compounds suggests a uniquely different approach to the generation of diazonium ions. Study of appropriate reactions offers the possibility of providing valuable new mechanistic information about the intriguing questions associated with deamination chemistry. This is now under investigation.

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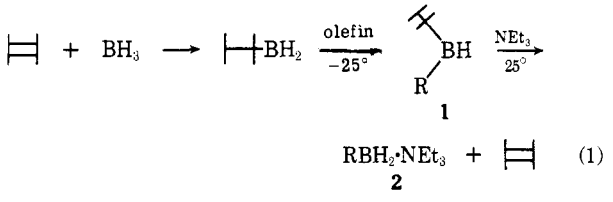
Remarkably Facile and Selective Dehydroboration of Tetramethylethylene from Thexylmonoalkylboranes under the Influence of Triethylamine. A Novel, Convenient Synthesis of Monoalkylboranes as Triethylaminates

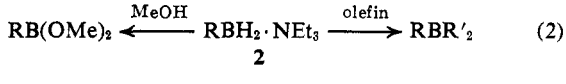
Sir:

Thexylmonoalkylboranes (**1**), readily obtainable by the hydroboration of olefins with an equimolar quantity of thexylborane,[1] react rapidly at 25° with triethylamine to produce the corresponding triethylamine–monoalkylboranes (**2**) in nearly quantitative yields (eq 1).



(1)

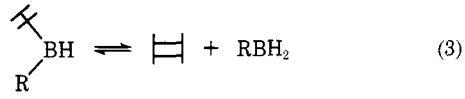
Thus tetramethylethylene serves as a temporary blocking agent to achieve the simple monoalkylation of borane. The triethylamine–monoalkylboranes (**2**) function as monoalkylboranes in disguise. They can readily be solvolyzed to form the corresponding boronic acids and their derivatives, and can hydroborate olefins to produce a variety of mixed trialkylboranes (eq 2).



(2)

Partially alkylated boranes and mixed organoboranes are essential to the maximum application of organoborane chemistry to organic synthesis.[2] Except with a very limited number of olefins, such as tetramethylethylene (TME),[3] simple hydroboration does not lead to predominant formation of monoalkylboranes.[4] We recently reported the first general synthesis of free monoalkylboranes.[5] However, a simpler, more convenient synthesis has been desired.

While studying the reaction of thexylborane with olefins, we observed dehydroboration to minor extents of TME from thexylmonoalkylboranes even at 0° (for example, 5 and 25% with isobutylene and cyclohexene, respectively).[1b] If this involved an equilibrium reaction, as shown in eq 3, either distillation of the



(3)

volatile TME or selective complexation of the monoalkylboranes would provide a simple synthesis of monoalkylboranes or their addition compounds. Our attempts to obtain pure monoalkylboranes by the removal of TME have not been successful. Addition of pyridine to thexyl(2-methylcyclopentyl)borane results in an instantaneous and complete formation of complexes as indicated by ir. However, no extensive dehydroboration of TME takes place. Evidently, pyridine quenches the entire reaction mixture.

On the other hand, treatment of thexyl(2-methylcyclopentyl)borane with 4 equiv of triethylamine at 25° for 1 hr results in the regeneration of 98% of TME without the concurrent formation of 1-methylcyclopentene. Oxidation[6] of the reaction mixture with alkaline hydrogen peroxide provides *trans*-2-methylcyclopentanol in 97% yield along with traces (≤1% each) of the cis isomer, 2,3-dimethyl-1-butanol, and 2,3-dimethyl-2-butanol. Evaporation of the volatile substances at 15 mm for 2 hr produces triethylamine–(2-methylcyclopentyl)borane (**3**): pmr (benzene, TMS) δ 0.86 (t, J = 7 Hz, 9 H), 1.28 (d, J = 6 Hz, 3 H), 1.4–2.2 (m, *ca.* 8 H), and 2.46 (q, J = 7 Hz, 6 H) ppm; ir (neat) 2350 (s) cm^{-1}. The following procedure is adaptable to all cases reported. To 5.65 ml (10 mmol) of 1.77 M thexylborane[1] was added 0.82 g (10 mmol) of 1-methylcyclopentene at −25°. One hour later 5.6 ml (40 mmol) of triethylamine was added and the mixture was stirred for 1–2 hr at 25°. For most purposes direct use of this reaction mixture is satisfactory as described later. Clearly, the present synthesis is exceedingly simple and convenient.

