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Reaction of Organoboranes with Lead(IV) Acetate Azide. A Synthesis of Azidoalkanes from Alkenes *via* Hydroboration

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Trialkylboranes prepared from alkenes *via* hydroboration react with lead(IV) acetate azide in dichloromethane at −25 °C to form the corresponding azidoalkanes in a one-pot manner. One or two of the alkyl groups of trialkylboranes are utilized in the reaction. For example, 1-azidohexane is afforded from 1-hexene in 50% yield based on the alkene employed.

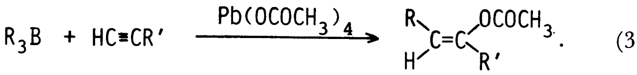
For several years, the authors have been studying the combination of alkyl groups of organoboranes[1] with ligands of metal compounds *via* the severance of carbon–boron linkage, by redox reaction of organoboranes with metal compounds.[2]

In the course of study on such oxidative transformations of trialkylboranes by metal compounds, the authors have found that lead(IV) acetate has interesting characteristics for reactions with organoboranes.

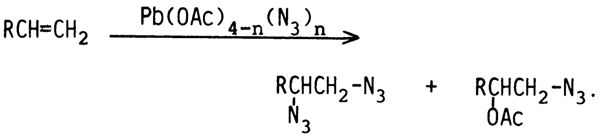
For example, it affords alkyl acetates from saturated trialkylboranes (Eq. 1),[3] 1-halo-1,2-dialkylethylenes from (1-halo-1-alkenyl)dialkylboranes (Eq. 2),[4] and (*Z*)-enol acetates from mixtures of trialkylborane and 1-alkyne (Eq. 3):[5]

$$R_3B + 2\ Pb(OCOCH_3)_4 \longrightarrow 2\ ROCOCH_3 + RB(OCOCH_3)_2 + 2\ Pb(OCOCH_3)_2 \quad (1)$$

$$R_2BCX{=}CHR' \xrightarrow{Pb(OCOCH_3)_4} RCX{=}CHR'\ (\ Z\ \text{or}\ E\ ) \quad (2)$$

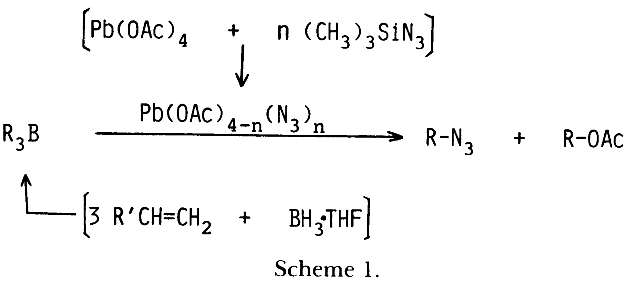

(3)

Lead(IV) acetate azide $Pb(OAc)_{4-n}(N_3)_n$, readily prepared by reaction of lead(IV) acetate with azidotrimethylsilane at −40 to −20 °C, transfers its acetoxy and azido groups to alkenes, giving a mixture of disubstituted alkanes consisting of *vic*-diazido and *vic*-acetoxy azido compounds (Eq. 4):[6]


(4)

$$RCH{=}CH_2 \xrightarrow{Pb(OAc)_{4-n}(N_3)_n} \underset{N_3}{RCH}CH_2\text{-}N_3 + \underset{OAc}{RCH}CH_2\text{-}N_3. \quad (4)$$

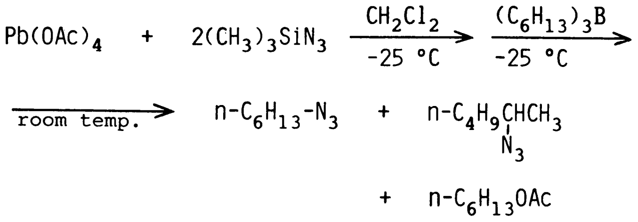
From these results it seemed probable that azidoalkane and/or alkyl acetate would be formed in the reaction of trialkylborane with lead(IV) acetate azide (Scheme 1).



