enabling us to extract the excess *d* enantiomer:[15] refluxing the photoproduct with pentane, decanting, and cooling the solution at 0° for 2 days gave a mixture of needlelike and rhombic crystals, the needles[14] showing a specific rotation of +31.4° (*c* 0.5, ether). To confirm that the enantiomeric crystals of **6** have a solubility different from that of the racemic compound, we prepared samples containing an excess of one enantiomer independently by chromatography of a *d,l*-meso mixture of **6** (from reduction of acetophenone with Al–Hg[16]) through cellulose-2.5-acetate.[17] With pentane we extracted an enriched enantiomer of high optical rotation from the optically active samples thus obtained, while extracts from the original inactive mixtures had zero rotations. To confirm that the induction had occurred during the step forming the central carbon–carbon bond of **6**, and not by asymmetric destruction after *d,l*-pinacol formation or by some resolution process, we subjected a solution of *d,l*-*meso*-**6** (ratio 1.8) in DAB after a storage period at room temperature of 16 hr and an irradiation period below 0° of 18 hr to exactly the work-up procedure described above. The pinacol recovered quantitatively was inactive and contained the *d,l* and meso diastereomers in an unaltered ratio.

Preliminary experiments indicate that photoreductions leading to secondary alcohols with asymmetric carbinol carbons can also be asymmetrically induced when carried out in the presence of **5**.

[15] *Cf.* T. Leigh, *Chem. Ind.* (*London*), 1016 (1970).

[16] K. Sisido and H. Nozaki, *J. Amer. Chem. Soc.*, 70, 776 (1948).

[17] For this method see comments by A. Lüttringhaus and R. Cruse, translators, in E. L. Eliel, "Stereochemie der Kohlenstoffverbindungen," Verlag Chemie, Weinheim/Bergstr., Germany, 1966, p 73, footnote 38b. Meso, *l*, and *d* isomer-enriched fractions were eluted consecutively with benzene.

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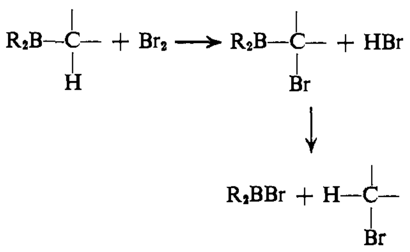
Rearrangement of α-Bromoethyldiethylborane Induced by Nucleophilic Reagents. An Unusually Facile Rearrangement Applicable to the Synthesis of Carbon Structures

Sir:

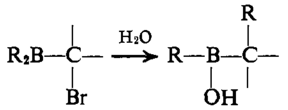
α-Bromoethyldiethylborane is readily synthesized by the photochemical reaction of triethylborane with bromine in the absence of water. It is quite stable in the absence of added nucleophiles, but is rapidly rearranged to derivatives of *sec*-butylethylborane by nucleophilic reagents, such as pyridine, water, methanol, acetonitrile, propylene oxide, and tetrahydrofuran. 2,6-Lutidine, 2,6-di-*tert*-butylpyridine, and diethyl ether are less effective than less-hindered nucleophiles, indicating that the rearrangement involves coordination of the nucleophile with the boron atom of the α-bromoorganoborane. This essentially quantitative formation of carbon–carbon bonds under such mild conditions has major implications for synthesis.

It was recently reported that the reaction of trialkylboranes with bromine in inert solvents, such as cyclohexane and methylene chloride, appears to involve a relatively rapid free-radical substitution in the α position to produce the α-bromoorganoborane and hydrogen bromide in the initial stage.[1,2] These then react to produce the alkyl bromide[1a] (eq 1). However,



$$R_2B\text{—}\underset{H}{\overset{|}{C}}\text{—} + Br_2 \longrightarrow R_2B\text{—}\underset{Br}{\overset{|}{C}}\text{—} + HBr \;\Big\downarrow\; R_2BBr + H\text{—}\underset{Br}{\overset{|}{C}}\text{—} \qquad (1)$$

if water is present, the protonolysis is avoided and a facile rearrangement of an alkyl group from boron to carbon occurs[1b] (eq 2).



$$R_2B\text{—}\underset{Br}{\overset{|}{C}}\text{—} \xrightarrow{H_2O} R\text{—}\underset{OH}{B}\text{—}\underset{|}{\overset{R}{C}}\text{—} \qquad (2)$$

Previously, chloromethyldimethylborane was prepared and isolated.[3] The authors treated this derivative with water, but did not report any rearrangement of the kind postulated above. Matteson and Mah did report rearrangement of *B*-alkyl-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinates, but utilized sodium butoxide to achieve it.[4] Consequently, it appeared desirable to undertake to prepare and isolate[5] an α-bromotrialkylborane in order to confirm the fact that the postulated rearrangement can occur under the exceptionally mild conditions of the earlier bromination experiments.

