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CONVENIENT SYNTHESES OF ALKYL THIOCYANATES AND ALKYL SELENOCYANATES FROM STERICALLY HINDERED OLEFIN VIA HYDROBORATION. SELECTIVE REACTIONS OF SECONDARY OR TERTIARY ALKYL GROUP IN MIXED TRIALKYLBORANES WITH FERRIC THIOCYANATE OR FERRIC SELENOCYANATE

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Mixed trialkylboranes, prepared by the successive reactions of BH_3 in THF with a sterically hindered internal olefin and a terminal olefin, reacted with either aqueous ferric thiocyanate or aqueous ferric selenocyanate to give corresponding secondary or tertiary alkyl thiocyanates or selenocyanates selectively.

Previously, we reported one-pot syntheses of alkyl thiocyanates[1) and alkyl selenocyanates[2) from olefin via reactions of trialkylboranes with ferric thiocyanate or ferric selenocyantate(1).

$$\text{Olefin} \xrightarrow[\text{THF}]{BH_3} R_3B \xrightarrow[H_2O]{^-XCN,\ Fe^{3+}} 2RXCN + (HO)_2BR \qquad X{=}S,\ Se \tag{1}$$

Either in the thiocyanation or selenocyanation of trialkylboranes derived from terminal olefins, the composition study of the reaction products suggested that the reactivity of alkyl groups of trialkylboranes toward thiocyanate or selenocyanate decreased in the sequence secondary $>$ primary.[3) We were interested in this difference in the reactivity, because the selective thiocyanation or selenocyanation of the secondary alkyl group might be expected when the reaction was applied to mixed trialkylboranes, containing a useful secondary alkyl group and a primary alkyl group on a boron atom(2).[4)

$$(\text{sec-}R)_2B(\text{prim-}R) \xrightarrow[H_2O]{^-XCN,\ Fe^{3+}} 2\ \text{sec-}RXCN + (HO)_2B(\text{prim-}R) \qquad X{=}S,\ Se \tag{2}$$

Thus, we explored both the thiocyanation and selenocyanation for mixed trialkylboranes, prepared by the successive reactions of BH_3 in THF with an internal olefin and a terminal olefin, by using a required amount of thiocyanating agents or selenocyanating agents. The results are shown in Table 1.

In all cases examined, secondary alkyl thiocyanates or selenocyanates were afforded in good yields, and they were easily isolated from the reaction mixtures

Table 1. Secondary Alkyl Thiocyanates and Secondary Alkyl Selenocyanates from Internal Olefins

$$\text{Internal olefin} \xrightarrow{BH_3} (s\text{-}R)_2BH \xrightarrow{\text{terminal olefin}} (s\text{-}R)_2B(p\text{-}R) \xrightarrow[H_2O]{^-XCN,\ Fe^{3+}} 2\ s\text{-}RXCN + (HO)_2B(p\text{-}R) \qquad X=S,\ Se$$

Internal olefin	Terminal olefin	Thiocyanation[a)]			Selenocyanation[b)]		
		Product[c)]	Yield[d)] (%)	n_D^{20}	Product[c)]	Yield[d)] (%)	n_D^{20}
2-Methyl-2-butene	Propene	1,2-Dimethylpropyl thiocyanate	68	1.4664	1,2-Dimethylpropyl selenocyanate	58	1.4918
2-Methyl-2-butene	1-Hexene	1,2-Dimethylpropyl thiocyanate	69		1,2-Dimethylpropyl selenocyanate	60	
Cyclohexene	Propene	Cyclohexyl thiocyanate	67	1.5051	Cyclohexyl selenocyanate	56	1.5218
1-Methylcyclohexene	1-Hexene	2-Methylcyclohexyl thiocyanate	62	1.5022	2-Methylcyclohexyl selenocyanate	63	1.5072
α-Pinene	1-Butene	trans-3-Pinanyl thiocyanate	68	1.5124	trans-3-Pinanyl selenocyanate	61	1.5322
α-Pinene	1-Hexene	trans-3-Pinanyl thiocyanate	71		trans-3-Pinanyl selenocyanate	68	

a) Reaction was carried out at 55°C for 24 hr using 10 mmol of mixed trialkylborane and 40 mmol of ferric thiocyanate. b) Reaction was carried out at 45°C for 12 hr using 10 mmol of mixed trialkylborane and 40 mmol of ferric selenocyanate. c) Isolated by column chromatography. d) Based on internal olefin employed.

Table 2. Tertiary Alkyl Thiocyanates and Tertiary Alkyl Selenocyanates from Internal Olefins

$$\text{Internal olefin} \xrightarrow{BH_3} (t\text{-}R)BH_2 \xrightarrow{\text{terminal olefin}} (t\text{-}R)B(p\text{-}R)_2 \xrightarrow[H_2O]{^-XCN,Fe^{3+}} t\text{-}RXCN + HO\text{-}B(p\text{-}R)_2 \qquad X=S,\ Se$$