Treatment of the reaction mixture containing 10 mmol of triethylamine–(2-methylcyclopentyl)borane (**3**) with 40 mmol (100% excess) of methanol evolves 19.8 mmol (99%) of hydrogen within 30 min at 25° indicating the presence of 2 equiv of active hydride per boron. Glpc examination of the methanolysis product on a 2-ft SE-30 reveals the presence of 18.6 mmol (93%) of dimethyl 2-methylcyclopentylboronate (**4**). These results clearly support the formation of **3** as an essentially pure substance. Unlike free monoalkylboranes[5] triethylamine–monoalkylboranes appear quite stable to disproportionation. Thus, no noticeable disproportionation of **3** is observed at least for 1 week at 25° as evidenced by glpc after methanolysis. The experimental results of the preparation and characterization of triethylamine–monoalkylboranes are summarized in Table I.

These triethylamine–monoalkylboranes have proven to be highly useful intermediates. Thus, distillation

(1) (a) G. Zweifel and H. C. Brown, *J. Amer. Chem. Soc.*, **85**, 2066 (1963); (b) unpublished results with E. Negishi and J. J. Katz. We have not so far been able to obtain thexylmonoalkylboranes cleanly from monosubstituted terminal olefins.

(2) See, for example, H. C. Brown, *Proc. Int. Congr. Pure Appl. Chem., XXIIIrd*, **2**, 27 (1971).

(3) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962).

(4) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

(5) H. C. Brown and S. K. Gupta, *J. Amer. Chem. Soc.*, **93**, 4062 (1971).

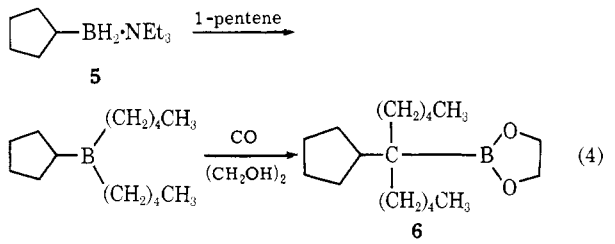
(6) *Caution!* Hydrogen peroxide (30%) should be added after completing the destruction of active hydride (25°, 0.5–1 hr) with 3 N sodium hydroxide. Premature addition of hydrogen peroxide to the unhydrolyzed monoalkylborane can result in minor explosions.

Table I. The Preparation and Characterization of Triethylamine–Monoalkylboranes[a]

Olefin	Triethylamine–monoalkylborane[b] Alcohol,[c,d] mmol	TME dehydroborated,[c] mmol	Dimethyl alkaneboronate[e] Yield, % Glpc	Yield, % Isolated	Bp, °C (mm)	n^{20}D
trans-3-Hexene	10.0	9.5	96	75	52–53 (15)	1.4075
2-Methyl-1-pentene	9.3	8.8	90	70	56–57 (15)	1.4092
Cyclopentene	9.6	10.0	98		*f*	
Cyclohexene	9.8	10.0	95	77	75–76 (17)	1.4375
2-Methyl-2-butene	9.5	9.5			*g*	
1-Methylcyclopentene	9.7	9.8	93	80	60–61 (15)	1.4290

[a] Prepared by the reaction of 10 mmol of thexylmonoalkylborane and 40 mmol of triethylamine. [b] All exhibit a strong, broad ir absorption centered at *ca.* 2350 cm^{-1} and satisfactory pmr spectra. The glpc yield of triethylamine was 100–105%. [c] By glpc. [d] Alcohol corresponds to the olefin used. Less than 0.5 mmol of 2,3-dimethyl-2-butanol and less than 0.1 mmol of 2,3-dimethyl-1-butanol were observed except with 2-methyl-1-pentene. In the case of 2-methyl-1-pentene, 1.0 mmol of 2,3-dimethyl-2-butanol was observed. [e] Satisfactory pmr and ir data were obtained. On oxidation, the corresponding alcohol was obtained in 100 ± 5% yields. [f] Triethylamine–cyclopentylborane was identified by the conversion in 70% to 2-(cyclopentyldi-*n*-pentylcarbinyl)-2-bora-1,3-dioxolane, bp 127–128° (0.7 mm); n^{20}D 1.4675. [g] Triethylamine–(3-methyl-2-butyl)borane was identified by the conversion in 72% to 2-[(3′-methyl-2′-butyl)dicyclopentylcarbinyl]-2-bora-1,3-dioxolane, bp 130–131° (0.8 mm); n^{20}D 1.4996.