It appeared possible that bromination of triethylborane in the absence of water, with rapid removal of the hydrogen bromide, prior to its reaction with the intermediate (eq 1), might provide the desired α-bromoorganoborane. Indeed, this proved to be practical, and the desired α-bromoethyldiethylborane could be isolated by distillation at low pressures.

A dry 200-ml flask, equipped with a septum inlet, magnetic stirrer with Teflon collar, reflux condenser connected to a water aspirator, and a dropping funnel was flushed with nitrogen. The flask was charged with 50 ml of dry *n*-pentane and 14.2 ml (100 mmol) of triethylborane.[6] Then 2.5 ml (50 mmol) of bromine in 10 ml of *n*-pentane was slowly added to the reaction mixture illuminated with a 150-W light bulb. A slow nitrogen stream and moderate suction with an aspirator were utilized to remove the hydrogen bromide as rapidly as possible. Distillation gave 6.2 g (35 mmol) of α-bromoethyldiethylborane (**1**), bp 57–58° (20 mm), a yield of 70% based on the bromine introduced (eq 3).

[1] (a) C. F. Lane and H. C. Brown, *J. Amer. Chem. Soc.*, **92**, 7212 (1970); (b) C. F. Lane and H. C. Brown, *ibid.*, **93**, 1025 (1971).

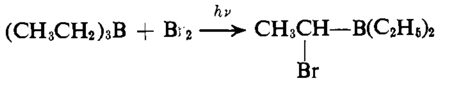
[2] J. Grotewold, E. A. Lissi, and J. C. Sianiano, *J. Organometal. Chem.*, **19**, 431 (1969).

[3] R. Schaeffer and L. J. Todd, *J. Amer. Chem. Soc.*, **87**, 488 (1965).

[4] D. S. Matteson and R. W. H. Mah, *ibid.*, **85**, 2509 (1963).

[5] α-Haloalkylboranes, RCHXBH$_2$, have been formed as intermediates in the hydroboration of certain vinyl chlorides. For example, hydroboration of 1-chloro-2-methylpropene yields α-chloroisobutylborane: H. C. Brown and R. L. Sharp, *ibid.*, **90**, 2915 (1968); D. J. Pasto, J. Hickman, and T.-C. Cheng, *ibid.*, 90, 6259 (1968). See also D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2773 (1966); D. J. Pasto and J. Hickman, *J. Amer. Chem. Soc.*, **89**, 5608 (1967). However, we have been unable to find any report for the preparation and isolation of an α-haloorganoborane other than the chlorotrimethylborane of Schaeffer and Todd.[3]

[6] Excess triethylborane was used to minimize polybromination.

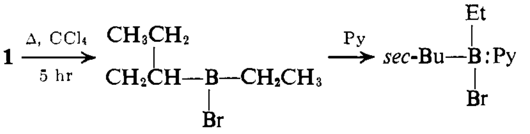


$$\mathrm{(CH_3CH_2)_3B + Br_2 \xrightarrow{h\nu} CH_3\underset{\displaystyle Br}{\underset{|}{C}}H{-}B(C_2H_5)_2} \quad (3)$$

1

The product is a colorless liquid which must be protected from oxygen and water vapor. Remarkably, it fumes strongly when exposed to water vapor, with liberation of hydrogen bromide, in the manner observed for reactive acyl bromides. Properly protected, it showed no significant change in 3 days at room temperature. It could be stored at 0° for relatively long periods of time without apparent change.

