1-Methyl-2-nitronaphthalene (23). This compound was prepared by reduction of **22** according to the literature procedure[19] to give 57% of **23**: mp 59–60 °C (lit.[19] mp 56 °C); IR (KBr) 6.59, 7.40, 12.30, 12.56, 13.30 μm; NMR ($CDCl_3$) δ 3.77 (3 H, s), 8.4–7.5 (6 H, m).

1-(*N,N*-Dimethylamino)-2-(2-nitro-1-naphthyl)ethene (24) and 3*H*-Benz[*e*]indole (1). A solution of 2.60 g (17.7 mmol) of dimethylformamide diethyl acetal and 3.30 g (17.6 mmol) of **23** in 10 mL of dry dimethylformamide was heated to 155 °C for 3 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure to yield crude **24** as a dark red oil: IR (neat) 6.14, 6.60, 7.30, 9.14, 12.50, 13.25 μm; NMR ($CDCl_3$) δ 2.80 (6 H, s), 5.66 (1 H, d, J = 13.7 Hz), 6.40 (1 H, d, J = 13.7 Hz). This material was used in the following step without additional purification.

The material obtained above was dissolved in 50 mL of benzene in a Parr hydrogenation vessel and 0.25 g of 5% palladium on carbon was added. This material was hydrogenated at 40 psi hydrogen pressure until the solution turned to a clear yellow. The reaction mixture was filtered through Celite and the filtrate was concentrated under reduced pressure. The residue was chromatographed on silica gel (ether–hexane eluent) to yield 0.70 g (24% based on 1-methyl-2-nitronaphthalene) of 3*H*-benz[*e*]indole (1). This material was identical in all respects with that described above.

Acknowledgment. We are indebted to the Public Health Service for grants from the Institute of General Medical Sciences and National Cancer Institute which supported this investigation.

Registry No.—1, 232-84-8; **4**, 91-59-8; **5**, 63017-82-3; **8**, 134-32-7; **9**, 34774-85-1; **11**, 2246-44-8; **15**, 63017-83-4; **16**, 18505-87-8; **17**, 63017-84-5; **18**, 57582-31-7; **19**, 63017-85-6; **20**, 90-12-0; **21**, 6627-78-7; **22**, 63017-86-7; **23**, 63017-87-8; **24**, 63017-88-9; 1-methyl-2-aminonaphthalene, 771-13-1; methylthio-2-propanone, 14109-72-9; methylthioacetaldehyde, 23328-62-3; dimethylformamide diethyl acetal, 1188-33-6.

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Hydroboration of Alkenes and Alkynes by 1,3,2-Dithiaborolane

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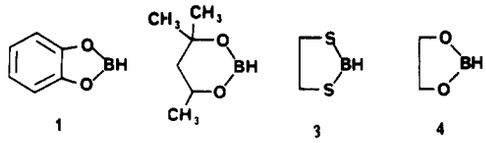
Treatment with diethyl ether–trifluoroborane or trichloroborane liberates 1,3,2-dithiaborolane (3) from its complex with trimethylamine. At 50 °C in benzene, hydroboration by 1,3,2-dithiaborolane efficiently converts a representative group of alkenes and alkynes into alkyl- and alkenyl-1,3,2-dithiaborolanes. Hydrolysis of these products yields the corresponding boronic acids.

From studies of boronic acids and their derivatives have come several important developments. Meriting special attention is the observation that certain derivatives of benzeneboronic acid accumulate in tumors of the brain.[1] Since ^{10}B has an unusually large cross section for the capture of thermal neutrons and since subsequent nuclear fission of $^{11}_{5}B$ releases locally lethal amounts of energy, neutron irradiation can be used to destroy the cells of tumors selectively.[2] The powerful, reversible inhibition of α-chymotrypsin and subtilisin by 2-phenylethaneboronic acid and benzeneboronic acid has given boronic acids a role to play in the study of specific inhibitors of enzymes.[3] Finally, boronic acids are useful intermediates in syntheses: for example, terminal alkynes can be converted into *trans*-vinyl iodides and *cis*-vinyl bromides;[4a] oxidation of boronic acids $RB(OH)_2$ with ammoniacal silver oxide gives simple coupled products R–R;[4b] a cross-coupling reaction mediated by boronate complexes derived from boronic esters and vinyllithium reagents can be used to prepare substituted olefins;[4c] and the reactions of carbonyl compounds with lithium bis(ethylenedioxyboryl)methide and then with hydrogen peroxide yield the homologous aldehydes.[4d]

An old, general method for preparing boronic acids and esters employs the reaction of appropriate organometallic compounds with esters of boric acid.[5] Redistribution reactions of trialkylboranes[6] or tetraalkylstannanes[7] with trichloroborane and redistribution reactions of trialkylboranes with esters of boric acid[8] produce derivatives of boronic acids, but frequently more efficient is the direct hydroboration of alk-

enes and alkynes by one of the following reagents: 1,3,2-benzodioxaborole (1),[9] 4,4,6-trimethyl-1,3,2-dioxaborinane (2),[10]



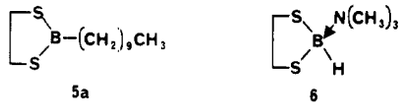
1 2 3 4

chloroborane,[11] and dichloroborane.[12] Now, 1,3,2-dithiaborolane (3) can be added to this list.

