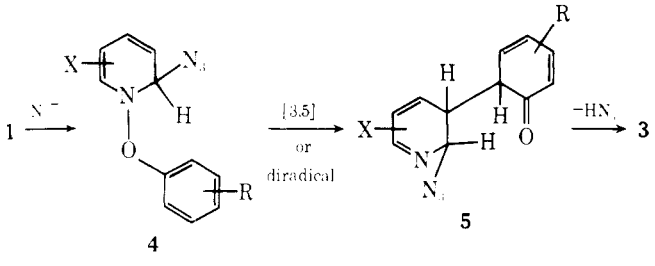
Table I. Rearrangement of 1 to 3 with Azide Ion in Acetonitrile

R	X	mp (3), °C	% yield
4-NO_2	H	294–298 dec	70.3
4-CN	H[a]	283–285 dec	70
4-NO_2	5-Br	192–193	50.4
4-NO_2	5-Me	>360	60
4-NO_2	4-Ph[a]	274–275	31
4-NO_2	4-OMe[a]	194–195	59

[a] Reaction carried out in boiling acetonitrile

The rearrangement appears to be quite general, at least for *N*-(aryloxy)pyridinium salts bearing electron-withdrawing substituents in the benzene ring. For example, **1** (X = 3-Br; R = 4-NO_2) and azide ion gave **3** (X = 5-Br; R = 4-NO_2) (50.4%): mp 192–193 °C; *O*-acetate, mp 128–129 °C; NMR ($CDCl_3$) δ 8.05 (d, 1, $J_{4,6}$ = 3 Hz, H_6), 7.97 (d, 1, J = 2 Hz, H_2), 7.69 (m, 2, H ortho to NO_2), 7.30 (m, 1, H_4), 6.78 (d, 1, J = 9 Hz, H ortho to AcO), 1.92 (s, 3, CH_3). These and other rearrangements are summarized in Table I.

Assuming that the nucleophile adds mainly[8,9] at C-2 to give (**4**),[9] this could undergo a [3,5] sigmatropic shift to yield the 2,3-dihydro derivative **5**, which would eliminate HN_3 and aromatize to **3**. Alternatively, **4** could undergo homolysis to a tight radical pair (to account for the good yields of products) followed by radical recombination to give **5**. In support of the



intervention of *some* radical pathway is the isolation of pyridine (6.7%) (as the picrate) and *p*-nitrophenol (1.9%) from the reaction of **1** (X = H; R = 4-NO_2) with azide in dry CH_3CN. It is conceivable that the radical and concerted pathways are in competition with each other. Studies are under way to distinguish between these and other possible mechanisms.

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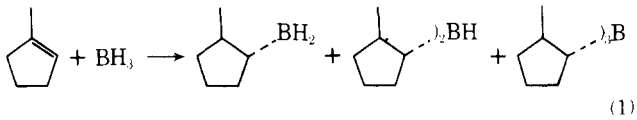
An Improved Synthesis of Monoalkylborane Derivatives via Bis(Thexylborane)-*N,N,N',N'*-tetramethylethylenediamine

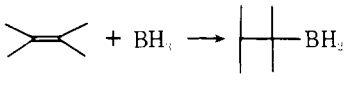
Summary: Bis(thexylborane)-*N,N,N',N'*-tetramethylethylenediamine (2ThBH$_2$·TMED) reacts with olefin with the facile displacement of tetramethylethylene and the formation of the corresponding bis(monoalkylborane)–tetramethylethylenediamine adducts in nearly quantitative yield. Treatment of the adducts with boron trifluoride etherate quantitatively precipitates TMED·2BF_3 and liberates free monoalkylborane providing a convenient general synthesis for such monoalkylboranes.

