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The Selective Elimination of Secondary Alkyl Group from Trialkylborane by the Successive Treatments with Anisole and Dimethyl Sulfoxide. A Supply of the Synthetic Intermediate for Primary Alkyl Derivatives

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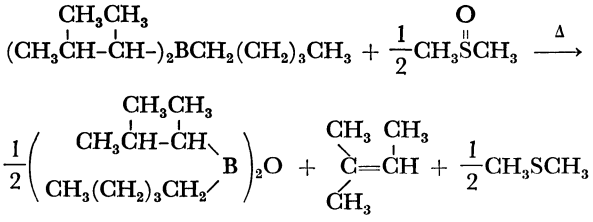
Synopsis. Secondary alkyl group of trialkylborane, derived from terminal olefin and borane, was selectively eliminated by the successive treatments with anisole and dimethyl sulfoxide. By the use of the resulting trialkylborane as the synthetic intermediate for primary alkyl derivatives, the contaminations of secondary alkyl derivatives were greatly reduced.

In the hydroboration of simple straight-chain terminal olefins, boron atom is placed on the terminal carbon atom, 95%, and on the internal carbon atom, 5%,[1] giving a mixture of trialkylboranes. For example, 1-pentene gives a mixture of tripentylborane (91%), dipentyl(1-methylbutyl)borane (6%), and pentylbis(1-methylbutyl)borane and tris(1-methylbutyl)borane (3%).[2] Accordingly, when these trialkylboranes are used as the synthetic intermediates, in some cases, contamination of the secondary alkyl derivative to the primary alkyl derivative is unavoidable.[3]

The authors previously reported that the mixed trialkylborane, which contained the primary and the secondary alkyl groups on the same boron atom, eliminated the secondary alkyl group preferentially to the primary alkyl group on heating in dimethyl sulfoxide (Eq. 1).[4]



(1)

The present work was undertaken with a view to obtain trialkylboranes in which the amount of the secondary alkyl group was considerably small by the selective elimination of the secondary alkyl group of the trialkylboranes, prepared from terminal olefins by the hydroboration with borane.

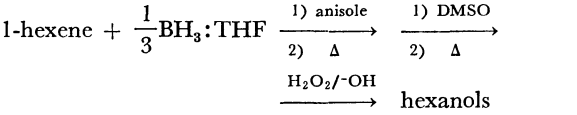
To achieve the selective and effective elimination of the secondary alkyl group from the mixed trialkylborane, several reaction procedures were examined by using the reaction of trihexylborane, prepared from 1-hexene, with dimethyl sulfoxide. After the reaction, the amounts of hexyl and 1-methylpentyl group were estimated from the amounts of hexanols obtained by the alkaline hydrogen peroxide oxidation of the reaction mixture.

By the direct reaction only with dimethyl sulfoxide, it was not able to obtain a satisfactory result (Table 1). This insufficient result seemed to be caused by the progress of the isomerization of the primary alkyl group to the secondary alkyl group in nearly neat trihexylborane during the elimination reaction with dimethyl sulfoxide.[5] Accordingly, anisole, which had a significant effect on the migration of the boron atom from the terminal carbon atom to the internal carbon atom,[5] was used as shown in Scheme 1. Thus, trihexylborane was heated in anisole followed by the reaction with dimethyl sulfoxide.

Table 1. Residual hexyl groups after the reaction with dimethyl sulfoxide[a]

Anisole[b] (ml)	DMSO / R_3B (mmol) / (mmol)	Temperature, °C (treatment with DMSO)	Residual hexyl group (%)	Hexyl/1-Methylpentyl
None	0.5 / 4	160	87.1	95 / 5
None	1 / 4	160	85.1	95 / 5
None	4 / 4	160	81.8	96 / 4
None	12 / 4	160	67.0	97 / 3
2	0.2 / 4	160	97.5	98 / 2
2	0.2 / 4	170	97.5	99 / 1
2	0.5 / 4	170	84.3	99 / 1

a) Carried out for 2 h. b) Pretreatment with anisole was carried out at 170 °C for 2 h.



Scheme 1.

By this procedure, the ratio of hexyl group and 1-methylpentyl group was greatly improved to 99:1, and 97.5% of hexyl group remained on the boron atom (Table 1).

By the same procedure, high proportions of the primary alkyl group were also realized in the reactions of trialkylboranes derived from other terminal olefins. The results are listed in Table 2.

Actually, the 1-alkanols thus formed by the oxidation with alkaline hydrogen peroxide, could be separated from the reaction mixtures effectively by column chromatography. For example, 1-octanol was obtained in 89% yield accompanied by only 0.5% of 2-octanol.

On the other hand, neat trialkylboranes could be distilled from the reaction mixtures. For example, essentially pure tripentylborane was distilled from the reaction mixture in 85% yield (75—76 °C/12 mmHg).