1,3,2-Dithiaborolane, first prepared by the reaction of diborane with 1,2-ethanedithiol in diethyl ether and characterized by Egan et al.,[13] is a colorless, crystalline solid which is only slightly soluble in tetrahydrofuran. The pure solid does not undergo disproportionation below 90 °C.[13] Measurement of the molecular weight in the gas phase and examination of the infrared spectra of the vapor and the solid showed that 1,3,2-dithiaborolane is monomeric in the gas phase and suggested that quaternization of boron occurs in the solid through intermolecular coordinate bonds between boron and sulfur.[13] 1,3,2-Dithiaborolane is a stronger Lewis acid than its close relative 1,3,2-dioxaborolane (4), since trimethylamine–1,3,2-dithiaborolane shows no tendency to dissociate at 25 °C, but trimethylamine–1,3,2-dioxaborolane is dissociated completely in the gas phase at 25 °C.[13]

Results and Discussion

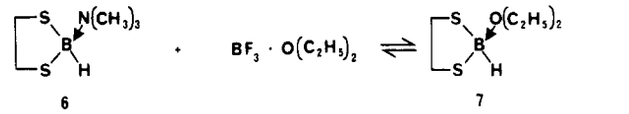
Because of the simplicity of its synthesis, its stability, and the strength of its Lewis acidity, 1,3,2-dithiaborolane promised to be a superior reagent for the preparation of boronic acids. To learn whether or not a solution of 1,3,2-dithiaborolane in fact could be prepared and used to effect the hydroboration of alkenes and alkynes, we performed the following experiment. When a solution of tetrahydrofuran–borane in tetrahydrofuran was treated at 0 °C with an equimolar amount of ethanedithiol and warmed to 25 °C, 2 molar equiv of hydrogen were liberated rapidly. Reaction of the homogeneous mixture with 1-decene at 25 °C for 15 h led, after oxidation of the products, to a 74% yield of 1-decanol. But only part of this 1-decanol could have been derived from the expected intermediate, 2-decyl-1,3,2-dithiaborolane (5a), since



5a 6

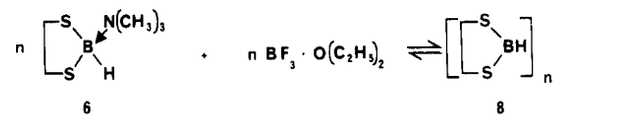
analysis of the reaction mixture showed that a significant amount of tridecylborane was present before oxidation. Reversing the order in which borane and ethanedithiol were combined and changing the temperatures of various steps in this sequence did not reveal conditions for a more efficient synthesis of compound **5a**. Disproportionation of thioboranes produced by the initial reaction of borane with ethanedithiol may regenerate borane and account for the formation of tridecylborane, since borane should compete successfully with 1,3,2-dithiaborolane for 1-decene.[11b]

Entirely satisfactory results, however, were obtained when 1,3,2-dithiaborolane was generated in a less direct manner. Its trimethylamine complex **6**, reported by Egan et al.,[13] can be prepared conveniently as a crystalline solid by the sequential treatment of tetrahydrofuran–borane in tetrahydrofuran with ethanedithiol and trimethylamine. Since trimethylamine–1,3,2-dithiaborolane (6) is thermally stable below 100 °C even under high vacuum, we were not surprised to find that it failed to react with 1-decene in boiling benzene, and we attempted to prepare a more active reagent by removing trimethylamine from the complex. Treatment of a solution of trimethylamine–1,3,2-dithiaborolane (6) in chloroform-d_1 at 25 °C with an equimolar amount of diethyl ether–trifluoroborane yielded a mixture which initially was homogeneous. Immediate examination by ^{1}H NMR spectroscopy revealed the presence of trimethylamine–trifluoroborane (broad singlet at δ 2.67), which could be isolated and characterized, and showed that less than 5% of the original amounts of diethyl ether–trifluoroborane and trimethylamine–1,3,2-dithiaborolane (6) remained. The other signals, a triplet at δ 1.20, a broad singlet at δ 3.30, and a quartet at δ 3.52, could be attributed to a weak complex 7 of diethyl ether and 1,3,2-dithiaborolane (reaction 1) or to a mixture of diethyl ether and an oligomer 8 of 1,3,2-dithiaborolane (reaction 2). Formation of oligomer 8 seems more likely, however, since the