Scheme 1.

Results and Discussion

To a dichloromethane solution of 2 mmol of lead(IV) acetate was added 4 mmol of azidotrimethylsilane at −25 °C over 10 min. After 15 min, 2 mmol of trihexylborane was added to this solution at −25 °C and the solution was stirred at this temperature for several hours. The solution was allowed to warm up to room temperature (20 °C). GLPC analysis of the reaction mixture revealed that 1.26 mmol of 1-azidohexane was formed as the major product accompanied by 2-azidohexane and hexyl acetate as the minor products (Scheme 2).

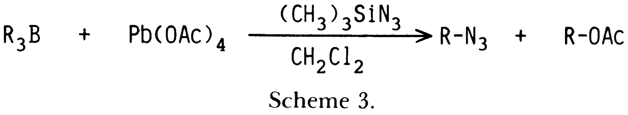


Scheme 2.

In any of blank experiments using pairs of trihexylborane and azidotrimethylsilane, hexyl acetate and azidotrimethylsilane, and hexyl acetate and lead(IV) acetate azide, no azidohexane was obtained. Accordingly, it is apparent that azidohexanes are formed by the reaction of lead(IV) acetate azide with trihexylborane.

The yield of azidoalkanes did not increase after the reaction over 6 h at −25 °C. This fact seems attributable to a decomposition of lead(IV) acetate azide during such a long reaction time.[6] The exchange reaction of the acetoxy group of lead(IV) acetate by the azido group was rapid at −40 to −20 °C,[6] and the reaction of trialkylboranes with lead(IV) acetate was very sluggish at temperatures below 0 °C.[3]

Accordingly, the following procedure, in which lead(IV) acetate azide was produced in the presence of trihexylborane in a one-pot manner, was examined to minimize the possibility of the unfavorable decomposition of lead(IV) acetate azide and to increase the yield of azidohexane. Thus, lead(IV) acetate was added to a solution of 2 mmol of trihexylborane in



Scheme 3.

dichloromethane, and then 2 mmol of azidotrimethylsilane was slowly added at −25 °C (Scheme 3). The results are shown in Table 1.

In this case, the reaction was fairly rapid and the maximum yield of azidohexanes was obtained after the reaction at −25 °C for 4 h. In Expt 4, a total 1.74 mmol (87%, based on R_3B) of 1-azidohexane and 2-azidohexane is formed, indicating that one of the three hexyl groups of trihexylborane is utilized for the reaction.

Table 2 shows how the yield varies with the amounts of lead(IV) acetate and azidotrimethylsilane. In the course of this experiment, it was recognized that a very slow addition of azidotrimethylsilane increased the yield of azidohexanes appreciably (for example, see the difference between Expts 9 and 10). Thus this step was carried out over a period of 1.5 or 2 h.

In the reactions with 2 mmol of the Pb(IV) compound (Expts 6 and 7), the total amounts of azidohexanes and hexyl acetate formed in each reaction were 1.96 and 1.93 mmol, respectively, suggesting that one equivalent of the Pb(IV) compound is required for the reaction of the first alkyl group in trihexylborane. The reaction of the second alkyl group in trihexylborane was rather sluggish compared with that of the first one. However, in the reaction with two or more equivalents of the lead(IV) compound to R_3B (2 mmol), the total amounts of the products formed in the reaction mixture exceeded 2 mmol and reached about 3.5 mmol in some cases, indicating that the second alkyl group in trihexylborane can also participate in the reaction, but not the third one.

The difference in the ratio of azide to acetate anions in the lead(IV) compound shows a small but evident effect on the product distribution. Thus, in Expts 7, 11, and 12, where the ratio is 2 or 4, the amounts of the azidohexanes are more than those in Expts 6, 10, 13, and 14, where the ratio is 1.

