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A simple general synthesis of dialkylboranes

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The reduction of aryl dialkylborinates with lithium aluminum hydride in hexane provides the dialkylboranes in high yield and purity. Since aryl dialkylborinates are now readily available through redistribution of the corresponding trialkylboranes with aryl borates[1], the present reaction sequence now provides a simple convenient general synthesis of dialkylboranes with a wide variety of structures.

The ready availability of dialkylboranes would have immense potential in the rapidly expanding applications of organoboranes in organic synthesis. Thus such dialkylboranes are useful in selective reductions[2]. Bromination of such dialkylboranes and their derivatives provides a new route to the synthesis of secondary and tertiary alcohols★. Hydroboration of suitable olefins provides a route to mixed organoboranes useful for the synthesis of tertiary alcohols via the carbonylation reaction[3]. Many other applications are highly promising[4].

Unfortunately, the original synthesis of such dialkylboranes, actually *sym*-tetraalkyldiboranes, via the redistribution of diborane and trialkylboranes, as developed by Schlesinger and coworkers[5], appears to be impractical for synthetic application. Attempts to achieve the synthesis of dialkylboranes by the hydroboration of olefins with diborane in the stoichiometric ratio fail[6], except in the case of certain olefins and dienes where special structural features favor the formation of relatively stable dialkylboranes[7].

We recently reported that the reaction of methyl dialkylborinates with lithium aluminum hydride in the presence of olefins gives mixed trialkylboranes in high yield[8]. Presumably the dialkylborane, produced *in situ*, is rapidly captured by the olefin to give the desired product (eq. 1)[8].

$$3\,R_2BOCH_3 + LiAlH_4 + 3\text{ olefin} \rightarrow 3\,R_2BR' + LiAlH(OCH_3)_3 \qquad (1)$$

When this reaction was performed in the absence of olefin, a heterogeneous mixture resulted, from which the desired dialkylborane could not be separated. An alternate route was developed involving the pyridine–dialkylboranes as intermediates[3]. However, a convenient direct synthesis eluded us.

The discovery that the redistribution of organoboranes with aryl borates is especially facile and clean (eq. 2)[1] led us to reopen the search for a convenient one-step synthesis of dialkylboranes.

★Research in progress with C.F. Lane. See footnote 4 in ref. 1.

$$2\,R_3B + (ArO)_3B \xrightarrow[100^\circ,\ 2\ h]{\text{cat. } H_3B/THF} 3\,R_2BOAr \qquad (2)$$

Indeed, we discovered that the reaction of aryl dialkylborinates with lithium aluminum hydride in hexane proceeds rapidly to give the desired dialkylboranes directly. The lithium triaryloxyaluminohydride product is insoluble, providing a supernatant solution containing almost pure dialkylborane (eq. 3).

$$3\,R_2BOAr + LiAlH_4 \xrightarrow[0^\circ,\ 30\ min]{\text{hexane}} 3\,R_2BH + LiAlH(OAr)_3\downarrow \qquad (3)$$

The purity of the several representative dialkylboranes prepared by the present method was confirmed by their IR spectra, their ready conversion to easily identified pyridine–dialkylboranes, and their reaction with 1-pentene to give the corresponding mixed trialkylborane. An examination of the results indicated that the purity of these dialkylborane preparations was generally greater than 95%. However, these preparations should be used as soon as possible, since such dialkylboranes undergo redistribution relatively easily[9].

The following synthesis of dicyclopentylborane will be illustrative of the general experimental methods enployed. A clear solution of lithium aluminum hydride in ethyl ether (1.5 *M*, 2.3 ml, 3.45 mmol) was placed in a flask which had been flushed with nitrogen. The solvent was then evaporated off at 25° under the vacuum of a water pump. To the crystalline lithium aluminum hydride thus obtained, dry hexane (10 ml) was added. Pure *o*-tolyl dicyclopentylborinate★ (2.56 g, 10 mmol), dissolved in hexane (10 ml), was then added to it at 0°, and the resulting heterogeneous mixture★★ was stirred for 30 min. The NMR analysis of the supernatant liquid at this time indicated the absence of any aromatic protons. The supernatant solution was subsequently siphoned out with the aid of a hypodermic syringe. The examination by IR showed a strong band at 1580 cm^{-1} (B–H–B, bridge). No other bands were discernible in 2600–1800 cm^{-1} range, indicating the absence of any B–H (terminal), and Al–H bond containing impurities. Upon the addition of water, 9.1 mmol of hydrogen gas was evolved.