6 7

$$+ BF_3 \cdot N(CH_3)_3 \quad (1)$$

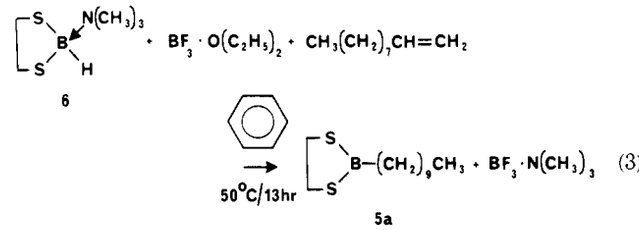


6 8

$$+ n\,O(C_2H_5)_2 + n\,BF_3 \cdot N(CH_3)_3 \quad (2)$$

chemical shifts of the triplet and quartet are very nearly the same as those of diethyl ether itself in chloroform-d_1.

Oligomer 8 proved to be significantly more reactive than trimethylamine–1,3,2-dithiaborolane (6), and the addition of an equimolar amount of diethyl ether–trifluoroborane to mixtures of trimethylamine–1,3,2-dithiaborolane (6) and 1-decene had a dramatic and beneficial effect: after 13 h at 50 °C, 1-decene had been consumed completely, and the product was simply a mixture of 2-decyl-1,3,2-dithiaborolane (5a) and trimethylamine–trifluoroborane (reaction 3). When complex 6 was treated with 1-decene and diethyl ether–trifluoroborane in benzene or chloroform and kept at 25 °C for 24 h, the major product, 2-decyl-1,3,2-dithiaborolane (5a), was contaminated with tridecylborane. Since an appropriate control experiment demonstrated that compound 5a is stable, the tridecylborane probably is derived from diborane generated by disproportionation of oligomer 8 or complex 7. A similarly impure product was isolated when a solution of trimethylamine–



6 5a

$$+ BF_3 \cdot O(C_2H_5)_2 + CH_3(CH_2)_7CH{=}CH_2 \xrightarrow[50°C/13hr]{} + BF_3 \cdot N(CH_3)_3 \quad (3)$$

1,3,2-dithiaborolane (6) and 1-decene in chloroform at 25 °C was treated with trichloroborane; a minor advantage of this procedure was the immediate and quantitative precipitation of trimethylamine–trichloroborane.

Application of the satisfactory conditions of reaction 3 to a representative series of alkenes and alkynes gave the results summarized in Figure 1. The physical properties and chemical behavior of compounds **5a–f** were those of derivatives of 1,3,2-dithiaborolane substituted at boron, a few examples of which already had been prepared by the reaction of boranes with ethanedithiol and by the reaction of 2-halo-1,3,2-dithiaborolanes with organometallic reagents.[14] Hydrolysis of compounds **5a** and **5b** in aqueous tetrahydrofuran very rapidly and efficiently yielded boronic acids, and hydrolysis followed by oxidation with aqueous hydrogen peroxide and base converted compounds **5a** and **5c** into the corresponding alcohols. In addition, the ^{1}H NMR spectra of these dithiaborolanes in chloroform-d_1 exhibited in all cases a sharp singlet at δ 3.2