The amounts 12 and 13% of 2-azidohexane in Expts 11 and 12, respectively, indicate that most of the secondary hexyl groups in trihexylborane are converted to 2-azidohexane, whereas the amounts 105 and 104% of 1-azidohexane indicate that a considerable portion of the primary hexyl groups remains unreacted. These facts suggest that in this reaction the secondary alkyl group is more reactive than the primary one when they are on the same boron atom.[7] This characteristic of the reaction is well shown in Expt 29, where dicyclohexylhexylborane was employed (Table 3). However, the preference of the secondary alkyl group to the primary one is not so excellent compared to that observed in the reaction of trialkylboranes with lead(IV) acetate.[3]

In tetrahydrofuran, acetonitrile, benzene, diethyl ether, and hexane, a certain amount of 1-azidohexane could be formed, but the yields could not exceed those obtained in dichloromethane.

Similar reactions were carried out by using several alkenes as substrates in dichloromethane. The results are shown in Table 3.

In these reactions the formation of a small amount of alkyl acetate cannot be avoided. However, azidoalkanes can be isolated easily from the reaction mixture by applying simple column chromatography using silica

Table 1. Reaction[a] of trihexylborane with lead (IV) acetate azide in dichloromethane (1)

Expt No.	Reaction time/h	Yield of product/mmol(%)[b]		
		1-Azidohexane	2-Azidohexane	Hexyl acetate
1	0.5	1.30 (65)	0.10 (5)	0.14 (7)
2	1	1.42 (71)	0.12 (6)	0.12 (6)
3	1.5	1.52 (76)	0.18 (9)	0.10 (5)
4	4	1.60 (80)	0.14 (7)	0.08 (4)
5	6	1.58 (79)	0.16 (8)	0.10 (5)

a) The reactions were carried out in dichloromethane (8 ml) at −25 °C by using 2 mmol of trihexylborane, 2 mmol of lead(IV) acetate, and 4 mmol of azidotrimethylsilane. b) Determined by GLPC, based on trihexylborane.

Table 2. Reaction[a] of trihexylborane with lead (IV) acetate azide in dichloromethane (2)

Expt No.		$Pb(OAc)_4$	$(CH_3)_3SiN_3$	Yield of product/mmol(%)[b]		
		mmol	mmol	1-Azidohexane	2-Azidohexane	Hexyl acetate
6	$(n\text{-}C_6H_{13})_3B$	2	2	1.56 (78)	0.16 (8)	0.24 (12)
7	(2 mmol)	2	4	1.62 (81)	0.20 (10)	0.11 (6)
8		2.4	4.8	1.80 (90)	0.18 (9)	0.16 (8)
9[c]		4	4	1.96 (98)	0.18 (9)	0.32 (16)
10		4	4	2.32 (116)	0.18 (9)	0.30 (15)
11		4	8	2.10 (105)	0.24 (12)	0.22 (11)
12		4	16	2.08 (104)	0.26 (13)	0.14 (7)
13		6	6	2.84 (142)	0.20 (10)	0.40 (20)

a) Carried out in dichloromethane (Expts 6—8, 8 ml; 9—12, 10 ml; 13, 12 ml) by stirring for 4 h at −25 °C, then with a rise from −25 °C to room temperature over 2h, and finally for 4 h at room temperature. Azidotrimethylsilane was added very slowly (Expts 6—8 and 10, 1.5 h; 11—13, 2h). b) Determined by GLPC, based on R_3B. The yields are expressed so as to become 300% when all alkyl groups of R_3B have reacted completely. c) Azidotrimethylsilane was added over 10 min.