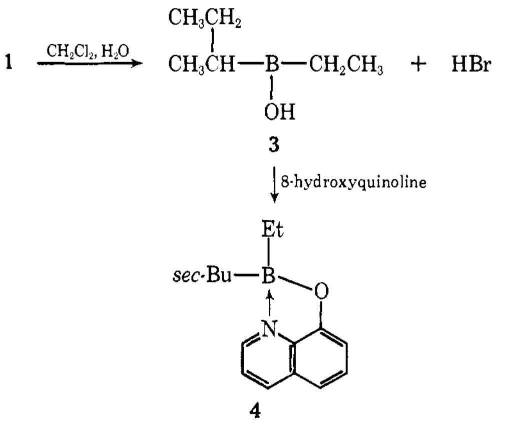
The assigned structure **1** is supported by the pmr spectrum and the reactions. The 60-MHz pmr spectrum of **1** (in CCl_4) reveals a quartet at δ 4.13 (1 H, $J = 6$ Hz), a doublet at 1.73 (3 H, $J = 6$ Hz), and a complex multiplet at 1.60–0.90 (10 H). When a solution of **1** in carbon tetrachloride was heated under reflux, there was observed over 5 hr a disappearance of the signals at δ 4.13 and 1.73 and the appearance of signals characteristic of *sec*-butylethylboron bromide (eq 4). Addition of pyridine gave the addition compound **2**.



$$\mathbf{1} \xrightarrow[5\ \mathrm{hr}]{\Delta,\ \mathrm{CCl_4}} \mathrm{\overset{\displaystyle CH_3CH_2}{\overset{|}{CH_2CH}}{-}\underset{\displaystyle Br}{\underset{|}{B}}{-}CH_2CH_3} \xrightarrow{\mathrm{Py}} sec\text{-}\mathrm{Bu{-}\overset{\displaystyle Et}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{B}}}}{:}Py} \quad (4)$$

2

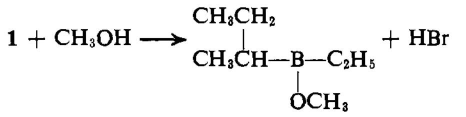
Treatment of **1** in methylene chloride with water results in the practically instantaneous formation of an equimolar quantity of hydrogen bromide in the water phase. Oxidation of the product with alkaline hydrogen peroxide yields 1 mol equiv of 2-butanol and ethanol. Alternatively, treatment of the hydrolyzed **1** with 8-hydroxyquinoline[7] gives **4**, bp 139–140° (0.5 mm), in essentially quantitative yield. Therefore, water must rearrange **1** almost instantaneously to *sec*-butylethylborinic acid (**3**) (eq 5).



(5)

The effect of various nucleophiles on the rearrangement of **1** was explored by adding the nucleophile to **1** in carbon tetrachloride and observing the change in the pmr spectra with time. When the rearrangement had been completed, the reaction mixture was treated with water, the organic layer was separated, and the product was isolated and identified as the 8-hydroxyquinolinate.

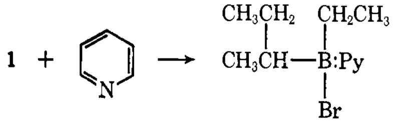
Methanol also causes the rearrangement of **1** (eq 6).



$$\mathbf{1} + \mathrm{CH_3OH} \longrightarrow \mathrm{\overset{\displaystyle CH_3CH_2}{\overset{|}{CH_3CH}}{-}\underset{\displaystyle OCH_3}{\underset{|}{B}}{-}C_2H_5} + \mathrm{HBr} \quad (6)$$

The reaction is slower than that caused by water, but still quite rapid (half-life, 5 min).

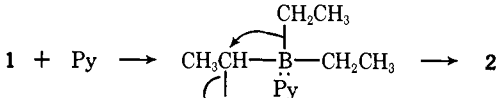
Pyridine brings about an almost instantaneous rearrangement (eq 7), resulting in the formation of the



2

(7)

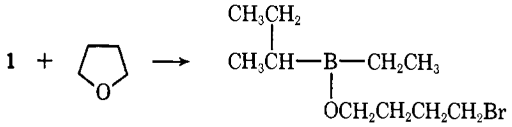
pyridine addition compound previously mentioned, **2**. The rearrangement is considerably slower with 2,6-lutidine (half-life, 20 min), and even slower with 2,6-di-*tert*-butylpyridine (half-life, 24 hr), suggesting that the rearrangement must be preceded by coordination of the nucleophile to the boron atom (eq 8). At this time, it is not possible to state whether the rearrangement occurs simultaneously with coordination, or proceeds in a fast subsequent stage.