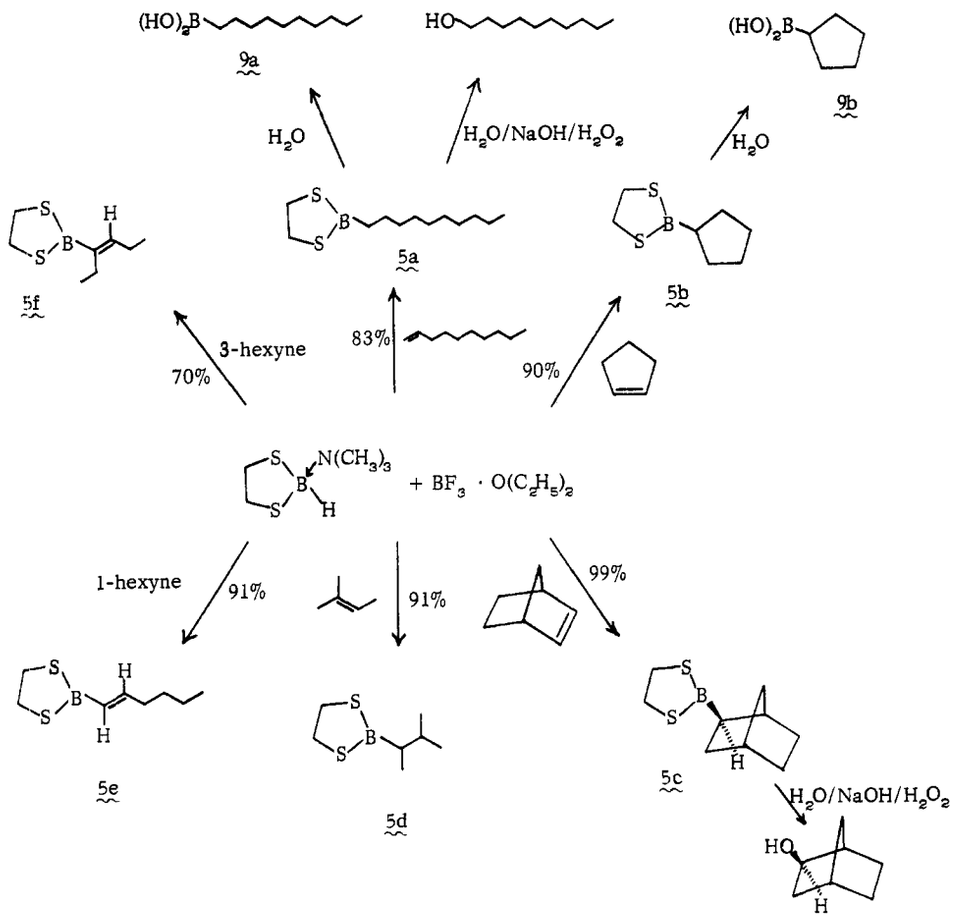


Figure 1. Products from the reaction of trimethylamine–1,3,2-dithiaborolane (**6**) with diethyl ether–trifluoroborane and a representative series of alkenes and alkynes in benzene at 50 °C.

attributed previously to the hydrogens of the dithiaborolane ring.[14c,d] Finally, the structures assigned to compounds **5a–d** were consistent with their mass spectra, which revealed prominent ions arising from the loss of the elements of 1,3,2-dithiaborolane by dehydroboration.

Simple derivatives of boronic acids have been prepared directly by the reactions of alkenes and alkynes with 1,3,2-benzodioxaborole (**1**),[9] 4,4,6-trimethyl-1,3,2-dioxaborinane (**2**),[10] chloroborane,[11] and dichloroborane.[12] Unfortunately, compounds **1** and **2** react sluggishly with alkenes; only at temperatures above about 100 °C do these hydroborations occur at satisfactory rates. The disadvantages of the chloroboranes, which are more reactive alternatives, are their instability and the intricacy of their preparation. We believe that the reactivity of 1,3,2-dithiaborolane, the stability of its trimethylamine complex, and the simplicity of its synthesis make trimethylamine–1,3,2-dithiaborolane a particularly effective reagent for the synthesis of boronic acids by hydroboration.

Experimental Section

General Procedures. All infrared (IR) spectra were recorded on a Perkin-Elmer Model 137 spectrometer. Varian A-60, T-60, HA-100, and XL-100 spectrometers were used to obtain ^1H nuclear magnetic resonance (NMR) spectra. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane (δ). An AEI MS-9 double-focusing spectrometer was used to obtain mass spectra (MS) at 70 eV. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points (mp) were measured on a Thomas-Hoover capillary apparatus and are uncorrected. Vapor-phase chromatographic analyses were performed on columns of 2% Apiezon L (5 ft × 0.25 in.), 10% SE-30 (6 ft × 0.25 in.), and 10% Carbowax-20M (5 ft × 0.25 in.) on Chromosorb W in a Varian Aerograph Model 1420 instrument equipped with a thermal-conductivity detector. All glassware was dried at 120 °C and cooled under dry N_2 immediately before use. Benzene and hexane were dried over sodium wire, and tetrahydrofuran was distilled from the sodium ketyl of benzophenone. A solution of tetrahydrofuran–borane in tetrahydrofuran was obtained from the Ventron Corporation. All other reagents were commercial products of the highest purity obtainable.