TABLE 3. REACTION[a] OF TRIALKYLBORANES WITH LEAD (IV) ACETATE AZIDE IN DICHLOROMETHANE (**3**)

Expt No.	R_3B (2 mmol) R=	$Pb(OAc)_4$ mmol	$(CH_3)_3SiN_3$ mmol	Yield of product/mmol(%)[b] RN_3		ROAc
				1-Azidoalkane	2-Azidoalkane	
14	Butyl	6	6	2.56 (128)	0.16 (8)	0.38 (19)
10	Hexyl	4	4	2.32 (116)	0.18 (9)	0.30 (15)
13		6	6	2.84 (142)	0.20 (10)	0.40 (10)
15[c]	(10 mmol)	30	30	13.6 (136)	1.01 (10)	—
16	Octyl	4	4	2.10 (105)	0.18 (9)	0.34 (17)
17		6	6	2.25 (113)	0.20 (10)	0.36 (18)
18[c]	(10 mmol)	30	30	10.6 (106)	0.90 (9)	—
19	Cyclopentyl	4	16	2.16 (108)		0.16 (8)
20[c]	(10 mmol)	20	80	10.4 (102)		—
21	Cyclohexyl	2	4	1.44 (72)		0.24 (12)
22		4	8	1.92 (96)		0.30 (15)
23		4	16	3.40 (170)		0.26 (13)
24[c]	(10 mmol)	20	80	16.2 (162)		—
25	Cyclooctyl	4	16	1.76 (88)		0.16 (8)
26[c]	(10 mmol)	20	80	8.50 (85)		—
27	Norbornyl	4	16	*exo*-, 2.24 (112) *end*-, 0		0.42 (21)
28[c]	(10 mmol)	20	80	10.3 (103)		—
29	Dicyclohexylhexyl	2	4	hexyl, 0.24 (12) cyclohexyl, 1.16 (58)		hexyl, 0.08 (4) cyclohexyl, 0.38 (19)

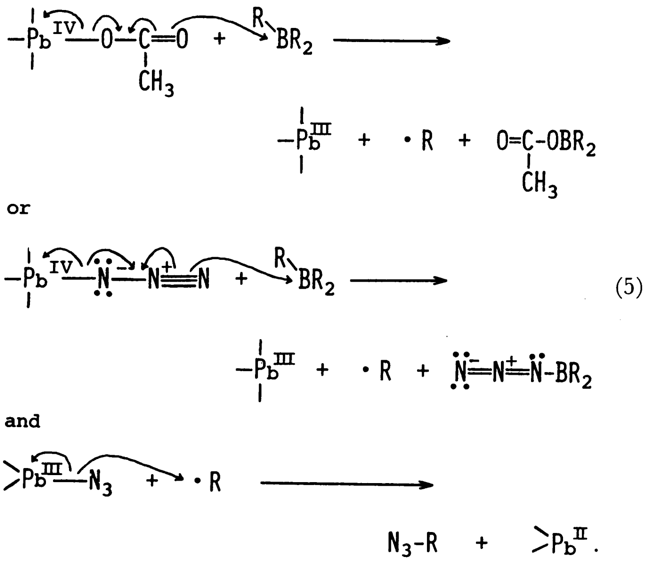
a) Carried out in dichloromethane (8—12 ml, except Expt Nos. marked with c) for 4 h at −25 °C, then with a rise from −25 °C to room temperature over 2 h, and finally 4 h at room temperature. Azidotrimethylsilane was added very slowly (over 1.5—2 h). b) Determined by GLPC (except Expt Nos. marked with c) based on R_3B used and expressed so as to become 300% when all alkyl group of R_3B have reacted completely. c) Preparative experiments. Azidoalkanes were isolated by column chromatography.

gel. Thus, the present reaction can be used as a general synthetic method for azidoalkanes.

The formation of azidoalkanes was moderately depressed when the reaction was carried out in the presence of added garvinoxyl (20 mol% to R_3B), a reagent for trapping radicals. Therefore, the reaction seems to proceed *via* a radical process.

When the reaction of trialkylborane involves a radical mechanism, the secondary alkyl group tends to react more easily than the primary one.[2,3] There is the same tendency in the present reactions as mentioned above.

From these results, the mechanism of the present reaction may be written as follows (Eq. 5):



(5)

Next we offer some characteristic features of the present reaction, in comparison with reactions which have hitherto been reported.