In another experiment, *o*-tolyl dicyclopentylborinate (10 mmol) was treated with lithium aluminum hydride in hexane in a similar manner. After 30 min at 0°, the supernatant liquid was withdrawn and pyridine (2 ml, 20 mmol) was added to it. After stirring the resulting solution for 15 min at 0°, the solvent was distilled off to give a colorless liquid. This was redissolved in hexane (50 ml) and then filtered. The filtrate upon evaporation left a colorless liquid. This was dried at 25° (0.2 mm) for 30 min to give the desired pyridine–dicyclopentylborane, 2.1 g (90%), as a colorless liquid: n_D^{20} 1.5250; IR (neat) 2300, 1620 cm^{-1}.

Alternatively, the dicyclopentylborane can be used to hydroborate simple olefins,

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★We utilized the *o*-tolyl dialkylborinates because the redistribution reaction involving the liquid *o*-tolyl borate proved to be especially convenient.

★★In contrast to this result, a clear, homogeneous reaction mixture was obtained when ethyl ether was not evaporated off prior to this addition. This mixture, after stirring at 0° for 20 to 30 min deposited a white precipitate, presumably the lithium triaryloxyaluminohydride product, generally in 90 to 95% yield. The supernatant liquid thus contains the desired dialkylborane, but also small amounts of the aluminum compound. The present procedure circumvents this difficulty.

TABLE 1

THE PREPARATION OF DIALKYLBORANES AND PYRIDINE–DIALKYLBORANES FROM THE CORRESPONDING *o*-TOLYL DIALKYLBORINATES[a]

R	R_2BH		Pyridine–dialkylborane,	
	yield (%)	IR (B–H–B)[c]	yield (%)	n_D^{20}
1-Butyl	91[d]	1560 (CCl_4)	90	1.4880
1-Butyl[b]	95[d]	1560 (CCl_4)	92	1.4880
2-Butyl	88[d]	1590 (CCl_4)	85	1.4920
Isobutyl	93[d]	1580 (CCl_4)	95	1.4830
Isobutyl[b]	95[d]	1580 (CCl_4)	95	1.4840
Cyclopentyl	90[e]	1590 (CCl_4)	85	1.5250
Cyclopentyl[b]	93[e]	1590 (hexane)	90	1.5250
Cyclohexyl	90[e]	1590 (hexane)		
exo-Norbornyl	92[e]	1590 (hexane)		

[a] Unless otherwise mentioned, the crude *o*-tolyl dialkylborinates obtained from the redistribution of the corresponding trialkylborane and *o*-tolyl borate were used directly without further purification. [b] Pure *o*-tolyl dialkylborinates were used. [c] The solvent is given in parentheses. [d] By GLPC analysis, based on their reaction with 1-pentene and the identification of the resulting n-$C_5H_{11}BR_2$. [e] By GLPC analysis, based on their reaction with 1-octene and the total utilization of the olefin in the hydroboration reaction.

such as 1-pentene, to produce the mixed organoborane, dicyclopentyl-n-pentylborane, or to hydroborate functionally substituted olefins, such as 11-dodecenenitrile, to produce the corresponding functionally substituted mixed organoborane[3].

Since the isolation of certain high molecular weight *o*-tolyl dialkylborinates by distillation from the redistribution reaction mixture may not be practical, the direct use of the crude product obtained from the redistribution of the corresponding trialkylborane with *o*-tolyl borate was then explored. Fortunately, this procedure also proceeds quite satisfactorily, giving the desired dialkylboranes in excellent yields, with purities in the range of 85 to 92% (eq. 4).

$$2\,R_3B + (ArO)_3B \xrightarrow[100^\circ,\ 2\ h]{cat.\ H_3B{:}THF} 3\,R_2BOAr \xrightarrow[hexane]{LiAlH_4} 3\,R_2BH + LiAlH(OAr)_3 \downarrow \tag{4}$$

The purity of these preparations was checked by their conversion to mixed trialkylboranes and the identification of the resulting organoboranes by GLPC analysis using the previously identified samples[3]. Although these purities are somewhat lower than those realized with the distilled *o*-tolyl dialkylborinates, they should be adequate for many applications.

The results of a series of representative transformations of *o*-tolyl dialkylborinates, providing the corresponding dialkylboranes and pyridine–dialkylboranes, are summarized in Table 1★.

The present development provides, for the first time, a simple and easily

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★ All the compounds were analyzed by IR and NMR spectroscopy. All the new compounds, in addition, gave concordant elemental analyses.

performed procedure for the direct synthesis of reasonably pure samples of dialkylboranes from the readily available trialkylborane intermediates.

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