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# PREPARATION OF TRIETHYLAMINE-BORANE OR PYRIDINE-BORANE IN LIQUID SULFUR DIOXIDE AND REDUCTION OF ARALKYL HALIDES WITH BASE-BORANE COMPLEX IN LIQUID SULFUR DIOXIDE OR IN NITROMETHANE

Shoichi Matsumura and Niichiro Tokura

Department of Applied Chemistry, Faculty of Engineering, Osaka University,
Suita, Osaka, Japan.

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Rapid progresses have been made in selective reduction using diborane and metallic borohydride which greatly simplified the synthetic problems of organic chemistry. The reductive cleavage of episulfones by metallic aluminum- and borohydride has been examined by the present authors.[1] In this communication, we wish to report the preparation of triethylamine-borane or pyridine-borane in liquid sulfur dioxide and the use of the amine-borane complexes for the reduction of aralkyl halides to the corresponding hydrocarbons in liquid sulfur dioxide or in nitromethane.

The amine-borane complex has been prepared by the reaction of amine hydrochloride with sodium borohydride,[2] or by the reduction of trialkyl-boranes in the presence of a tertiary amine.[3] H. C. Brown et al., obtained the complex by mixing triethylamine with diborane.[4] However, the preparation and use in liquid sulfur dioxide is superior in its yield and convenience.

The reduction of aralkyl halides by the borane complexes has not been reported. To explore the possibility of the reduction in liquid sulfur dioxide, the present authors investigated the reaction of such reducing agents as sodium or lithium borohydride with triethylamine or pyridine in liquid sulfur dioxide. The reaction in liquid sulfur dioxide at 0°C proceeded instantaneously and the triethylamine-borane complex was separated by distillation at 76°C (4mm Hg), the yield being over 85 percent.

$$NaBH_4 + NR_3 \xrightarrow[0°C]{liq.SO_2} H_3B{\cdot}NR_3 + \text{inorganic product} \qquad (1)$$

Since sulfur dioxide is a weaker acid than other Lewis acids such as $BF_3$, sulfuric acid and HCl, the triethylamine-borane complex is prepared in good yield and has moderate stability in liq.$SO_2$. On the other hand, pyridine-borane complex is not so stable as triethylamine complex and reduces the sulfur dioxide to sulfur when the complex is kept in sulfur dioxide. Therefore pyridine-borane complex separated from the reaction mixture was dissolved in nitromethane for use as the reducing agent.

The results of the reduction of aralkyl halides by these reagents together with the results in other solvents are summarized in Table 1. The rates and the yields of the reaction depend on the stability of carbonium ions derived from the halides and decrease in the following order:

$$Ph_3CCl > Ph_2CHBr > Ph_3CHCl \approx (CH_3)_3CI \gg (CH_3)_3CCl \approx PhCH_2Cl$$

While the reduction by sodium borohydride in water under solvolytic condition as reported by H. C. Brown et al.,[5] gives a mixture of the corresponding hydrocarbon and alcohol in a low yield, the reduction by the amine-borane does not afford the alcohol from the chloride.

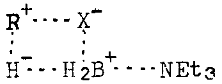
Inspection of the results in Table 1 reveals the distinguished difference between the solvents used. The nucleophilic solvents such as DMF (dimethylformamide) and THF (tetrahydrofuran) failed to afford the reduction products whereas liquid sulfur dioxide, an ionizing and electrophilic solvent, gave an excellent yield in the reduction of benzhydryl chloride. Both sulfur dioxide and nitromethane are very unique solvents which stabilize the cationic species and favor the reactions.

Secondly, the applicability of the reduction procedure is limited within tertiary and secondary halides and no reduction product is possible with primary halides. The solvent effect coupled with above fact, will account for the following reaction mechanism, i.e., the rate determining ionization of RX, eq. (2), followed by a nucleophilic attack of hydride ion derived from the amine-borane complex.

$$RX \longrightarrow R^{+}\cdots X^{-} \qquad (2)$$

$$R^{+}\cdots X^{-} + H_3B\cdot NEt_3 \longrightarrow RH + XH_2B\cdot NEt_3 \qquad (3)$$

Alternatively, following four center mechanism for the reduction is another possibility.



$$\begin{array}{lll} R^{+}\cdots & X^{-} & \\ \vdots & \vdots & \\ H^{-}\cdots & H_2B^{+}\cdots & NEt_3 \end{array} \qquad (4)$$

## REFERENCES

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TABLE 1 REDUCTION OF ALKYL HALIDES BY TRIETHYLAMINE-BORANE IN VARIOUS SOLVENTS

| RX | Solvent | Temp.(°C) | Reaction Period(hr) | RH | Yield(%) |
|---|---|---|---|---|---|
| $(C_6H_5)_3CCl$ | liq-$SO_2$-Ether* | Room Temp. | 1 | $(C_6H_5)_3CH$ | 98 |
| | Ether | 〃 | 100 | 〃 | 90 |
| $(C_6H_5)_2CCl_2$ | liq-$SO_2$ | 〃 | 5 | $(C_6H_5)_2CH_2$ | 50 |
| $(C_6H_5)_2CHBr$ | liq-$SO_2$ | 0 | 1 | 〃 | 99 |
| | Nitromethane | Room Temp. | 5 | 〃 | 100 |
| | Nitromethane** | 〃 | 5 | 〃 | 85 |
| $(C_6H_5)_2CHCl$ | liq-$SO_2$ | 〃 | 10 | 〃 | 81 |
| | DMF | 〃 | 50 | 〃 | Trace |
| | THF | 〃 | 50 | 〃 | 0 |
| $C_6H_5C(CH_3)_2Cl$ | liq-$SO_2$ | 〃 | 5 | $C_6H_5CH(CH_3)_2$ | 57 |
| $(CH_3)_3CCl$ | liq-$SO_2$ | 〃 | 30 | $(CH_3)_3CH$ | 0 |
| $(C_6H_5)CH(CH_3)Br$ | liq-$SO_2$ | 〃 | 30 | $C_6H_5CH_2(CH_3)$ | 0 |
| $(C_6H_5)CH(CH_3)Cl$ | liq-$SO_2$ | 〃 | 30 | 〃 | 0 |
| $C_6H_5CH_2Cl$ | Nitromethane | 100 | 8 | $C_6H_5CH_3$ | 15 |

* This reaction was very fast, so it is necessary to moderate the reaction velocity by adding ether to the system.

** Pyridine-borane was used.