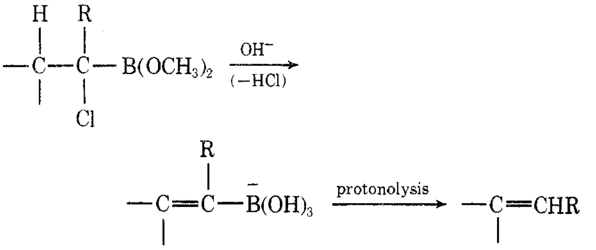
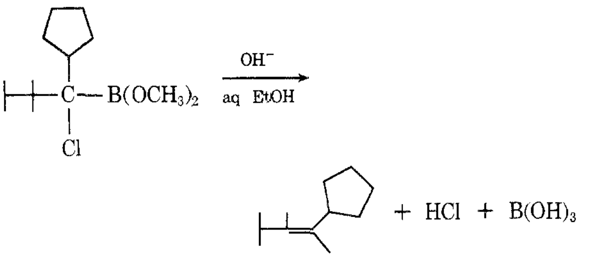
However, the same olefins were produced. The possibility was next considered that the reaction might proceed through an E2 elimination of hydrogen chloride, followed by protonolysis of the resulting vinylboronate (eq 3). This possibility was excluded on the basis of the following observations. (1) The methyl migration obtained in the thexylcyclopentyl case would be difficult to rationalize in terms of a vinylboronate intermediate (eq 4). (2) Protonolysis of vinylboronates is a very slow process under alkaline conditions.[2] (3) No deuterium is incorporated into the olefinic side products in the oxidation of the reaction products from both methyl bis(*trans*-2-methylcyclopentyl)borinate and methyl thexylcyclopentylborinate with DCME and base in deuterium oxide. Finally, (4) hydrolysis of 1 in 50% aqueous ethanol at 60° in the absence of base also yields the olefin (eq 1).



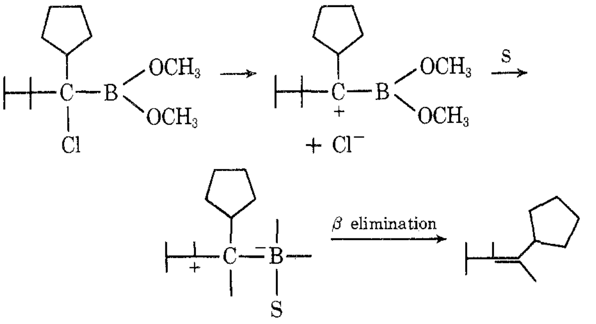
$$\text{—}\overset{\overset{H}{|}}{\underset{|}{C}}\text{—}\overset{\overset{R}{|}}{\underset{\underset{Cl}{|}}{C}}\text{—}B(OCH_3)_2 \xrightarrow[(-HCl)]{OH^-} \text{—}\underset{|}{C}{=}\overset{\overset{R}{|}}{C}\text{—}\overset{-}{B}(OH)_3 \xrightarrow{\text{protonolysis}} \text{—}\underset{|}{C}{=}CHR$$

(3)



(4)

A possible explanation for these results is a mechanism involving the ionization of the chlorine substituent to produce the corresponding carbonium ion which then undergoes fast hydride (or methide) migration, followed by β elimination (eq 5).



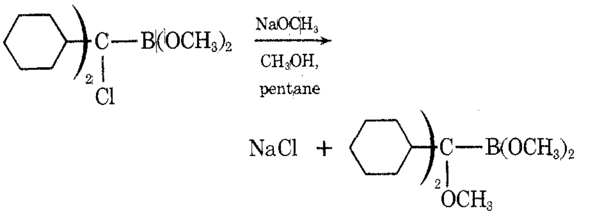
(5)

This mechanism is also compatible with the facile vapor phase decomposition of these tertiary α-chloroboronates.[3]

If this carbonium ion mechanism is indeed the pathway, it appeared possible that the reaction could be facilitated by aqueous silver nitrate. Indeed, addition of a molar equivalent of silver nitrate to a solution of α-chloroboronate in ethanol leads to instantaneous precipitation of silver chloride. Analysis of the reaction mixture by NMR and gas chromatography reveals the presence of olefins in yields above 80%/ The results are summarized in Table II.

