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A NEW ROUTE TO ALKYL SELENOCYANATE FROM OLEFIN VIA HYDROBORATION. REACTION OF ORGANOBORANES WITH FERRIC SELENOCYANATE

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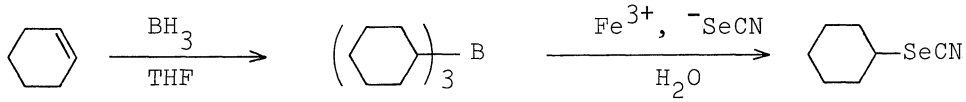
Trialkylboranes, prepared by hydroboration of terminal or internal olefins, react with ferric selenocyanate in an aqueous tetrahydrofuran to give corresponding primary or secondary alkyl selenocyanates.

Previously we reported that, when trialkylboranes were stirred in an aqueous solution of ferric thiocyanate, alkyl thiocyanates were obtained in good yield.[1)]

With an expectation to find a general one-pot procedure for the syntheses of various alkyl pseudohalides from olefin, we examined similar reactions of trialkylboranes by using aqueous mixtures of ammonium ferric sulfate as a source of Fe^{3+} and alkali pseudohalides such as sodium azide, potassium cyanide, potassium cyanate, and potassium selenocyanate. In the first place, tricyclohexylborane, obtained by hydroboration of cyclohexene, was subjected to the reactions. In each cases of sodium azide,[2)] potassium cyanide, and potassium cyanate, any remarkable reaction product was not obtained. However, in the case of potassium selenocyanate, cyclohexyl selenocyanate was afforded.[3)] It was readily isolated from the reaction mixture.



Thus, we examined the selenocyanation reaction using several trialkylboranes. The products were isolated by either distillation or column chromatography. Representative results are shown in Table 1.

Table 1. Reaction[a] of Trialkylboranes with Ferric Selenocyanate in Aqueous Tetrahydrofuran Solution

Olefin	Product	Yield (%)	Bp. °C/mmHg	n_D^{20}
1-Butene	Butyl selenocyanate	43.6[c]	86/12	1.4920
	s-Butyl selenocyanate	5.0[c]		
2-Butene	*s*-Butyl selenocyanate	47.4[c]	77/12	1.4923
2-Methylpropene	Isobutyl selenocyanate	43.6[d]		1.4910
2-Methyl-2-butene	1,2-Dimethyl selenocyanate	45.0[d]		1.4924
1-Hexene	Hexyl selenocyanate	44.0[c]	62/1.5	1.4927
	1-Methylpentyl selenocyanate	5.7[c]		
Cyclohexene	Cyclohexyl selenocyanate	40.0[c]	102/2	1.5218
Norbornene	2-Norbornyl selenocyanate[e]	41.7[d]		1.5441

a) Reaction was carried out at 40°C for 24 hr using 30 mmol of $Fe_2(NH_4)_2(SO_4)_4 \cdot 24 H_2O$ and 60 mmol of KSeCN. b) Based on olefin employed. c) Isolated by distillation. d) Isolated by elution with benzene on silica gel column. e) From pmr spectrum, the product seems to be substantially pure *exo*-norbornyl selenocyanate.

In the present reactions, the yields of alkyl selenocyanates are not always superior to those (40-60%) in the reaction of alkyl halides with potassium selenocyanate, which has been employed as a general procedure for the preparation of alkyl selenocyanates.[3),4)] However, it is found that the selenocyanation of trialkylboranes is applicable for the synthesis of secondary alkyl selenocyanates, of which synthesis has never been reported in the reaction of alkyl halides with potassium selenocyanate.

In order to clarify the stoichiometry of the reaction, we carried out the reaction using tricyclohexylborane with varying amounts of selenocyanating agents. The results are shown in Table 2. It was found that two moles of Fe^{3+} and two moles of ^-SeCN were required in the formation of one mole of cyclohexyl selenocyanate. In experiments 1 and 2, color change of the solution was observed. The dark brown color due to ferric ion turned pale yellowish green, suggesting the reduction of Fe^{3+} ion to Fe^{2+} ion. Consequently, the reaction is considered to obey the stoichiometry as shown in Eq. 1.

Table 2. Stoichiometric Study of Reaction[a] of Tricyclohexylborane with Ferric Selenocyanate in Aqueous Tetrahydrofuran Solution

Exp. no.	$Fe_2(NH_4)_2(SO_4)_4 \cdot 24H_2O$ mmol	KSeCN mmol	Yield of cyclohexyl selenocyanate, mmol[b]
1	2	30	1.9
2	5	30	4.3
3	10	30	9.0
4	10	60	9.2
5	10	20	9.1
6	10	10	4.2

a) Carried out at 40°C for 24 hr using 10 mmol of tricyclohexylborane.

b) Determined by glpc.

$$\text{>B—R} + 2Fe^{3+} + 2^{-}SeCN + H_2O \longrightarrow RSeCN + 2\,Fe^{2+} + HSeCN + \text{>BOH} \quad (1)$$

The reaction mechanism has not been clarified. However, the stoichiometric study seems to suggest that the role of Fe^{3+} ion in the selenocyanation resembles that of Cu^{2+} ion and Fe^{3+} ion in the reaction of trialkylboranes with cupric[5] and ferric[1] halides, respectively.

The following reaction procedure is representative. In an argon flushed 200ml flask provided with a septum inlet, reflux condenser, and a magnetic stirring bar, 30 mmol of 2-butene in 30 ml THF was hydroborated by 10 mmol of BH_3 in THF. To the solution, 70 ml of aqueous solution of 30 mmol of ammonium ferric sulfate and 60 mmol of potassium selenocyanate were added, and then the solution was stirred at 40°C for 24 hr. The reaction mixture was extracted with petroleum ether several times. The combined extracts were washed with water and dried over anhydrous magnesium sulfate. Distillation at 77°C under 12 mmHg gave 14.2 mmol of s-butyl selenocyanate. Pmr(CCl_4): δ=0.98(t, 3H), 1.63(d, 3H), 1.71(m, 2H) and 3.37(m, 1H). Ir(film): ν_{SeCN}=2150 cm^{-1}. Mass spectrum: m/e=163(M^+).

The reaction described in this paper is applicable for the synthesis of alkyl selenocyanates from several types of olefins, such as terminal, internal and ring ones, in an one-pot process. In addition, isolation of alkyl selenocyanate from the reaction mixture is successfully performed by such a simple procedure as distillation or column chromatography. Thus, although few methods have been reported on the synthesis of alkyl selenocyanate,[3),4),6)] the selenocyanation of trialkylboranes seems to be a convenient and general synthetic procedure of alkyl selenocyanates from olefin *via* hydroboration.

REFERENCES AND NOTES

1) A. Arase, Y. Masuda, and A. Suzuki, Bull. Chem. Soc. Japan, 47, 2511 (1974).

2) Trialkylboranes have been found to react with sodium azide in the presence of Fe^{3+} and H_2O_2 to give corresponding alkyl azides. Private communication from Professor A. Suzuki.

3) Cyclohexyl selenocyanate was identified by the direct comparison with an authentic sample obtained by the method described in the following literature: W. E. Weaver and W. H. Whaley, J. Amer. Chem. Soc., 68, 2125 (1925).

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