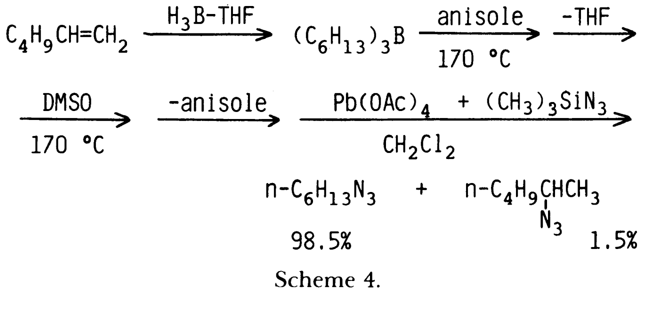
(1) Azidoalkanes are usually prepared by reactions using haloalkanes or diazo compounds as starting materials,[8] while the present reaction makes use of alkene.

(2) Azidoalkanes have also been synthesized by reactions of alkenes with mercury(II) azide[9] where the azido group is introduced in the "Markownikoff" fashion,[10] while the present reaction is in the "anti-Markownikoff" fashion.

(3) A method for synthesis of azidoalkanes using organoboranes, iron(II) azide, and hydrogen peroxide has been reported.[11] Yields of our reaction are mostly higher than those of the above reaction.

(4) As described above (Scheme 1), diazido compounds and acetoxy azido compounds[6] are formed by the reaction of olefin with lead(IV) acetate azide,[12] while in the pesent reaction these compounds are not detected, but mainly azidoalkane is formed.

In the present reaction, contamination of 1-azidoalkane by 2-azidoalkane cannot be avoided when trialkyl-



$$C_4H_9CH{=}CH_2 \xrightarrow{H_3B\text{-}THF} (C_6H_{13})_3B \xrightarrow[170\ ^\circ C]{anisole} \xrightarrow{-THF} \xrightarrow[170\ ^\circ C]{DMSO} \xrightarrow{-anisole} \xrightarrow[CH_2Cl_2]{Pb(OAc)_4\ +\ (CH_3)_3SiN_3} \underset{98.5\%}{n\text{-}C_6H_{13}N_3} + \underset{1.5\%}{n\text{-}C_4H_9\underset{N_3}{C}HCH_3}$$

Scheme 4.

boranes from 1-alkenes are employed.7) 2-Azidoalkane must come from the secondary alkyl groups which are originally present in trialkylboranes. Thus, to minimize the amount of 2-azidoalkane, most of the secondary alkyl groups in the trialkylborane were converted to primary alkyl groups or removed from trialkylborane by successive treatments of trialkylboranes with anisole and dimethyl sulfoxide before the reaction with lead(IV) acetate azide (Scheme 4).13)

Although the yield was caused to be lowered a little by using this trialkylborane, the amount of 2-azidoalkane could be markedly reduced and highly isomerically pure 1-azidoalkane was obtained (97—99%).

Experimental

Instruments. GLPC was performed using a NEVA Model 1400. ^{1}H NMR spectra were obtained on a Hitachi R-20A spectrometer (60 MHz). Infrared spectra were recorded on a Hitachi 285 spectrometer. Mass spectra were obtained on a Hitachi M-52 mass spectrometer.

Materials. Commercial 1-hexene, 1-octene, cyclopentene, cyclohexene, cyclooctene, and tetrahydrofuran were dried over lithium aluminium hydride and used after distillation in an argon atmosphere. Commercial 2-norbornene and 1-butene were used without any purification. Dichloromethane was dried over phosphorus pentoxide and used after distillation in an argon atmosphere. Anisole and dimethyl sulfoxide were dried over Molecular Sieve 5A and distilled before use.

The tetrahydrofuran solution of borane,14) lead(IV) acetate15) (purity>98%),16) and azidotrimethylsilane17) (bp 93—95 °C; lit 95 °C) were prepared by the methods described in the literature.