A representative procedure follows. To 5.0 mmol of the α-chloroboronate dissolved at room temperature in 5 ml of absolute ethanol under nitrogen is added 5.5 mmol of silver nitrate in 5 ml of distilled water. An immediate precipitate forms. The mixture is stirred an additional hour at 25°. The mixture (after addition of 5 ml of pentane) can be analyzed by GLC, using a hydrocarbon as internal standard. Alternatively, the olefin can be isolated by first filtering the silver chloride and then washing the precipitate with 2 × 10 ml of water and 2 × 10 ml of pentane. Distillation of the dried organic layer yields the olefin. The physical properties of the olefins, as well as their structures, are similar to those reported in the pyrolysis of α-chloroboronic esters.[3]

The elimination reaction could be avoided and substitution[4] of the chloride atom successfully accomplished by treating a 1.0 *M* solution of α-chloroboronate in pentane with 1 equiv of sodium methoxide in anhydrous methanol (eq 6). The product, dimethyl (dicyclohexylmethoxycarbinyl)boronate, mp 68–70°, is obtained in 87% yield. NMR confirmed the product to be the α-methoxy derivative. A singlet at δ 3.28 (3 H) was observed for the *C*-methoxy protons and another singlet at δ 3.63 (6 H) for the *B*-methoxy protons. Such replacement of the chlorine atom by a methoxy group, prior to the oxidation by alkaline hydrogen peroxide, avoids significant formation of olefins as side products and markedly improves the yields of ketone over those reported in Table I. Thus, it is possible by variation in the reaction conditions to achieve a facile conversion of α-chloroboronic esters to olefins or to the α-methoxy derivatives, readily oxidized to ketones.



(6)

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(3) J.-J. Katz, B. A. Carlson, and H. C. Brown, *J. Org. Chem.*, **39,** 2817 (1974).
(4) D. S. Matteson and R. W. Mah, *J. Am. Chem. Soc.*, **85,** 2599 (1963).
(5) Graduate research assistant on Grant GM 10937 supported by the National Institutes of Health.
(6) Graduate research assistant on Grant GP 41169X supported by the National Science Foundation.

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A General One-Carbon Homologation of Organoboranes via α-Thioorganoborate Anions

Summary: The reaction of trialkylboranes with thiomethoxymethyllithium or 2-lithiothiomethoxy-1,3-thiazoline, followed by the treatment of the resultant α-thioorganoborate complexes with methyl iodide, produces the one-carbon homologated organoboranes in high yields.

Sir: We wish to report a novel procedure for the one-carbon homologation of organoboranes via α-thiorganoborate anions.[1]

The reaction of tri-*n*-butylborane with the α-lithio derivatives of methyl phenyl sulfone,[2] dimethyl sulfoxide,[3] and dimethyl sulfide[4] produces the corresponding organoborate complexes **1**, **2**, and **3**, as judged by ^{1}H NMR[5] [(THF–hex-

Table I
One-Carbon Homologation of Organoboranes via the Reaction of α-Thioorganoborate Anions with Methyl Iodide[a]

Organoborane	Homologation reagent[b] (equiv)	Product after oxidation[c] (mmoles)
Tri-*n*-butyl-	A (1)	*n*-Pentanol (9.7), *n*-butanol (19.3)[d,e]
	B (1)	*n*-Pentanol (8.9), *n*-butanol (19.7)[d]
Tris-(2-methylpentyl)-	B (3)	2-Methylhexanol (9.2), 2-methylpentanol (20.8)
Tricyclopentyl-	B (1)	Cyclopentylmethanol (7.1), cyclopentanol (22.1)
	B (2)	Cyclopentylmethanol (8.2), cyclopentanol (20.5)
	B (3)	Cyclopentylmethanol (9.7), cyclopentanol (21.0)
Trinorbornyl-	A (3)[f]	2-Norbornylmethanol (8.3), 2-norbornanol (20.5)
	B (3)	2-Norbornylmethanol (6.6), 2-norbornanol (22.0)
Thexyldi-*n*-pentyl-[g]	A (2)[h]	*n*-Hexanol (8.8), *n*-pentanol (11.0), thexyl alcohol (9.7)[i]
Disiamyl-*n*-pentyl-[j]	A (1)	*n*-Hexanol (2.1), *n*-pentanol (7.2), 2,3-dimethyl-1-butanol (6.7), 2-methyl-2-butanol (12.9)
B-Phenyl-9-BBN[k]	A (3)[f]	Benzyl alcohol (7.3), phenol (1.8), 1,5-cyclooctanediol (8.3) 5-hydroxycyclooctylmethanol (1.1)
B-(*p*-Methoxyphenyl)-9-BBN[k]	A (2)[h]	*p*-Methoxybenzyl alcohol (8.4), *p*-methoxyphenol (1.1), 1,5-cyclooctanediol (8.0), 5-hydroxycyclooctylmethanol (1.2)
Disiamyl-*trans*-1-hexenyl-[j]	A (3)[f]	*trans*-2-Hepten-1-ol[l] (7.2), 1-hepten-3-ol (0.5), 2,3-dimethyl-1-butanol (2.9), 2-methyl-2-butanol (17.4)[m]