Preparation of Trimethylamine–1,3,2-Dithiaborolane (6). Under dry N_2, a stirred solution of tetrahydrofuran–borane in tetrahydrofuran (56 mL, 1.0 M, 56 mmol) at 0 °C was treated dropwise during 30 min with freshly distilled 1,2-ethanedithiol (5.3 g, 56 mmol). The mixture, from which gas issued vigorously, was stirred at 0 °C for 2 h. Then after an excess of trimethylamine had been introduced by the slow distillation of a liquid sample (6 mL at 0 °C) into the reaction vessel, the mixture was kept at 0 °C for an additional 2 h. Removal of solvent by evaporation at 25 °C in vacuo left complex **6** as a mass of colorless crystals, and sublimation of this material at 50 °C and 0.004 Torr efficiently provided an analytically pure sample of trimethylamine–1,3,2-dithiaborolane in the form of glassy prisms (7.0 g, 43 mmol, 77%): mp 100–101 °C dec; IR (solution in CH_2Cl_2) 2405 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.65 (s, 9 H), 2.93 (s, 4 H); MS *m/e* (rel intensity) 104 (36), 103 (12), 76 (16), 61 (12), 60 (52), 59 (44), 58 (100). Anal. Calcd for $C_5H_{14}BNS_2$: C, 36.82; H, 8.65; B, 6.63; N, 8.59; S, 39.31. Found: C, 36.99; H, 8.70. Trimethylamine–1,3,2-dithiaborolane (**6**) dissolved readily in organic solvents like benzene, chloroform, and tetrahydrofuran at 25 °C, and solutions with concentrations greater than 0.80 M could be prepared.

Preparation of 2-Decyl-1,3,2-dithiaborolane (5a). Under dry N_2, a solution of trimethylamine–1,3,2-dithiaborolane (**6**; 246 mg, 1.50 mmol) and freshly distilled 1-decene (213 mg, 1.52 mmol) in benzene (5.0 mL) was stirred at 50 °C, treated dropwise during 2 min with freshly distilled diethyl ether–trifluoroborane (190 μL, 1.50 mmol), and then heated at 50 °C for 13 h. After the mixture had been cooled to 25 °C, solvent was removed by evaporation in vacuo and the residue was treated with hexane (5.0 mL). A colorless solid which failed to dissolve was separated by filtration under dry N_2; the IR spectrum and MP of this material could not be distinguished from those of a sample of trimethylamine–trifluoroborane prepared by the method of Amster and Taylor.[15] Evaporation of hexane from the filtrate at 25 °C in vacuo left a colorless liquid residue of 2-decyl-1,3,2-dithia-

borolane (**5a**; 306 mg, 1.25 mmol, 83%) in which no contaminants could be detected spectroscopically. Molecular distillation of this material at 85 °C and 0.2 Torr provided a sample which was analytically pure: IR (liquid film) 2940, 2850, 1280, 900, 840 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.9 (m, 3 H), 1.3 (m, 18 H), 3.23 (s, 4 H); MS *m/e* (rel intensity) 244 (7), 140 (7), 96 (29), 76 (20), 61 (93), 60 (100), 59 (71), 58 (36). Anal. Calcd for $C_{12}H_{25}BS_2$: C, 59.00; H, 10.32; B, 4.43; S, 26.25. Found: C, 58.76; H, 10.14.

Reactions of 2-Decyl-1,3,2-dithiaborolane (5a). a. Under dry N_2, 2-decyl-1,3,2-dithiaborolane (**5a**; 212 mg, 0.868 mmol) was treated with tetrahydrofuran (2.0 mL) and water (2.0 mL), and the mixture was stirred at 25 °C for 2 h. Removal of the volatile components by evaporation in vacuo at 25 °C left a colorless solid residue of decyldihydroxyborane (**9a**; 146 mg, 0.785 mmol, 90%). A sample of this material which had been recrystallized twice from a 1:1 mixture of nitromethane and ethyl acetate melted at 76–77 °C (lit.[16] 76–78 °C).

b. Under dry N_2, a mixture of 2-decyl-1,3,2-dithiaborolane (**5a**; 114 mg, 0.467 mmol), tetrahydrofuran (1.5 mL), and water (1.5 mL) was stirred at 25 °C for 75 min. After the volatile components of this mixture had been removed by evaporation in vacuo, the residue was treated with tetrahydrofuran (3.0 mL), aqueous NaOH (3 N, 500 μL), and aqueous H_2O_2 (30%, 500 μL) and heated at 50 °C for 30 min. After the mixture had been cooled and partitioned between diethyl ether and water, the ethereal phase was washed with water and saturated aqueous NaCl and then was dried over K_2CO_3. Evaporation of the solvent under reduced pressure left a residue of 1-decanol (58 mg, 0.37 mmol, 78%) containing no impurities which could be detected by spectroscopy or vapor-phase chromatography.

