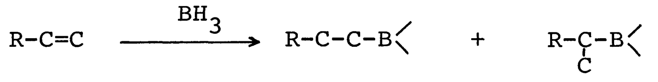
CHEMISTRY LETTERS, pp. 419-422, 1975. Published by the Chemical Society of Japan

A NEW ROUTE TO DIALKYL SELENIDE FROM OLEFIN VIA HYDROBORATION

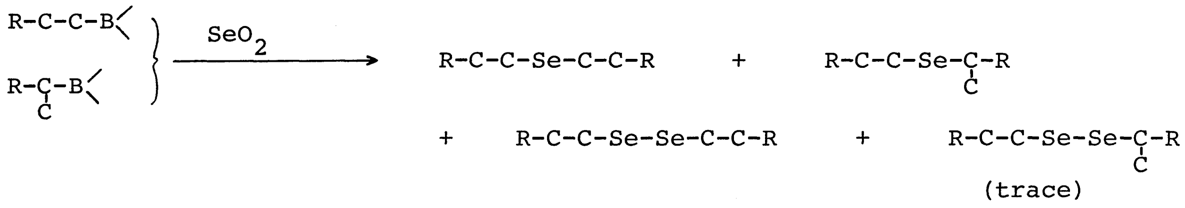
Akira ARASE and Yuzuru MASUDA
Kitami Institute of Technology, Kitami, Hokkaido 090

The reaction of trialkylboranes, prepared from olefin via hydroboration, with selenium dioxide was studied. In the aqueous selenium dioxide solution, trialkylboranes give the mixtures of dialkyl selenide and dialkyl diselenide, whereas in the suspension of selenium dioxide in tetrahydrofuran, trialkylboranes give dialkyl selenides selectively under the condition where the reaction time and the amount of selenium dioxide are controlled.

In the study of the reactions of organoboranes with the oxidizing agents, the authors recently found that dialkyl selenide and dialkyl diselenide were formed in the reaction of trialkylboranes with selenium dioxide (Eq. 2).



$$\mathrm{R{-}C{=}C} \xrightarrow{\mathrm{BH_3}} \mathrm{R{-}C{-}C{-}B}\!< \;+\; \mathrm{R{-}\underset{C}{C}{-}B}\!< \qquad (1)$$



$$\left.\begin{array}{l}\mathrm{R{-}C{-}C{-}B}\!< \\ \mathrm{R{-}\underset{C}{C}{-}B}\!<\end{array}\right\} \xrightarrow{\mathrm{SeO_2}} \mathrm{R{-}C{-}C{-}Se{-}C{-}C{-}R} + \mathrm{R{-}C{-}C{-}Se{-}\underset{C}{C}{-}R} + \mathrm{R{-}C{-}C{-}Se{-}Se{-}C{-}C{-}R} + \underset{\text{(trace)}}{\mathrm{R{-}C{-}C{-}Se{-}Se{-}\underset{C}{C}{-}R}} \qquad (2)$$

This type of the reaction has never been found in the reaction of organoboranes with oxidizing agents.

A reaction was first tried in the aqueous selenium dioxide solution using tricyclohexylborane. Thus, 10 mmol of tricyclohexylborane in tetrahydrofuran, obtained by hydroboration of cyclohexene, was allowed to react with 10 mmol of aqueous selenium dioxide at 70°C and the reaction was followed by glpc. Two compounds, formed after the reaction of three days, were isolated by preparative glpc, and they were identified as dicyclohexyl selenide and dicyclohexyl diselenide by their ir, pmr and mass spectra. The yields were 3.5 mmol for dicyclohexyl selenide and 0.9 mmol for dicyclohexyl diselenide. These yields were increased up to 5.7 mmol for the former and 2.6 mmol for the latter respectively by using 30 mmol of selenium dioxide for 10 mmol of tricyclohexylborane. Thus, it was expected that the reaction had a possibility to be a new method for the synthesis of organoselenium compounds. We examined the reaction using some trialkylboranes. The results are shown in Table 1.

Table 1. Reaction[a] of trialkylboranes with aqueous selenium dioxide solution

R_3B(10 mmol) from olefin	Time day	Product[b]	Yield,[c] mmol		Yield,[c] mmol
Cyclohexene	3	Dicyclohexyl selenide	5.7	Dicyclohexyl diselenide	2.6
1-Butene	5	Dibutyl selenide	1.5	Dibutyl diselenide	2.0
		Butyl 1-methylpropyl selenide	0.4		
2-Butene	5	Di-1-methylpropyl selenide	1.5	Di-1-methylpropyl diselenide	1.6
2-Methylpropene	5	Di-2-methylpropyl selenide	1.6	Di-2-methylpropyl diselenide	1.6
1-Hexene	5	Dihexyl selenide	1.0	Dihexyl diselenide	1.5
		Hexyl 1-methylpentyl selenide	0.3		

a) Carried out at 70°C by using 30 mmol of selenium dioxide and 10 mmol of R_3B.
b) Isolated by preparative glpc. c) Determined by glpc.