[a] In THF–hexane at ~25° after addition of methyl iodide at 0°. A threefold excess of methyl iodide was used unless otherwise stated. [b] A, thiomethoxymethyllithium–TMEDA; B, 2-lithiothiomethoxythiazoline. The numbers in parentheses are the amount of the reagent relative to that of the organoborane. [c] The amount of each product is based on 10 mmol of the organoborane used. [d] The amount of 1-butanol includes ~1.5 mmol of 2-butanol. Only a trace of 2-methyl-1-butanol was present. [e] The yield of di-*n*-butylmono-*n*-pentylborane containing minor amounts (~15%) of two other by-products was 93% by GLC (SE-30). [f] A ninefold excess of methyl iodide was used. [g] thexyl, 2,3-dimethyl-2-butyl. [h] A sixfold excess of methyl iodide was used. [i] Only a trace of 2,2,3-trimethyl-1-butanol was present. [j] siamyl, 3-methyl-2-butyl. [k] 9-BBN, 9-borabicyclo[3.3.1]nonane. [l] Only a trace of the cis isomer was present. [m] A few other minor unidentified products were present.

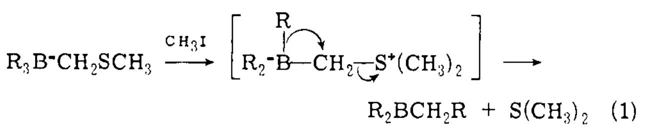
$Li[n\text{–}C_4H_9)_3BCH_2SO_2Ph]$ $Li[n\text{–}C_4H_9)_3BCH_2SOCH_3]$

1 2

$Li[n\text{–}C_4H_9)_3BCH_2SCH_3]$

3

ane, benzene) δ −0.45 to ca. +0.25 (6 H for α-methylene protons) ppm relative to $(CH_3)_4Si$ and ir[5,6] [(THF–hexane) ~2740 cm^{-1} for α-methylene C–H stretching]. Whereas treatment of 1 with alkylating agents, such as methyl fluorosulfonate, induces an *intermolecular* carbon–carbon bond formation producing ethyl phenyl sulfone, the corresponding reaction of 3 results in an *intramolecular* carbon–carbon bond formation producing di-*n*-butylmono-*n*-pentylborane[7] (4) in nearly quantitative yield (93%).[8] When a 1:1 mixture of tri-*n*-butylborane and tri-*n*-pentylborane was used, none of the cross-over products, such as di-*n*-butylmono-*n*-hexylborane, was detected by GLC, indicating the intramolecular nature of the carbon–carbon bond formation (eq 1).



$$R_3B^-CH_2SCH_3 \xrightarrow{CH_3I} \left[R_2\overset{R}{\overset{|}{B^-}}\text{—}CH_2\text{—}S^+(CH_3)_2\right] \longrightarrow R_2BCH_2R + S(CH_3)_2 \quad (1)$$