Preparation of 2-Cyclopentyl-1,3,2-dithiaborolane (5b). To a solution of trimethylamine–1,3,2-dithiaborolane (**6**; 1.59 g, 9.74 mmol) and cyclopentene (681 mg, 10.0 mmol) in benzene (15.0 mL), stirred under dry N_2 at 50 °C, freshly distilled diethyl ether–trifluoroborane (1.20 mL, 9.77 mmol) was added dropwise. After the mixture had been heated at 50 °C for 13 h and cooled to 25 °C, volatile components were removed by evaporation in vacuo and the residue was extracted with hexane (10.0 mL). Removal of hexane from the filtered extracts by evaporation in vacuo left a colorless liquid residue of 2-cyclopentyl-1,3,2-dithiaborolane (**5b**; 1.51 g, 8.77 mmol, 90%). Molecular distillation of this material at 55 °C and 0.7 Torr yielded a sample which was analytically pure: IR (liquid film) 2940, 2860, 1280, 880, 840 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.6 (m, 9 H), 3.25 (s, 4 H); MS *m/e* (rel intensity) 172 (93), 144 (47), 116 (25), 104 (93), 103 (29), 76 (25), 68 (100), 67 (28), 61 (60), 60 (57), 59 (27). Anal. Calcd for $C_7H_{13}BS_2$: C, 48.85; H, 7.61; B, 6.28; S, 37.26. Found: C, 48.76; H, 7.57.

Preparation of Cyclopentyldihydroxyborane (9b). A mixture of 2-cyclopentyl-1,3,2-dithiaborolane (**5b**; 334 mg, 1.94 mmol), tetrahydrofuran (2.0 mL), and water (2.0 mL) was stirred under N_2 at 25 °C for 2 h. Removal of the volatile components by evaporation in vacuo at 25 °C left a colorless solid residue of cyclopentyldihydroxyborane (**9b**; 212 mg, 1.86 mmol, 96%). A sample of this material which had been recrystallized twice from water and dried over anhydrous sulfuric acid was analytically pure: mp 90–92 °C; IR (KBr) 3300, 2950, 2860, 1370 cm^{-1}; ^1H NMR (60 MHz, Me_2SO-d_6) δ 1.6 (m, 9 H). Anal. Calcd for $C_5H_{11}BO_2$: C, 52.70; H, 9.73; B, 9.49; O, 28.08. Found: C, 52.89; H, 9.77.

Preparation of 2-(*exo*-2-Bicyclo[2.2.1]heptyl)-1,3,2-dithiaborolane (5c). To a solution of trimethylamine–1,3,2-dithiaborolane (**6**; 1.45 g, 8.88 mmol) and bicyclo[2.2.1]hept-2-ene (0.840 g, 8.92 mmol) in benzene (15.0 mL), stirred under dry N_2 at 50 °C, freshly distilled diethyl ether–trifluoroborane (1.10 mL, 9.11 mmol) was added dropwise. After the mixture had been heated at 50 °C for 13 h and cooled to 25 °C, volatile components were removed by evaporation in vacuo and the residue was extracted with hexane (10.0 mL). Removal of hexane from the filtered extracts by evaporation in vacuo left a colorless liquid residue of 2-(*exo*-2-bicyclo[2.2.1]heptyl)-1,3,2-dithiborolane (**5c**; 1.75 g, 8.83 mmol, 99%). Molecular distillation of this material at 75 °C and 0.7 Torr provided a sample which was analytically pure: IR (liquid film) 2950, 2860, 1280, 900, 840, 825 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.3, 1.5 (m, 9 H), 2.3 (m, 2 H), 3.20 (s, 4 H); MS *m/e* (rel intensity) 198 (72), 170 (77), 169 (59), 130 (44), 95 (26), 94 (100), 81 (33), 76 (28), 67 (38), 66 (31), 61 (67), 60 (100), 59 (44). Anal. Calcd for $C_9H_{15}BS_2$: C, 54.55; H, 7.63; B, 5.45; S, 32.36. Found; C, 54.62; H, 7.57.

A mixture of 2-(*exo*-2-bicyclo[2.2.1]heptyl)-1,3,2-dithiaborolane (**5c**; 536 mg, 2.70 mmol), tetrahydrofuran (4.0 mL), and water (4.0 mL) was stirred under N_2 for 2 h at 25 °C. After volatile components of this mixture had been removed by evaporation in vacuo, the residue was treated with tetrahydrofuran (4.0 mL), aqueous NaOH (3 N, 1.0 mL), and aqueous H_2O_2 (30%, 1.0 mL) and heated at 50 °C for 90 min. After the mixture had been cooled and partitioned between diethyl ether and water, the ethereal phase was washed with water and saturated aqueous NaCl and then was dried over K_2CO_3. Evaporation of the solvent under reduced pressure left a residue of *exo*-2-bicyclo[2.2.1]-heptanol (189 mg, 1.68 mmol, 62%) containing no impurities which could be detected by IR or NMR spectroscopy; analysis by gas chromatography revealed that less than 3% of the endo isomer was present.