Sir: Hydroboration of olefins with THF·BH_3[1] or Me_2S·BH_3[1] generally proceeds rapidly past the monoalkylborane stage to the dialkylborane or trialkylborane stage.[2,3] Consequently, it is generally not possible to synthesize monoalkylboranes by the direct reaction of olefins with borane (eq 1). Only in the

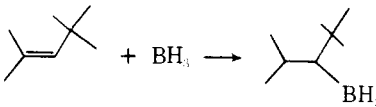


(1)

case of certain highly hindered olefins, such as tetramethylethylene (TME) or 2,4,4-trimethyl-2-pentene (diisobutylene-2 ≡ DIB-2), is it possible to control the hydroboration so as to achieve the synthesis of the monoalkylborane (RBH$_2$).[4,5] In this way, thexylborane (ThBH$_2$)[6] and diisobutylene-2-borane (DIBBH$_2$)[7] are readily prepared (eqs 2, 3).



(2)



(3)

ThBH$_2$·NEt$_3$ reacts with olefins with displacement of TME and formation of the corresponding adduct, RBH$_2$·NEt$_3$.[8] Treatment with THF·BH_3[9] or Et_2O·BF_3[10] produces the corresponding free monoalkylborane. Unfortunately, the byproducts, Et_3N·BH_3 and Et_3N·BF_3, are highly soluble and cannot easily be separated from the desired product. A further difficulty is the liquid nature of the RBH$_2$·NEt$_3$ adducts, rendering difficult their purification.

We recently observed that both monoisopinocampheylborane and BF_3 form crystalline bisadducts with TMED.[11] Accordingly, we undertook to explore the displacement reaction with TMED. Indeed, we observed that in refluxing ethyl ether TME is rapidly displaced from a mixture of 2ThBH$_2$·TMED and selected olefins, providing the crystalline bisadducts 2RBH$_2$·TMED in excellent yields. Moreover, BF_3 rapidly and quantitatively precipitates TMED·2BF_3 from the

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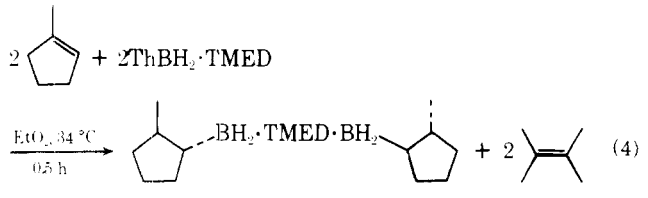
Table I. Reaction of $2ThBH_2$·TMED (1.0 M) with Various Olefins in Et_2O at 34 °C[f]

olefin	time, h	TME[a] displaced, mmol	ROH[b,c] found, mmol	$2RBH_2$·TMED[d] isolated, %	mp,[e] °C
α-pinene	6	9.6	9.9	95	140–141
1-methylcyclopentene	0.5	9.6	9.9	98	123–124
2-methyl-2-butene	1	9.6	9.8	84	90–92
cyclohexene	1	9.7	9.9	98	100–101
norbornene	1	9.7	9.9	97	118–119
cyclopentene	1	9.6	9.8	96	105–106
trans-3-hexene	1	9.7	9.9	90	27–29

[a] Analysis after methanolysis via GLC on SE-30 and CW-20M columns.[1] [b] Analysis via GLC on CW-20M column after alkaline hydrogen peroxide oxidation of the reaction mixture.[1] [c] R corresponds to the olefin used. [d] The crude adduct is isolated by pumping off the volatiles from the reaction mixture at 12 mmHg. Alternatively, modestly lower yields are realized by direct crystallization of the adducts from the chilled reaction mixtures. [e] Melting points are uncorrected and were obtained in sealed capillary tubes after recrystallization of the adducts. [f] 10-mmol scale.

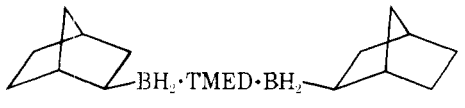
adducts in a variety of solvents, giving the pure RBH_2 for ready isolation or further application.[12] In view of this promising development, we undertook to explore the scope of this new general synthesis of the $2RBH_2$·TMED and free RBH_2.