(8)

Acetonitrile is also an effective nucleophile, but the rearrangement is relatively slow (half-life, 40 min). Presumably, this lower effectiveness is the result of the weaker donor properties of this species.

The importance of steric effects on the coordination of donors is also indicated by the contrasting results with ethyl ether and tetrahydrofuran. The addition of ethyl ether to **1** does not induce the rearrangement. However, both propylene oxide and tetrahydrofuran bring about the rearrangement, with concurrent opening of the ring system (eq 9). The results are summarized in Table I.



(9)

Table I. Rearrangement of α-Bromoethyldiethylborane with Various Nucleophiles[a]

Nucleophile	Half-life of rearrangement,[b] min	Yield of *sec*-butylethylborinic acid,[c] %
Water	0[d]	95
Methanol	5	93
Pyridine	0[d]	96
2,6-Lutidine	20	90
2,6-Di-*tert*-butylpyridine	1440	92
Acetonitrile	40	95
Propylene oxide	60	90
Tetrahydrofuran	120	92
Ethyl ether	NR[e]	

[a] Solutions of α-bromoethyldiethylborane in carbon tetrachloride, 0.87 M, were treated with an equimolar quantity of the nucleophile at 25°. [b] Time of the disappearance of the pmr signals at δ 4.13 and 1.73. [c] As the 8-hydroxyquinoline derivative, determined by pmr. [d] Very fast, almost instantaneous. [e] No change observed in 120 min.

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[7] This reagent converts dialkylborinic acids into derivatives that are relatively stable to oxygen and water. Research in progress with Dr. S. K. Gupta.

Perhaps the most remarkable feature of this rearrangement is the great speed of the reaction and the mildness of the reagents that can induce the change. The formation of carbon–carbon bonds under such mild conditions in essentially quantitative yields must hold great promise for the synthesis of complex organic structures. We are currently exploring such possibilities.

[8] Postdoctorate research associate on Grant No. GM-10937 from the National Institutes of Health and Grant No. GP-27742X from the National Science Foundation.

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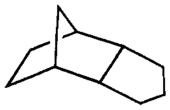
Preparation of Diamondoid Hydrocarbons by Rearrangement Employing a Chlorinated Platinum–Alumina Catalyst

Sir:

The use of Lewis acids such as $AlCl_3$ and $AlBr_3$, singly or in combination with alkyl halides and/or hydrogen halides (the so-called "sludge" method), as catalysts for the conversion of strained tricyclic hydrocarbons containing ten or more carbon atoms into adamantanes has been extensively investigated following the discovery in 1956 by Schleyer and Donaldson[1] of the first example of adamantane formation by rearrangement of *endo*-tetrahydrodicyclopentadiene (**1**) with $AlCl_3$.[2,3] The yields in this reaction are low (15–20%);[4] apparently $AlCl_3$ is catalytically unselective inasmuch as fragmentation processes and other side reactions produce hundreds of by-products. Several attempts have been made to improve on this method: replacement of $AlCl_3$ by BF_3–HF gives 30% yields of adamantane with the disadvantage, however, that a nonglass inert apparatus must be employed,[5] and yields of up to 40% have been realized with an $AlCl_3$–HCl system under 40 atm pressure of hydrogen.[6] The only gas-phase process recorded gives 6–13% yields of adamantane and at least 40 acyclic, alicyclic, and aromatic by-products from **1** on an aluminosilicate catalyst at 450–475°.[7]

Within the last few years several solid catalysts capable of isomerizing *n*-butane, *n*-pentane, and *n*-hexane to near their equilibrium isomer distributions at low temperatures have been described.[8] The essential feature of the catalytic activity of these materials is the introduction of chlorine into platinum–alumina by reaction with various chlorinating agents such as carbon tetrachloride or thionyl chloride. We have examined the reactivity of one of these catalysts toward several hydrocarbons all of which are known to give adamantanes under conventional aluminum halide catalysis,[2,9] and we now disclose that there is a dramatic increase in selectivity for adamantane formation.