Preparation of 2-(1,2-Dimethylpropyl)-1,3,2-dithiaborolane (5d). Freshly distilled diethyl ether–trifluoroborane (420 μL, 3.38 mmol) was added dropwise to a solution of trimethylamine–1,3,2-dithiaborolane (**6**; 554 mg, 3.40 mmol) and 2-methyl-2-butene (250 mg, 3.56 mmol) in benzene (5.0 mL), stirred under N_2 at 50 °C. After the mixture had been heated at 50 °C for 20 h, a crude sample of 2-(1,2-dimethylpropyl)-1,3,2-dithiaborolane (**5d**; 542 mg, 3.11 mmol, 91%) was isolated in the usual manner. Molecular distillation of this material at 35 °C and 0.45 Torr provided a sample which was analytically pure: IR (liquid film) 2950, 2860, 1280, 880, 840 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.95 (d, 6 H, J = 6 Hz), δ 1.05 (d, 3 H, J = 6 Hz), δ 1.5 (m, 2 H), δ 3.23 (s, 4 H); MS *m/e* (rel intensity) 174 (96), 173 (33), 159 (46), 146 (35), 145 (40), 132 (99), 131 (78), 104 (77), 103 (45), 76 (29), 71 (63), 70 (100), 61 (94), 60 (88), 59 (33), 55 (67). Anal. Calcd for $C_7H_{15}BS_2$: C, 48.28; H, 8.68; B, 6.21; S, 36.83. Found: C, 48.46; H, 8.73.

Preparation of 2-[(*E*)-1-Hexenyl]-1,3,2-dithiaborolane (5e). Freshly distilled diethyl ether–trifluoroborane (240 μL, 1.95 mmol) was added dropwise to a solution of trimethylamine–1,3,2-dithiaborolane (**6**; 313 mg, 1.92 mmol) and 1-hexyne (159 mg, 1.94 mmol) in benzene (5.0 mL), stirred under N_2 at 50 °C. After the mixture had been heated at 50 °C for 12 h, 2-[(*E*)-1-hexenyl]-1,3,2-dithiaborolane (**5e**; 325 mg, 1.75 mmol, 91%) was isolated in the usual manner. Molecular distillation of this material at 55 °C and 0.45 Torr yielded a sample which was analytically pure: IR (liquid film) 2950, 2860, 1280, 990, 900, 840 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.9 (m, 3 H), 1.2 (m, 4 H), 2.2 (m, 2 H), 3.27 (s, 4 H), 6.11 (d, 1 H, J = 17 Hz), 6.69 (d of t, 1 H, J = 6, 17); MS *m/e* (rel intensity) 186 (100), 185 (25), 176 (33), 158 (34), 157 (33), 144 (90), 143 (29), 130 (90), 129 (34), 116 (42), 105 (30), 61 (92), 60 (96), 59 (55). Anal. Calcd for $C_8H_{15}BS_2$: C, 51.62; H, 8.12; B, 5.81; S, 34.45. Found: C, 51.79; H, 8.19.

Preparation of 2-(1-Ethyl-(*Z*)-1-butenyl)-1,3,2-dithiaborolane (5f). Freshly distilled diethyl ether–trifluoroborane (0.960 mL, 7.81 mmol) was added dropwise to a solution of trimethylamine–1,3,2-dithiaborolane (**6**; 1.20 g, 7.36 mmol) and 3-hexyne (0.634 g, 7.72 mmol) in benzene (10.0 mL), stirred under N_2 at 50 °C. After the mixture had been heated at its boiling point for 13 h, a colorless liquid (1.24 g) was isolated in the usual manner and shown to consist of a mixture of 2-(1-ethyl-(*Z*)-1-butenyl)-1,3,2-dithiaborolane (**5f**; 83%) and tris(1-ethyl-(*Z*)-1-butenyl)borane (**10**; 17%). Various changes in the conditions of reaction did not alter the composition significantly, and neither molecular distillation at 80 °C and 0.4 Torr nor preparative vapor-phase chromatography on Apiezon L cleanly separated the components. A sample of compound **10** was prepared independently by the reaction of a solution of tetrahydrofuran–borane in tetrahydrofuran (4.0 mL, 0.25 M, 1.0 mmol) with 3-hexyne (259 mg, 3.15 mmol) at 25 °C under dry N_2 for 24 h. Removal of volatile materials by evaporation in vacuo left a colorless, liquid residue of tris(1-ethyl-(*Z*)-1-butenyl)borane (**10**; 208 mg, 0.80 mmol, 80%): IR (liquid film) 2940, 2850, 1590 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.00 (t, 18 H, J = 7 Hz), 2.2 (m, 12 H), 5.70 (t, 3 H, J = 7 Hz); MS *m/e* 260.[17] The chromatographic behavior and spectroscopic properties of this sample could not be distinguished from those of the minor component of the mixture and were similar to those of the major product **5f**: IR (liquid film) 2940, 2850, 1605, 895, 840; ^1H NMR (60 MHz, $CDCl_3$) δ 1.00 (t, 6 H, J = 7 Hz), 2.2 (m, 4 H), 3.27 (s, 4 H), 6.37 (t, 1 H, J = 7 Hz); MS *m/e* 186 (95), 158 (45), 157 (51), 144 (97), 143 (39), 129 (32), 116 (44), 84 (31), 81 (36), 76 (31), 69 (47), 67 (40), 61 (100), 60 (100), 59 (84), 58 (38), 55 (94). The *Z* configuration has been assigned to compound **5f** since addition of 1,3,2-dithiaborolane to 1-hexyne is stereospecifically cis.