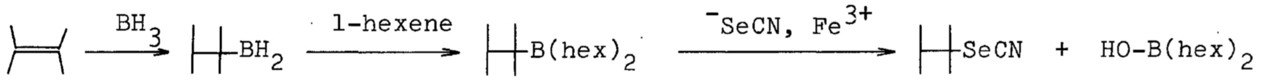
Internal olefin	Terminal olefin	Thiocyanation[a)]			Selenocyanation[b)]		
		Product[c)]	Yield[d)] (%)	n_D^{20}	Product[c)]	Yield[d)] (%)	n_D^{20}
2,3-Dimethyl-2-butene	1-Hexene	1,1,2-Trimethylpropyl thiocyanate	73	1.4693	1,1,2-Trimethylpropyl selenocyanate	67	1.4922
1,2-Dimethylcyclohexene	1-Hexene	1,2-Dimethylcyclohexyl thiocyanate	74	1.5021	1,2-Dimethylcyclohexyl selenocyanate	78	1.5223

a) Reaction was carried out at 55°C for 24 hr using 10 mmol of mixed trialkylborane and 20 mmol of ferric thiocyanate. b) Reaction was carried out at 45°C for 12 hr using 10 mmol of mixed trialkylborane and 20 mmol of ferric selenocyanate. c) Isolated by column chromatography. d) Based on internal olefin employed.

by column chromatography.[5] Any amount of primary alkyl derivatives was not observed. With larger amounts of additional thiocyanating or selenocyanating agent, primary alkyl thiocyanates or selenocyanates were formed. Consequently, it is obvious that, in these reactions, the secondary alkyl group reacts more preferentially than the primary one.

The marked difference in the reactivities between the primary alkyl group and the secondary one in such mixed trialkylboranes, led us to compare the reactivity of the tertiary alkyl group with the primary one. Thus, mixed trialkylboranes, obtained by the successive reactions of BH_3 in THF with a tetra substituted olefin and a terminal olefin, were subjected to the reactions.

As shown in Table 2, it is found that the tertiary alkyl group gave the product in preference to the primary one.[6] For example, dihexyl-1,1,2-trimethylpropylborane gave only 1,1,2-trimethylpropyl selenocyanate(3). It is a remarkable fact that 1,1,2-trimethylpropyl group can readily be converted to the product in preference to primary one under such a mild reaction condition as that applied in the thiocyanation or selenocyanation of tri-prim-alkylboranes,[1],[2] because this tertiary alkyl group shows extremely unreactive character due to its steric hindrance in most reactions of organoboranes.[7]



(3)

In all reactions examined, the distinct preference of secondary and tertiary alkyl group to primary one was observed,[8] and no difficulty was encountered in the isolation of the products. Thus, sterically hindered internal olefins were efficiently converted to the corresponding products by the sacrifice of the common and cheap terminal olefin(propene, etc.). These facts show that the present procedure is useful as the general and convenient method for the conversion of sterically hindered internal olefins to the corresponding alkyl thiocyanates and selenocyanates.

The following reaction procedure is representative. In an argon flushed 200 ml flask, provided with a septum inlet, a reflux condenser and a magnetic stirring bar, 10 mmol of dihexyl-1,1,2-trimethylpropylborane was prepared by the successive reaction of BH_3 in THF with 10 mmol of 2,3-dimethyl-2-butene at 0°C for 2 hr, and 20 mmol of 1-hexene at 0°C for 2 hr. To the solution, 70 ml of aqueous solution of 10 mmol of ammonium ferric sulfate and 60 mmol of potassium selenocyanate was added, and then the solution was stirred at 45° C for 12 hr. The reaction mixture was extracted with petroleum ether several times. The combined extracts were washed with water and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the reaction product was separated by column chromatography(silica gel). On elution with benzene, 1.3 g(67%) of 1,1,2-trimethylpropyl selenocyanate was obtained. Pmr(CCl_4, TMS): δ=1.04(d, 6H), 1.63(s, 6H) and 1.52-2.10(m, 1H). Ir(film): ν_{SeCN}=2150 cm^{-1}. Mass spectrum: m/e=191(M^+).

REFERENCES AND NOTES

1) A. Arase, Y. Masuda, and A. Suzuki, Bull. Chem. Soc. Japan, 47, 2511 (1974).
2) A. Arase and Y. Masuda, Chem. Lett., 785 (1976).
3) For example, trihexylborane, containing 94 % of hexyl group and 6 % of 1-methylpentyl group, gave 76 % of hexyl thiocyanate and 6 % of 1-methylpentyl thiocyanate.
4) The thiocyanation or selenocyanation of the third alkyl group of R_3B was extremely sluggish.
5) 1-Methylcyclohexene gave two stereoisomers of 2-methylcyclohexyl thiocyanate (or 2-methylcyclohexyl selenocyanate), whereas α-pinene gave pure trans-3-pinanyl thiocyanate (or trans-3-pinanyl selenocyanate). The stereochemistry of the reactions will be discussed elsewhere.
6) 1,2-Dimethylcyclohexene gave two stereoisomers of 1,2-dimethylcyclohexyl thiocyanate (or 1,2-dimethylcyclohexyl selenocyanate). The stereochemistry of the reaction will be discussed elsewhere.
7) For example, a) H. C. Brown and E. Negishi, J. Amer. Chem. Soc., 89, 5285 (1967). b) H. C. Brown and E. Negishi, J. Amer. Chem. Soc., 89, 5477 (1967). c) A. Pelter, A. Arase, and M. G. Hutchings, J. C. S. Chem. Commn., 346 (1974).
8) The preference of secondary and tertiary alkyl groups to primary one seems to suggest that the radical reaction mechanism is included in the reaction. The detailed mechanistic study will be presented elsewhere.

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