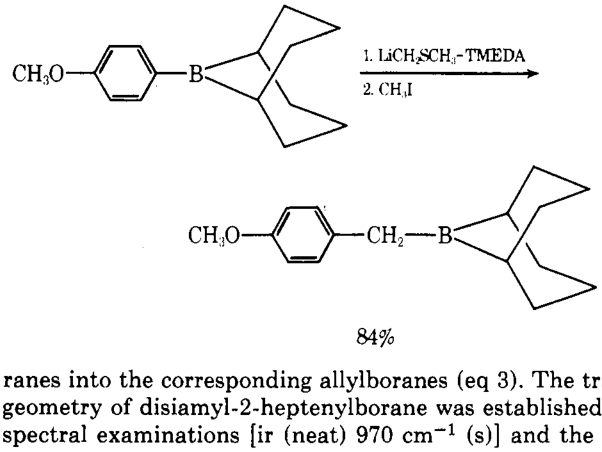
Although the reaction of organoboranes with certain ylides achieves a similar homologation,[9] there are major differences between the organoborane–ylide reaction and the organoborate–electrophile reaction. First, the latter is far less sensitive to the steric hindrance and is therefore of greater generality.[10] Second, the organoborane–ylide reaction can be complicated by the multihomologation. Such a multihomologation has not been observed in the latter even when excessive quantities of α-thioalkyllithiums and electrophiles were used. This makes possible to force the homologation reaction to go to completion.

The highest yields of homologated products have been observed with methyl iodide as an electrophile, although other reagents, such as methyl fluorosulfonate, benzyl chloride and benzoyl chloride, also give satisfactory results.

Although both thiomethoxymethyllithium–TMEDA[4] (5) and 2-lithiothiomethoxy-1,3-thiazoline[11] (6) are satisfactory as homologation reagents, the procedure using 5 appears to be less sensitive to the steric requirement of organoboranes. However, 6 can offer an advantage in that it can have an organic substituent on the methyl carbon atom.[12]

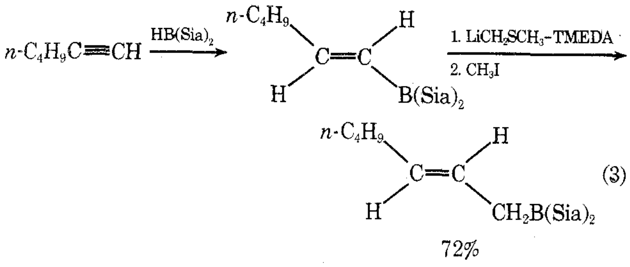
The homologation reaction reported here is general as indicated by the results summarized in Table I. It should be noted that the homologated organoboranes prepared in this study are not readily accessible by the simple hydroboration or transmetalation methods.

A few unique applications of the one-carbon homologation procedure are the conversion of arylboranes into the corresponding benzylboranes (eq 2) and that of alkenylboranes into the corresponding allylboranes (eq 3). The trans geometry of disiamyl-2-heptenylborane was established by spectral examinations [ir (neat) 970 cm^{-1} (s)] and the gas chromatographic comparison of 2-hepten-1-ol obtained after oxidation with its authentic sample. Since a variety of *trans*-alkenylboranes can be readily obtainable by the hydroboration of the corresponding acetylenes, the reaction offers, for the first time, a *stereoselective*[13] synthesis of stereochemically defined allylic organoboranes. We are cur-



(2)

84%



(3)

Sia = 3-methyl-2-butyl

rently exploring the scope and limitations of this highly promising synthesis as well as the possibility of applying the homologation procedure to the organoborane ring expansion.

The following procedure is representative. To a solution of 10 mmol of thiomethoxymethyllithium–TMEDA in hexane prepared by the literature procedure[4] and placed in a 100-ml flask equipped with a septum inlet, a magnetic stirring bar, and an outlet connected to a mercury bubbler was added 2.44 ml (10 mmol) of tri-*n*-butylborane in 10 ml of THF at 0°. After the mixture stirred for 1 hr at 0°, 1.87 ml (30 mmol) of methyl iodide was added at 0°, and the reaction mixture was stirred for 6 hr at 25°. After addition of *n*-hexadecane as an internal standard, the mixture was oxidized with 10 ml each of 3 *N* sodium hydroxide and 30% hydrogen peroxide. After the aqueous layer was saturated with potassium carbonate, GLC examination (Carbowax 20M) indicated the presence of *n*-pentanol (9.7 mmol), 1-butanol (17.8 mmol), 2-butanol (1.5 mmol), and a trace of 2-methyl-1-butanol. In a separate run, the reaction mixture was examined by GLC (SE-30) before oxidation. There was present di-*n*-butylmono-*n*-pentylborane (93%) accompanied by two minor by-products (~15% of the total products). This product was identified by GLC isolation followed by alkaline hydrogen peroxide oxidation which produced a mixture of the alcohols in a ratio almost identical with that reported above. Essentially no tri-*n*-butylborane remained unreacted.

