requires 2 molar equivalents of hydride (0.67 molar equivalent of borane) stoichiometrically: one equivalent of hydride for hydrogen evolution and another equivalent of hydride for reduction. The reduction of diphenyl sulfoxide was representative. As shown in Fig. 2, the results appeared that with 4 molar equivalents of hydride, the sulfoxide was reduced in the yield of 90% and with 3 molar equivalent of hydride, the reduction was slower, giving 73% yield both in 24 h. On the other hand, the sulfoxide was reduced quite slowly with stoichiometric amounts of hydride, giving 35% diphenyl sulfide in 24 h. Therefore, the reaction was performed with 4 molar equivalents of hydride in the presence of 10 mole percent triphenyl borate.

**Generality of the Reaction.** In order to

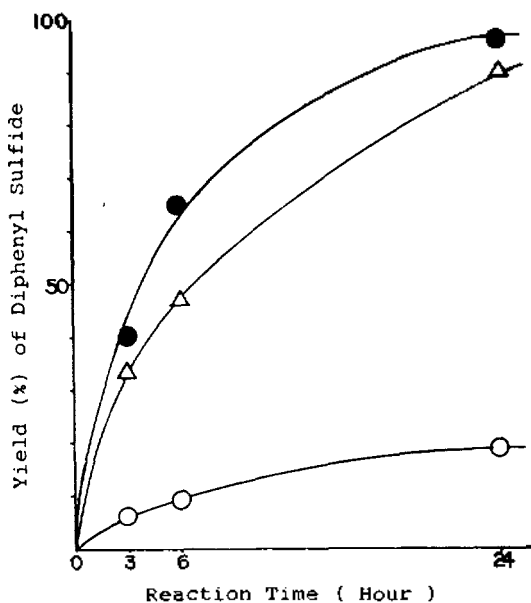


Fig. 1. Reduction of diphenyl sulfoxide with borane in THF at room temperature.  $(C_6H_5)_2SO/BH_3$ ; 1/1. 33,  $BH_3/(C_6H_5O)_3B$ ; 1/1(●), 1/0.1(△), 1/0(○)

test the generality of this reaction, the four more structurally different sulfoxides, namely tetramethylene sulfoxide, diethyl sulfoxide, dibenzyl sulfoxide and benzylphenyl sulfoxide were chosen and reduced under the same con-

ditions. The reduction of these five sulfoxides were also carried out with borane itself. As shown in Table 2, the catalytic effect of triphenyl borate was evident in all cases. For example, the complete reduction of dibenzyl sul-

Table 2. Reaction of representative sulfoxides with borane in the presence of 10 mole percent triphenyl borate in THF at room temperature.

Compounds <sup>a</sup>	(C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> B <sup>b</sup> mole %	Products <sup>c</sup>						
		5min	15min	0.5 h	1.0 h	3.0 h	6.0 h	24.0 h
Tetramethylene sulfoxide	10	100						
	None		70	88	95	100 <sup>d</sup>		
Diethyl sulfoxide	10	83	95	100				
	None			33	46	69	86	100
Dibenzyl sulfoxide	10		96	100				
	None			36	56	85	96	
Benzylphenyl sulfoxide	10			83	100			
	None			23	38	69	83	100
Diphenyl sulfoxide	10					34	48	90
	None					6	9	18

<sup>a</sup>Reaction mixtures were 0.25M in compounds and 1.0M in hydride. <sup>b</sup>10 mole percent catalysts to the concentration of borane were used. <sup>c</sup>Percent yields of products estimated by glpc analysis. <sup>d</sup>Yield at 2 h.