The catalyst was prepared from alumina and chloroplatinic acid (0.5% by weight in platinum) and was activated by sequential treatment with H_2, HCl, and $SOCl_2$, according to the method of Giannetti and Sebulsky.[8d] The rearrangement procedure was simply a "hot-tube" process whereby a stream of the hydrocarbon vapor in dry HCl was passed through an electrically heated glass tube containing the catalyst while the products were collected in a cold trap. The adamantane precursors investigated were **1**, its exo isomer **2**, *exo*-2,3-tetramethylenenorbornane (**3**), and perhydroacenaphthene (**4**) (a mixture of four stereoisomers). The reaction details and the products, which were identified by direct comparison with authentic samples, are summarized in Table I.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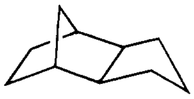
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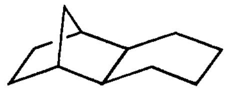
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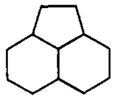
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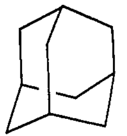
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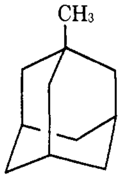

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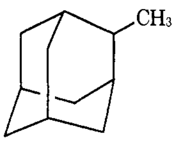

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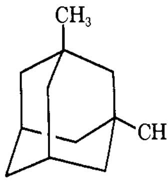

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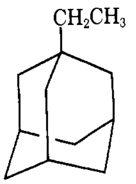

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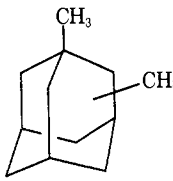

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It is immediately obvious that the catalyst exhibits a remarkable selectivity for adamantane formation in all four cases with by-product formation amounting to 1% or less, and with an essentially quantitative recovery of material. The rearrangement of **3** provided the most dramatic example; glpc analysis of the *crude* white crystalline product revealed that within the limits of detectability 1- and 2-methyladamantane were the sole products in quantitative yield. Similarly, in the C_{12} case the only products detected were the substituted adamantanes listed in Table I. Adamantane itself

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[1] P. von R. Schleyer, *J. Amer. Chem. Soc.*, **79**, 3292 (1957); P. von R. Schleyer and M. M. Donaldson, *ibid.*, **82**, 4645 (1960).

[2] *Cf.* the review article by R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

[3] The use of $AlBr_3$ "sludge" catalysts has been described by A. Schneider, R. W. Warren, and E. J. Janoski, *J. Org. Chem.*, **31**, 1617 (1966), and V. Z. Williams, Jr., P. von R. Schleyer, G. J. Gleicher, and L. B. Rodewald, *J. Amer. Chem. Soc.*, **88**, 3862 (1966).

[4] P. von R. Schleyer, M. M. Donaldson, R. D. Nicholas, and C. Cupas, *Org. Syn.*, **42**, 8 (1963).

[5] R. E. Ludwig, U. S. Patent 2, 937, 211 (1960); *Chem. Abstr.*, **54**, 19540c (1960).

[6] H. Koch and J. Franken, *Brennst.-Chem.*, **42**, 90 (1961); *Chem. Abstr.*, **55**, 21059i (1961).

[7] A. F. Plate, Z. K. Nikitina, and T. A. Burtseva, *Neftekhimiya*, **1**, 599 (1961); *Chem. Abstr.*, **57**, 4938a (1962).

[8] (a) A. G. Goble and P. A. Lawrence, *Prepr. Proc. Int. Congr. Catal., 3rd, 1964*, 320 (1965); (b) A. G. Goble, J. N. Haresnape, and T. C. O'May, Belgian Patent 634,142 (1964); *Chem. Abstr.*, **61**, 518h (1964); (c) M. D. Riordan and J. H. Estes, British Patent 1,021,587 (1966); *Chem. Abstr.*, **64**, 14088c (1966); (d) J. P. Giannetti and R. T. Sebulsky, *Ind. Eng. Chem., Prod. Res. Develop.*, **8**, 356 (1969); (e) J. P. Giannetti, H. G. McIlvreid, and R. T. Sebulsky, *Ind. Eng. Chem., Process Des. Develop.*, **9**, 473 (1970).

[9] A. Schneider, British Patent 1,068,518 (1967); *Chem. Abstr.*, **67**, 81859v (1967).