of the methanolysis product from **3** produces pure **4**[7] in 80% yield, thereby providing a new, low-temperature route to such boronic acid esters. In marked contrast with the corresponding trimethylamine or pyridine complexes, which show little tendency to hydroborate at 25°, triethylamine–monoalkylboranes hydroborate olefins at 25° at reasonable rates. Addition of 1.4 g (20 mmol) of 1-pentene to a crude mixture containing 10 mmol of triethylamine–cyclopentylborane (**5**) results in the uptake of greater than 90% of the 1-pentene in 16 hr at 25°. Carbonylation of the reaction mixture in the usual manner[8] yields the corresponding boronate[9] (**6**) in 70% yield (eq 4), bp 127–128° (0.7 mm); n^{20}D



(4)

1.4675. This result should be compared with our recent observation that the reaction of thexylcyclopentylborane with 2 equiv of 1-butene results in the displacement of only 1% of the thexyl group, failing to produce the corresponding cyclopentyldi-*n*-butylborane.[10] The hydroboration with triethylamine–monoalkylboranes can be greatly accelerated by carrying out the reaction in hexane in the presence of boron trifluoride etherate. In the absence of olefins, this reaction provides free monoalkylboranes in a manner similar to our recent procedure using pyridine–monoalkylboranes.[5]

The present novel, convenient synthesis of triethylamine–monoalkylboranes makes these derivatives easily available for the first time and should greatly facilitate the application of organoborane chemistry to organic synthesis.

(7) All isolated dimethyl alkaneboronates were identified and characterized by glpc analysis of the oxidation products, pmr, ir, boiling points, and refractive indices as summarized in Table I.

(8) H. C. Brown, E. Negishi, and S. K. Gupta, *J. Amer. Chem. Soc.*, **92**, 6648 (1970).

(9) The product yielded correct elemental analyses and spectral data.

(10) C. F. Lane and H. C. Brown, *J. Organometal. Chem.*, **34**, C29 (1972).

(11) Postdoctoral Research Associate on Grant No. DA 31-124 ARO(D) 453, supported by the U. S. Army Research Office (Durham).

(12) Graduate Research Assistant on Grant No. GM 10937, supported by the National Institutes of Health.

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The Use of Proton and Carbon-13 Nuclear Magnetic Resonance for Assignment of the Glycosylation Site in 3- and 5-Substituted 1-β-D-Ribofuranosyl-1,2,4-triazoles

Sir:

We report here the novel use of both ^{1}H (pmr) and ^{13}C (cmr) nmr to establish the glycosylation site in 1-β-D-ribofuranosyl-1,2,4-triazoles. To our knowledge, this is the first report of cmr used in this manner.

Several substituted 1-β-D-ribofuranosyl-1,2,4-triazoles have recently been shown to exhibit broad spectrum antiviral activity in tissue culture and in animal systems.[1,2] These nucleosides were prepared by both the silylation–glycosylation and the acid-catalyzed procedures which provided both the 3- and 5-substituted isomeric products.[3] The classical utilization of uv spectra to assign the position of ribose attachment was of no avail, since these compounds showed weak absorption.

The results of our nmr experiments are summarized in Table I. The pmr spectrum of 1,2,4-triazole base I has been reported and is a singlet at −8.33 ppm.[4a] The cmr spectrum, as previously noted,[4b] also shows

(1) R. W. Sidwell, J. H. Huffman, G. P. Khare, L. B. Allen, J. T. Witkowski, and R. K. Robins, *Science*, in press.

(2) J. H. Huffman, J. T. Witkowski, R. K. Robins, R. W. Sidwell, G. P. Khare, W. B. Jolley, L. N. Simon, L. P. Gebhardt, and D. G. Streeter, *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **31**, Abstracts 2035, 2036, 2037, 2038 (1972).

(3) J. T. Witkowski, R. K. Robins, and R. W. Sidwell, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, No. MEDI 19.

(4) (a) R. Jacquier, M-L. Roumestant, and P. Viallefont, *Bull. Soc. Chim. Fr.*, 2630 (1967); (b) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **90**, 3543 (1968).