Tetrahedron Letters No.5, pp. 363-365, 1969. Pergamon Press. Printed in Great Britain.

REDUCTION OF ARALKYL HALIDES WITH DIBORANE IN NITROMETHANE

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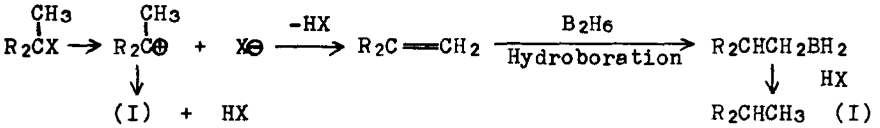
(Received in Japan 6 November 1968; received in UK for publication 23 December 1968)

In continuation of the work in a previously published paper,[1] we wish to report the effective reduction of aralkyl halides with diborane in nitromethane.[2] Because of the high solubility of diborane in tetrahydrofuran (THF), this solution is conveniently utilized for reductions by diborane. However, aralkyl halide could not be reduced to the corresponding hydrocarbon by diborane in THF.[3] The present results are summarized in TABLE I. On the basis of these results, it is interesting to note that the reduction is almost quantitative and would be quite useful for the conversion of alkyl halides into the corresponding hydrocarbons. As described in our previous communication,[1] the ionization of alkyl halides into the carbonium ions is the important factor of this reaction: tertiary > secondary > primary halides. This reduction is available not only to aralkyl halides, but to other alkyl halides, for example, when a Lewis acid such as aluminium chloride is used. The reduction products were the corresponding hydrocarbons and hydrogen halides, and not B-haloboranes (BH_2X).

$$\mathrm{RX} \xrightarrow[\text{in Nitromethane}]{B_2H_6} \mathrm{RH} + \mathrm{HX} + (\mathrm{BH})_n$$

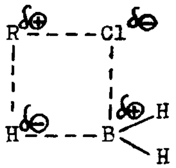
This suggests that B-haloborane decomposes into hydrogen halide and unknown remainders (represented as $(BH)_n$) in nitromethane, though B-haloborane is stable in THF,[4] and this result was confirmed by the fact that triethylamine-B-haloboranes decompose to triethylammonium halide in nitromethane; in our previous paper, the hydrocarbon, triethylammonium halide and unknown remainders were prepared by the reduction of alkyl halides with triethylamine-borane in nitromethane.

The evolved hydrogen halide will accelerate the rate of reaction by increasing the ionization of alkyl halides. Furthermore, this reduction gave the corresponding hydrocarbon in excellent yield.



For example, t-cumyl chloride gave cumene in a 87 % yield by diborane whereas α-methylstyrene (40 %) was prepared in addition to cumene (57 %) from t-cumyl chloride when the reduction was carried out with triethylamine-borane. (see also the TABLE I of the previous communication[1]).

As diborane is an electrophilic agent,[5] involving a symmetrical cleavage of diborane, but not an unsymmetrical cleavage in certain basic environments, so a mechanism involving simultaneous nucleophilic attack of halide on boron and electrophilic attack on hydrogen by the carbonium ion would be accepted. This four-centered reaction resembles the hydroboration and the hydrogen-halogen exchange reaction between trialkylsilanes and trityl halide.[6]



Similarly, diisocamphenylborane (IPC$_2$BH) also reduced trityl chloride to the corresponding hydrocarbon, triphenylmethane, under reflux conditions (>95 %)

We are now studying on the reduction in more details.

REFERENCES

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2. Sulfur dioxide reacts with diborane to give sulfur smoothly, so we carried out the reduction in nitromethane.
3. H. C. Brown, B. C. Subba Rao, J. Am. Chem. Soc., 82 681 (1960)
4. H. Nöth, H. Beyer, Ber., 93 2251 (1960)
5. Triethylamine-borane did not decompose into diborane in liquid sulfur dioxide or in nitromethane and this reagent is a nucleophile in contrast to diborane.
6. C. Y. Corey, R. West, J. Am. Chem. Soc., 85 2430 (1963)

TABLE I REDUCTION OF ALKYLHALIDES BY DIBORANE IN NITROMETHANE*

RX	Solvent	Temp.(°C)	Reaction Period(hr)	RH	Yield(%)
$(C_6H_5)_3CCl$	Nitromethane	15	6	$(C_6H_5)_3CH$	96
	Nitromethane**	110	6	$(C_6H_5)_3CH$	>95
$(C_6H_5)_2CHBr$	Nitromethane	15	6	$(C_6H_5)_3CH_2$	92
$(C_6H_5)_2CHCl$	Nitromethane	15	6	$(C_6H_5)_2CH_2$	90
	Tetrahydrofuran	15	6	$(C_6H_5)_2CH_2$	<2
$C_6H_5C(CH_3)_2Cl$	Nitromethane	15	6	$C_6H_5CH(CH_3)_2$	82
$C_6H_5CH_2Cl$	Nitromethane	50	10	$C_6H_5CH_3$	0

* Diborane scarcely dissolves in nitromethane. We carried out the experiments by the following procedure: alkyl halides (0.002 mole) in nitromethane (50 ml) were treated with externally evolved diborane ($NaBH_4$ 3 g, and $BF_3 \cdot Et_2O$ 16 g in Diglyme) for about 6 hours, and unreacted diborene was trapped by triethylamine.

** Diisocamphenylborane (IPC_2BH) was used.