Acknowledgment. We thank the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Syracuse University for support of this work.

References and Notes

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(3) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).

(4) D. J. Peterson, *J. Org. Chem.*, **32**, 1717 (1967).

(5) R. Damico, *J. Org. Chem.*, **29**, 1971 (1964).

(6) These complexes are stable at 25° for at least several hours. On heating, they undergo slow decomposition reactions. The precise courses of such reactions have not been examined in detail.

(7) Tri-*n*-butylborane contains ~15% of di-*n*-butylmono-*sec*-butylborane and 1–2% of mono-*n*-butyldi-*sec*-butylborane. Although two minor products that accompanied di-*n*-butylmono-*n*-pentylborane have not been identified, the GLC pattern is nearly identical with the original three-peak pattern.

(8) The reaction of **2** with methyl fluorosulfonate produced **4** in 14% yield: unpublished results obtained with K. W. Chiu.

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(11) K. Hirai, H. Matsuda, and Y. Kishida, *Tetrahedron Lett.*, 4359 (1971).

(12) Such a possibility is currently under investigation.

(13) A few stereospecific syntheses of stereochemically defined α-thioallyllithiums were reported recently: (a) J. F. Biellman and J. B. Ducep, *Tetrahedron Lett.*, 3707 (1969); (b) ref 11.

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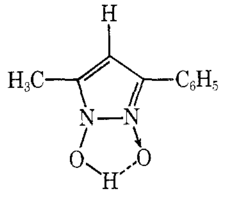
Isolation of a New 1-Hydroxypyrazole 2-Oxide via Chelation

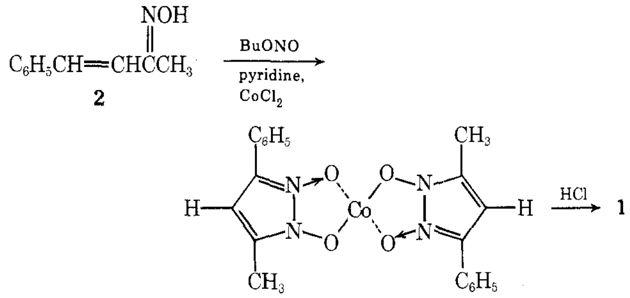
Summary: The isolation of 1-hydroxy-3(5)-phenyl-5(3)-methylpyrazole 2-oxide via a metal complex by nitrosation of benzalacetone oxime in the presence of cobaltous chloride is reported, and the intermediacy of this compound in the formation of 3,4-diazacyclopentadienone derivatives is demonstrated.

Sir: We wish to report the isolation of 1-hydroxy-3(5)-phenyl-5(3)-methylpyrazole 2-oxide (**1**). Although several 1-hydroxypyrazole 2-oxides have been prepared by Freeman and Gannon,[1] this is the first case in which the pyrazole ring is not fully substituted.



1

The procedure used in the isolation of **1** involved the preparation of a solution in aqueous ethanol of benzalacetone oxime (**2**), pyridine, and cobaltous chloride[2] in a molar ratio of 1:1:0.5. This solution was treated with 1.3 equiv of *n*-butyl nitrite which was added in three equal portions at 90-min intervals. The crude precipitate, chiefly the cobalt chelate (**3**),[3] was extracted with warm, concentrated HCl, and an insoluble by-product was filtered off.[4] Upon dilution of the filtrate with water and cooling, **1** was isolated in 33% yield.



2

3

The product was only sparingly soluble in most solvents, but with aqueous KOH it formed a stable salt which was readily purified by recrystallization from ether–tetrahydrofuran. A pure sample of **1** regenerated from the potassium salt was a white solid, melting with decomposition at 182°. (Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.14; H, 5.31; N, 14.72.