Reaction of Trialkylboranes with Lead(IV) Acetate Azide. The following procedure is representative. A dry, 100-ml round bottomed flask, equipped with a gas inlet, a magnetic stirring bar, a septum inlet, and a dropping funnel, was flushed with argon. In this flask 3.75 ml (30 mmol) of 1-hexene was hydroborated with 10 mmol of borane in tetrahydrofuran, and then the tetrahydrofuran was removed under reduced pressure at 25 °C. In an argon atmosphere, 13.3 g (30 mmol) of lead(IV) acetate in 40 ml of dichloromethane was added to trihexylborane14) at −25 °C and 4.20 ml (30 mmol) of azidotrimethylsilane in 10 ml of dichloromethane was added dropwise (for 2 h) through the dropping funnel. The solution was stirred at −25 °C for 4 h, then with a rise from −25 °C to room temperature over 2 h, and finally at room temperature for 4 h. The light brown color of the solution changed into white after the reaction. The reaction mixture was transferred into a separatory funnel together with 100 ml of diethyl ether and 30 ml of water. Then it was saturated with sodium chloride, and the lower aqueous layer was separated and extracted three times with diethyl ether. The combined organic layer and diethyl ether extracts were washed with a saturated aqueous sodium chloride solution, and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the products were separated by column chromatography (silica gel, 150 g). On elution with pentane (200 ml) and then with a mixture of pentane (200 ml) and dichloromethane (200 ml), 1.85 g of a mixture containing 13.6 mmol of 1-azidohexane and 1.01 mmol of 2-azidohexane was obtained. The GLPC retention times, n_D values, and IR, ^{1}H NMR, and mass spectra of these products were consistent with those obtained for authentic samples.8)

An analytical experiment was carried out by using smaller amounts of reagents, and the reaction mixture was analyzed by GLPC using the internal standard method (FFAP, supported on Diasolid M, was used as the liquid phase).

Reactions using tributylborane14) and trioctylborane14) were carried out under the same conditions as described above. From trioctylborane (10 mmol), on elution with hexane (200 ml) and a mixture of hexane (200 ml) and benzene (200 ml), 10.6 mmol of 1-azidooctane with 0.90 mmol of 2-azidooctane was obtained.

A reaction of tricycloalkylborane14) was carried out under the same conditions as described above by using 10 mmol of tricycloalkylborane, 20 mmol of lead(IV) acetate, and 80 mmol of azidotrimethylsilane. From tricyclopentylborane, on elution with pentane (200 ml) and with a mixture of pentane (200 ml) and dichloromethane (200 ml), 10.4 mmol of azidocyclopentane was obtained. From tricyclohexylborane, tricyclooctylborane, and trinorbornylborane, 16.2 mmol of azidocyclohexane, 8.5 mmol of azidocyclooctane, and 10.3 mmol of *exo*- 2-azidonorbornane, respectively, were obtained on elution with hexane (200 ml) and with a mixture of hexane (200 ml) and benzene (200 ml). The GLPC retention times, n_D values, and IR, ^{1}H NMR, and mass spectra of these azidocyclohexane and *exo*-2-azidonorbornane were consistent with those obtained from authentic samples.8,10)

Reaction of Trihexylborane with Lead(IV) Acetate Azide in the Presence of Garvinoxyl. The reaction was carried out under the same conditions as described above using 2 mmol of trihexylborane, 2 mmol of lead(IV) acetate, 4 mmol of azidotrimethylsilane, and 0.20 g (20 mol%) of garvinoxyl. The total yields of 1- and 2-azidohexane in this reaction and those in the absence of garvinoxyl (in parentheses) are as follows: 30 min, 24% (56%); 45 min, 32% (61%); 2.5 h, 34% (65%); 5 h, 37% (71%).