Then we undertook another reactions to confirm the usefulness of this procedure. Thus, after the treatments with anisole and dimethyl sulfoxide, trihexylborane was allowed to react with aqueous iron(III) chloride, aqueous copper(II) bromide and aqueous

Table 2. Residual alkyl group of some trialkylboranes after the successive treatments with anisole[a] and dimethyl sulfoxide[b]

R_3B (4 mmol) from olefin	Residual alkyl group (%)	*prim*-Alkyl/*sec*-Alkyl
1-Butene	86.3	99 / 1
1-Pentene	95.2	99 / 1
1-Octene	92.7	99 / 1
1-Dodecene	93.3	99 / 1

a) Carried out by using 2 ml of anisole at 170 °C for 2 h. b) Carried by using 0.2 mmol of DMSO at 170 °C for 2 h.

Table 3. Reactions of trihexylborane[a] with aqueous iron(III) chloride,[b] aqueous copper(II) bromide[c] and aqueous methyl vinyl ketone[d] after the treatments[e] with anisole and dimethyl sulfoxide

Reagent (mmol)	Product, mmol		Hexyl/1-Methylpentyl
Iron(III) chloride (24)	1-Chlorohexane	5.80	98 / 2
	2-Chlorohexane	0.09	
Copper(II) bromide (24)	1-Bromohexane	6.31	99 / 1
	2-Bromohexane	0.09	
Methyl vinyl ketone (6)	2-Decanone	2.41	98 / 2
	5-Methyl-2-nonanone	0.05	

a) 4 mmol of trihexylborane was used. b) The reaction was carried out at 55 °C for 48 h. c) The reaction was carried out at 55 °C for 48 h. d) The reaction was carried out at 20 °C for 2 h. e) The treatments were carried out by using 2 ml of anisole at 170 °C for 2 h, and then by using 0.2 mmol of DMSO at 170 °C for 2 h.

methyl vinyl ketone. The results are presented in Table 3.

As previously reported, the reactions of trialkylboranes with these reagents provide simple and convenient synthetic methods for chloroalkane,[3b] bromoalkane[3b] and 2-alkanone[3a] from various types of olefins. These reactions have a characteristic that the secondary alkyl group reacts with these reagents preferentially to primary alkyl group when both alkyl groups are on the same boron atom. Accordingly, in the direct reactions of these reagents with trialkylborane, prepared from terminal olefin and borane, appreciable amounts of secondary alkyl derivatives were involved in the reaction mixtures, that is, 8% of 2-chlorohexane, 5% of 2-bromohexane and 15% of 5-methyl-2-nonanone in the respective reactions. However, after the treatments with anisole and dimethyl sulfoxide, the proportions of the secondary alkyl derivatives were greatly reduced in the reactions with the same reagents.

We have not fully examined how trialkylboranes changed by the treatment with anisole. However, this procedure seems to have a practical value when trialkylboranes, derived from terminal olefins, are used as the synthetic intermediates for primary alkyl derivatives.

Experimental

Materials. Commercial 1-butene, 1-pentene, 1-hexene, 1-octene, 1-dodecene, anisole and dimethyl sulfoxide were dried over molecular sieve-5A and distilled before use. Commercial iron(III) chloride and copper(II) bromide were used without any purification.

Successive Treatments of Trialkylborane with Anisole and Dimethyl Sulfoxide. The following procedure is representative. A dry 50-ml flask, equipped with a magnetic stirring bar, a septum inlet and a reflux condenser, was flushed with argon. In the flask, 12 mmol of 1-hexene was hydroborated with 4 mmol of borane in tetrahydrofuran in the usual procedure.[6] After the addition of a 2 ml portion of anisole, tetrahydrofuran was removed under reduced pressure. Then the solution was heated at 170 °C for 2 h, followed by the reaction with 0.2 mmol of dimethyl sulfoxide at 170 °C fro 2 h. Then 4 ml of tetrahydrofuran was added to the solution and the solution was oxidized with alkaline hydrogen peroxide. The lower aqueous layer was separated and extracted with ethyl ether. The combined extracts and upper layer were analyzed by GLC, demonstrating that 11.6 mmol of 1-hexanol (96.7%) was obtained accompanied by 0.10 mmol of 2-hexanol (0.8%).

Isolation of 1-Octanol. From the organic layer, derived from 24 mmol of 1-octene in a similar manner as above, tetrahydrofuran and ethyl ether were removed. Then the reaction mixture was put on a dry silica gel column (Wako Q-50). Anisole was first eluted by benzene and then octanols were eluted by ethyl ether. Thus, 21.4 mmol of 1-octanol and 0.12 mmol of 2-octanol were obtained.

Reactions of Trihexylborane with Iron(III) Chloride, Copper(II) Bromide and Methyl Vinyl Ketone. After the treatments of trihexylborane with anisole and dimethyl sulfoxide as above, the aqueous solutions of these reagents were added to the solution respectively, and the reactions were carried out in similar manners as described in the previous reports.[3] The amounts of the reaction products were estimated by GLC.

References

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