The bisadduct, $2ThBH_2$·TMED, is readily obtained from thexylborane and the appropriate quantity of TMED.[12] Addition of 1-methylcyclopentene followed by reflux in ethyl ether for 0.5 h provided the crystalline bisadduct, mp 123–124 °C, in a yield >98% (eq 4).



(4)

In the same way, cyclohexene was converted into the TMED adduct of cyclohexylborane in 1 h in a yield of 98%, and norbornene was converted in 1 h into the TMED adduct of *exo*-norbornylborane in a yield of 97%. Both cyclopentene and *trans*-3-hexene were readily accommodated in the reaction. However, olefins of very low steric requirements, such



as 1-hexene, gave unsatisfactory results. On the other hand, olefins of very large steric requirements, such as α-pinene, could be used, but it was necessary to increase the reaction time to 6 h. The results are summarized in Table I.

These bisadducts are crystalline and readily recovered from the reaction mixture, in most cases, by merely chilling it to 0 to −5 °C. The products are stable in air and can be stored without special precaution for an appreciable time without apparent change.

The adducts are readily converted to the free RBH_2 by dissolving them in either THF, Et_2O, or pentane and adding the appropriate quantity of Et_2O·BF_3. A rapid precipitation of TMED·$2BF_3$ occurs, complete in <1 h at room temperature. Simple filtration (under nitrogen) provides the RBH_2 in solution. Removal of the volatile solvent under vacuum provides the pure RBH_2.

It was established that the structure of the products corresponded to that anticipated for a simple hydroboration. Thus oxidation of the methanolyzed RBH_2 from 1-methylcyclopentene yielded only the pure *trans*-2-methylcyclopentanol. Similarly, oxidation of the methanolyzed RBH_2 from norbornene yielded the pure *exo*-norbornanol.

The following procedure is representative. All operations were carried out under nitrogen.[1] Neat $ThBH_2$ was prepared by adding 1.2 mL of TME (10 mmol) to 1.0 mL of 10 M Me_2S·BH_3 (10 mmol) at 25 °C for 0.5 h.[3] To this reaction mixture, 0.75 mL of TMED (5 mmol) was added followed by the addition of 2.0 mL of Et_2O, providing a 1.0 M solution of 2 $ThBH_2$·TMED in Et_2O. The Et_2O solvent was refluxed (34 °C) and 1.1 mL of 1-methylcyclopentene (10 mmol) was added. The reaction mixture was stirred at 34 °C for 0.5 h. On cooling to 25 °C, the adduct crystallizes out. Solution IR of the supernatant liquid showed strong absorption at 4.2–4.4 μm (2381–2273 cm^{-1}) characteristic of *trans*-2-methylcyclopentylborane–tetramethylethylenediamine. Methanol, 1.6 mL (40 mmol; 100% excess), when added to the reaction mixture, liberated hydrogen quantitatively (~20 mmol) and gave dimethyl *trans*-2-methylcyclopentylboronate in 95% yield after solvent evaporation [25 °C (12 mmHg)]. Oxidation of the methanolyzed product with alkaline hydrogen peroxide[1] provided pure *trans*-2-methylcyclopentanol (10 mmol) by GLC analysis.

Alternatively, in place of methanolysis, the reaction mixture was transferred to a centrifuge tube. Methyl sulfide and TME were removed by centrifugation followed by decantation.[1] Solids were washed with pentane (3 × 5 mL) and dried under vacuum (12 mmHg) to provide 1.51 g (98%) of bis(*trans*-2-methylcyclopentylborane)–tetramethylethylenediamine adduct: mp 123–124 °C; NMR ($CDCl_3$, Me_4Si) δ 0.96 (d, 6 H, J = 7 Hz), 2.60 (s, 12 H), 3.20 (s, 4 H); ^{11}B NMR (THF, relative to Et_2O·BF_3) δ +0.22 (br s).

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