Reaction of Trialkylborane with Lead(IV) Acetate Azide after Successive Treatments with Anisole and Dimethyl Sulfoxide. In an argon-flushed flask equipped with the same apparatus as described above and a reflux condenser, 30 mmol of 1-hexene was hydroborated with 10 mmol of borane in tetrahydrofuran. After addition of 5 ml of anisole, the tetrahydrofuran was removed under reduced pressure (20 Torr) at 25 °C. The solution was heated at 170 °C for 2 h and allowed to react with 0.5 mmol of dimethyl sulfoxide at 170 °C for 2 h. The anisole was removed under reduced pressure (3 Torr, 1 Torr≈133.322 Pa) at 50 °C. Then the reaction of trihexylborane with 30 mmol of lead(IV) acetate and 30 mmol of azidotrimethylsilane was carried out in the same manner as described above. The products were separated by column chromatography (silica gel, 150 g). On elution with pentane (200 ml) and with a mixture of pentane (200 ml) and dichloromethane (200 ml), 9.55 mmol of 1-azidohexane with 0.18 mmol of 2-azidohexane was obtained.

Similarly, 9.20 mmol of 1-azidooctane with 0.28 mmol of 2-azidooctane was obtained from 30 mmol of 1-octene.

Analytical Data of Products. *1-Azidohexane*: IR (film) ν_{N_3} 2100 cm^{-1} (v.s.); ^{1}H NMR (CCl$_4$, TMS) δ=0.89 (t, 3H), 1.15—1.75 (m, 8H), and 3.20 (t, 2H); n_D^{20} 1.4320 (lit8) 1.4318). Found: C, 56.56; H, 10.29; N, 33.15%. Calcd for $C_6H_{13}N_3$: C, 56.66; H, 10.30; N, 33.04%.

1-Azidooctane: IR (film) ν_{N_3} 2100 cm^{-1} (v.s.); ^{1}H NMR (CCl$_4$, TMS) δ=0.87 (t, 3H), 1.15—1.70 (m, 12H), and 3.19 (t, 2H); n_D^{20} 1.4401 (lit8) 1.4368).

Azidocyclopentane: IR (film) ν_{N_3} 2100 cm^{-1} (v.s.); ^{1}H NMR (CCl$_4$, TMS) δ=1.5—1.9 (m, 8H), and 3.7—4.0 (m, 1H); MS *m/z* 111 (M$^+$); n_D^{20} 1.4660 (lit8) 1.4616).

Azidocyclohexane: IR (film) ν_{N_3} 2100 cm^{-1} (v.s.); ^{1}H NMR (CCl$_4$, TMS) δ=1.1—2.1 (m, 10H) and 3.0—3.5 (m, 1H); MS *m/z* 125 (M$^+$); n_D^{20} 1.4697 (lit8) 1.4693).

Azidocyclooctane: IR (film) ν_{N_3} 2090 cm^{-1} (v.s.); ^{1}H NMR (CCl$_4$, TMS) δ=1.1—2.2 (m, 14H) and 3.2—3.7 (m, 1H); n_D^{20} 1.4921.

exo-*2-Azidonorbornane*: IR (film) ν_{N_3} 2100 cm^{-1} (v.s.); ^{1}H NMR (CCl_4, TMS) δ=0.95—1.7 (m, 8H), 2.2—2.4 (m, 2H), and 3.25—3.55 (m, 1H); MS *m/z* 137 (M^+); n_D^{20} 1.4936 (authentic sample,[10]) 1.4893).

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7) Trialkylboranes prepared from 1-alkenes by hydroboration are mixtures in which a primary alkyl group and/or 1-methylalkyl group are bound to a boron atom. For example, from 1-pentene, a mixture of tripentylborane (91%), dipentyl(1-methylbutyl)borane (6%), and pentylbis(1-methylbutyl)borane and tris(1-methylbutyl)borane (3%) was obtained (A. Arase, Y. Masuda, M. Itoh, M. Itoh, and A. Suzuki, *Nippon Kagaku Kaishi*, **1972**, 395). The distribution of the trialklylborane isomers derived from 1-hexene is considered to be similar to that of the trialkylborane isomers from 1-pentene described above.

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