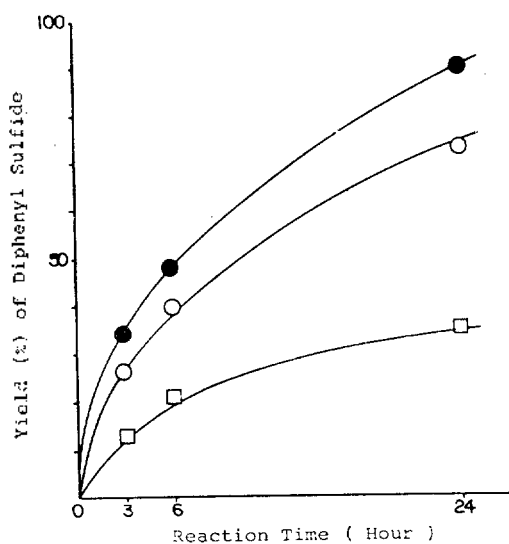


Fig. 2. Reduction of diphenyl sulfoxide with borane in the presence of 10 mole percent triphenyl borate in THF at room temperature. (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SO/hydride; 1/4(●) 1/3(○), 1/2(□).

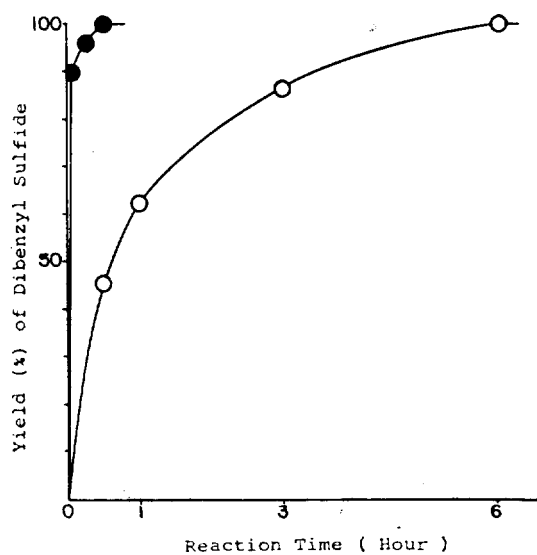


Fig. 3. Reduction of dibenzyl sulfoxide with borane and borane methyl sulfide in the presence of 10 mole percent triphenyl borate in THF at room temperature. (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>SO/BH<sub>3</sub>(●) or BMS(○); 1/1.33.

Table 3. Reaction of representative sulfoxides with borane in the presence of various catalysts in THF at room temperature.

Compounds <sup>a</sup>	Catalysts <sup>b</sup>	Products <sup>c</sup>						
		5min	15min	0.5 h	1.0 h	3.0 h	6.0 h	24.0 h
Tetramethylene sulfoxide	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> B	100						
	(EtO) <sub>3</sub> B	80	97	100				
	BF <sub>3</sub> ·OEt <sub>2</sub>	58	72	87	98			
	None		70	88	95	100 <sup>d</sup>		
Diethyl sulfoxide	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> B	83	95	100				
	(EtO) <sub>3</sub> B	43	63	80	100			
	BF <sub>3</sub> ·OEt <sub>2</sub>	30	47	62	82	97		
	None			33	46	69	86	100
Dibenzyl sulfoxide	(C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> B		96	100				
	(EtO) <sub>3</sub> B		31	51	78	100		
	BF <sub>3</sub> ·OEt <sub>2</sub>		20	40	62	95		
	None			36	56	85	96	
Benzylphenyl sulfoxide	(C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> B			83	100			
	(EtO) <sub>3</sub> B		28	40	70	100		
	BF <sub>3</sub> ·OEt <sub>2</sub>			21	37	78	93	100
	None			23	38	69	83	100
Diphenyl sulfoxide	(C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> B					34	48	90
	(EtO) <sub>3</sub> B					25	31	39
	BF <sub>3</sub> ·OEt <sub>2</sub>					14	31	36
	None					6	9	18

<sup>a</sup>Reaction mixtures were 0.25 M in compounds and 1.0 M in hydride. <sup>b</sup>10 mole percent catalysts to the concentration of borane were used. <sup>c</sup>Percent yields of products estimated by glpc analysis. <sup>d</sup>Yield at 2 h.

foxide with borane itself required 6 h, whereas the same yield was realized in 15 min in the presence of 10 mole percent the catalyst. In the case of dibenzyl sulfoxide, borane methyl sulfide (BMS) was also applied for the reduction. As shown in Fig. 3, dibenzyl sulfoxide was reduced rapidly in 0.5 h with BH<sub>3</sub>-THF, whereas the reduction with BMS was completed in 6 h.

