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REACTIONS OF ALKYLMAGNESIUM HALIDES AND ALKYLLITHIUMS WITH SELENIUM DIOXIDE. A NEW ROUTE TO DIALKYL SELENIDE

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Alkylmagnesium halides and alkyllithiums reacted with selenium dioxide, suspended in tetrahydrofuran, to afford dialkyl selenides in 30 — 62 % yields.

We have recently reported on the synthesis of dialkyl selenide by the reaction of trialkylborane with selenium dioxide.1) Strecker described that diphenyl selenide was afforded in the reaction of phenylmagnesium bromide with dichloroselenoxide.2) On the other hand, it has been reported that Grignard reagent reacted with sulfur dioxide to give dialkyl sulfide as a main reaction product.3) By analogy with these reactions it was expected that dialkyl selenide should be formed in the reaction of Grignard reagent with selenium dioxide.

In the first place, the reaction of butylmagnesium bromide, prepared from 1-bromobutane and magnesium, with selenium dioxide was examined. Then it was found that dibutyl selenide was formed in 62 % yield (based on 1-bromobutane) by the addition of the suspension of selenium dioxide in tetrahydrofuran to the diethyl ether solution of butylmagnesium bromide at 20°C. Butane (21 %), 1-butene (4 %) and octane (6 %) were also formed.

Then we undertook the reaction of some alkylmagnesium halides and alkyllithiums with selenium dioxide. Some results are shown in Table 1.

In all instances the yields were not so excellent. However, fortunately, the boiling points of these dialkyl selenides differ so largely from those of the by-products that the dialkyl selenides were isolated successfully by the distillation. Di-1-methylpropyl, dibutyl, dihexyl and dicyclohexyl selenides were identified by the direct comparison with authentic samples,4) and diethyl and di-1-methylethyl selenides were identified by mass apectra.

The following reaction procedure is representative. Into an argon flushed 100-ml flask, provided with a condencer, a dropping funnel and a stirring rod, 1.16 g of magnesium and 10 ml of diethyl ether were placed. Then 5.48 g (40 mmol) of 1-bromobutane in 20 ml of diethyl ether was added dropwise with stirring. To the stirred solution of resulting n-butylmagnesium bromide 4.44 g (40 mmol) of selenium dioxide, suspended in 30 ml of tetrahydrofuran was added slowly at 20°C. The stirring was continued for one hour at the same temperature. Then the reaction mixture was hydrolysed with 30 ml of water and extracted with petroleum ether several times. The combined extracts were washed with water and dried over anhydrous magnesium sulfate, followed by the distillation at 92°C/17 mmHg. Thus 1.85 g (9.6 mmol) of dibutyl selenide was obtained. Its ir, pmr and mass spectra were coincident with those of authentic dibutyl selenide.[4)]

Table 1. Reactions[a)] of Alkylmagnesium Halides and Alkyllithiums with Selenium Dioxide

RMgX from alkyl halide	Product	Yield,[b)] %	Bp. °C/mmHg
Bromoethane	Diethyl selenide	52[c)]	
2-Bromopropane	Di-1-methylethyl selenide	56[c)]	
1-Chlorobutane	Dibutyl selenide	45[c)]	
1-Bromobutane	Dibutyl selenide	62[c)] (48)[d)]	92/17
2-Bromobutane	Di-1-methylpropyl selenide	43[c)] (35)[d)]	85/16
1-Bromohexane	Dihexyl selenide	42[c)] (36)[d]	90/0.8
Chlorocyclohexane	Dicyclohexyl selenide	33[c)] (28)[d)]	92/0.7
RLi from alkyl halide			
1-Bromobutane	Dibutyl selenide	60[c)] (45)[d)]	92/17
1-Bromohexane	Dihexyl selenide	41[c)]	

a) Carried out by using 40 mmol of alkyl halide and 40 mmol of selenium dioxide, for one hour at 20°C for alkylmagnesium halide and -20°C for alkyllithium. b) Based on alkyl halide employed. c) Determined by glpc. d) Isolated by the distillation.

Several reactions for the synthesis of organoselenium compounds using Grignard reagent so far been reported. However this is the first case that selenium dioxide was applied in the reaction of Grignard reagent. This reaction seems to be useful as a new method for the synthesis of dialkyl selenide.

References

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4) The authentic samples were prepared by the method described in the following literature. M. L. Bird and F. Challenger, J. Chem. Soc., 570 (1942).

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