The reactions of acyclic trialkylboranes were considerably sluggish and furthermore roughly equal amounts of dialkyl selenide and dialkyl diselenide were formed.

These synthetically unfavorable facts led us to seek the reaction condition for the ready and selective formation of dialkyl selenide or dialkyl diselenide. Several attempts were made. After all, it was found that the addition of tetrahydrofuran solution of trialkylborane into the suspension of selenium dioxide in tetrahydrofuran, in the presence of small amount of added oxygen,[1] resulted in rapid and considerably selective formation of dialkyl selenide. Moreover, it was also found that in the case of acyclic trialkylboranes the yields were nearly three times those of the corresponding reactions, performed in the aqueous selenium dioxide solution. For example, 8.3 mmol of di-1-methylpropyl selenide was formed from 18.5 mmol of tri-1-methylpropylborane, obtained from 2-butene, in the reaction at 20°C for 1 hour. Dialkyl selenides thus formed were readily separated by extraction with petroleum ether from the reaction mixtures, followed by distillation. Some results are shown in Table 2.

The prolonged reaction time and the use of large excess of selenium dioxide reduced the amount of dialkyl selenide and caused the formation of dialkyl diselenide.

The reaction mechanism has not been clarified. However, the reaction was promoted by the addition of oxygen and inhibited by the presence of galvinoxyl. These facts suggest that a radical mechanism has an important role in the reaction.

Table 2. Reaction[a)] of trialkylboranes with selenium dioxide in the suspension in THF

R_3B(18.5 mmol) from olefin	Temp. °C	Time hr	Product[b)]	Yield mmol		Bp. °C/mmHg
Cyclohexene	0	0.5	Dicyclohexyl selenide	5.6[c)]	(6.2)[d)]	92/0.7
1-Butene	20	1	Dibutyl selenide	5.8[c)]	(7.8)[d)]	44-45/0.9[e)]
			Butyl 1-methylpropyl selenide	0.3[c)]	(0.6)[d)]	
2-Butene	20	1	Di-1-methylpropyl selenide	6.7[c)]	(8.3)[d)]	38-39/0.9
1-Hexene	20	1	Dihexyl selenide	6.3[c)]	(6.4)[d)]	90/0.8[e)]
			Hexyl 1-methylpentyl selenide	0.4[c)]	(0.5)[d)]	

a) Carried out by using 18.5 mmol of selenium dioxide and 18.5 mmol of R_3B, in the presence of 5 mmol of added oxygen.[1)] b) In all reactions dialkyl diselenides were formed in trace amount. c) Isolated by distillation. d) Determined by glpc. e) Two isomers were distilled as the mixture.

The following reaction procedure is representative. Into a nitrogen flushed 100-ml flask, provided with a septum inlet and magnetic stirring bar, 2.05 g (18.5 mmol) of finely powdered selenium dioxide and 20 ml of tetrahydrofuran were placed. Then 5 ml of oxygen[1)] was bubbled from a hypodermic syringe. To the stirred suspension 18.5 mmol of tricyclohexylborane in 20 ml of tetrahydrofuran, which was prepared by hydroboration of 55.5 mmol of cyclohexene with 18.5 mmol of BH_3, was added dropwise at 0°C. The stirring was continued for 0.5 hour at the same temperature. Then the reaction mixture was extracted with petroleum ether, and the extract was distilled at 92°C/0.7 mmHg. Thus 1.38 g(5.6 mmol) of dicyclohexyl selenide was obtained.

Dicyclohexyl selenide, dibutyl selenide, di-1-methylpropyl selenide and dihexyl selenide were identified by direct comparison with authentic samples.[2)] The other compounds were identified by their ir and mass spectra.

Several reactions for the synthesis of dialkyl selenide have so far been reported. However, there are few in which olefins are used as starting materials.[3,4)] This reaction seems not only interesting as a novel reaction of organoboranes but also useful as a new route to dialkyl selenides from olefins via hydroboration.

References

1) The role of oxygen has not been clarified. However, 3-10 ml amount of oxygen seems necessary for 18.5 mmol of trialkylboranes. The addition of too large amount of oxygen reduced the yields of dialkyl selenides.

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

3) H. Funk and W. Papenroth, J. Prakt. Chem., 8, 256 (1959).

4) F. Lautenschlaeger, J. Org. Chem., 34, 4002 (1969).

(Received February 8, 1975)