**Other Catalysts.** Since triphenyl borate is a boric acid ester and a Lewis acid, we wondered that triethyl borate and boron trifluoride etherate might also show the catalytic effect. We tested these possibilities. The five representative sulfoxides were reduced with borane under

the same conditions except that triphenyl borate was replaced by triethyl borate or boron trifluoride etherate. As shown in Table 3, and Fig. 4, the catalytic effects of triethyl borate and boron trifluoride etherate were also observed, but not so dramatic as triphenyl borate. It is interesting to note that the catalytic effects were in the order: triphenyl borate > triethyl borate > boron trifluoride etherate.

**Possible Mechanism.** From the results shown in Table 2 and Table 3, we suggest a possible mechanism as follows. A small quantity of Lewis acids, phenoxyborane species could be produced by a rapid mobile equilibrium involving disproportionation of borane and triphenyl

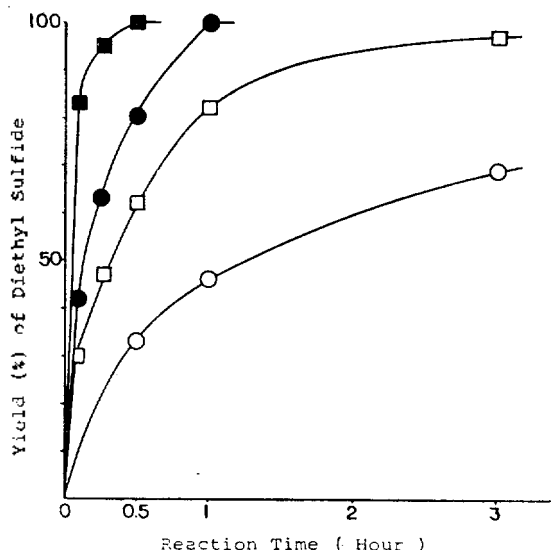
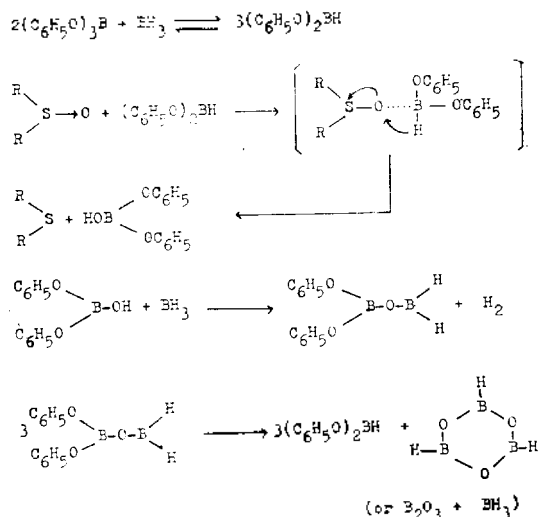


Fig. 4. Reduction of diethyl sulfide with borane in the presences of 10 mole percent various catalysts in THF at room temperature. diethyl sulfide/ $BH_3$ ; 1/1.33.  $BH_3$ /catalysts; 1/0.1. Catalysts;  $(C_6H_5O)_3$  (■),  $(EtO)_3B$  (●),  $BF_3 \cdot OEt_2$  (□), none (○).

borate.<sup>23</sup> The phenoxyborane species are expected to coordinate on the electron rich site, the oxygen of sulfoxide, and the coordinated sulfoxides are deoxygenated to form the stable borate *via* hydride transfer as following scheme.<sup>24</sup>



The catalytic effect of triphenyl borate suggests that the phenoxyborane species should be regenerated together with the formation of boroxine (or boron trioxide and borane).

### CONCLUSION

The presence of 10 mole percent triphenyl borate accelerated dramatically the rate of sulfoxide reduction with borane. This procedure provide a simple and synthetically useful method for the reduction of sulfoxides to the corresponding sulfides under mild conditions.

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