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Registry No.—**3**, 6675-41-4; **5a**, 63076-46-0; **5b**, 63076-47-1; **5c**, 63076-48-2; **5d**, 63076-49-3; **5e**, 63076-50-6; **5f**, 63104-21-2; **6**, 13291-21-9; **9b**, 63076-51,7; **10**, 63076-52-8; trimethylamine, 75-50-3; 1-decene, 872-05-9; cyclopentene, 142-29-0; bicyclo[2.2.1]hept-2-ene, 498-66-8; 2-methyl-2-butene, 513-35-9; 3-hexyne, 928-49-4; 1-hexyne, 693-02-7.

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Coupling Reactions of Diorganophosphides with Organic Halides. Evidence for a One-Electron Path

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The reactions of diorganophosphides with organic halides have been examined by ^{31}P CIDNP and product analysis. These reactions are shown to proceed in part by a radical mechanism and in part by a competing nonradical path. The preference for one mechanism or the other is highly dependent on the nature of the organic group, halide, and substituents bound to phosphorus. Thus, alkyl, allyl, and benzyl iodides and bromides react, to some degree, by a radical mechanism; alkyl chlorides follow an apparent S_N2 path. There is no evidence for radical participation in the reactions of dialkylphosphides with aryl halides or of diarylphosphides with alkyl halides. For those examples proceeding by a radical mechanism, the CIDNP data are consistent with an electron-transfer step, followed by coupling of the dialkylphosphinyl and organic radicals.

Diorganophosphide anions are useful precursors for the synthesis of *tertiary*[1] and polydentate phosphines.[1a,b,d,2] Their utility arises, in part, from their ready availability and because coupling reactions with organic halides generally proceed in high yields and tolerate substantial variation of phosphide or substrate.[1,2] To the inorganic chemist the primary asset of procedures employing these reagents is the ability to design ligands with specific electronic and steric properties or containing a functionality as a probe for ligand–metal interactions. Organophosphide ions are generally regarded as potent nucleophiles[1-4] and coupling reactions have long been assumed to proceed by an S_N2 mechanism with metal–halogen exchange as a competing or, in some cases, dominant factor.[1a,b,d,5]

In the course of preparing cyclopropylmethyldimethylphosphine from bromomethylcyclopropane and potassium dimethylphosphide, we noted the anticipated product was formed together with a comparable amount of 3-butenyldimethylphosphine. Inasmuch as this result suggested a predominant radical path, we were prompted to undertake a mechanistic study to determine whether one-electron steps were involved in these couplings and, if so, whether conditions could be found to enhance the S_N2 component. We report herein CIDNP and product distribution evidence that alkyl, allylic, and benzylic halides do, in fact, react with diorganophosphides via a mechanism involving substantial radical participation, the degree of which is highly sensitive to the nature of the phosphide, substrate, and halide employed.

Experimental Section

All manipulations and reactions were performed in an atmosphere of nitrogen. Solvents were distilled from sodium benzophenone ketyl before use. Benzene-d_6 and 1,2-dimethoxyethane-d_{10} were dried over calcium hydride and distilled in vacuo prior to use in NMR experiments.

1-Bromo-5-hexene was obtained from Tridom-Fluka and 1-chloro-5-hexene from ICN. Bromomethylcyclopropane was prepared by the literature method.[6] All other halides were readily obtainable from a number of common sources. Potassium diphenylphosphide,[7] *lithium dimethylphosphide*,[8] and *sodium dimethylphosphide*[8] were prepared by the literature procedures. ^{31}P and ^{1}H NMR experiments were performed on a Varian XL-100 spectrometer. Analysis of organophosphide/organic halide reactions was performed utilizing a Data General Nova 2 computer hardwired to an AEI MS 1073 dual-beam mass spectrometer/gas chromatograph. Mass spectra of isolated phosphines were obtained on an AEI MS-9 spectrometer. Product distribution analyses for the bromomethylcyclopropane and 1-halo-5-hexene reactions were performed on an F & M 720 gas chromatograph with a ¼ in. × 8 ft, 3.8% SE-52 column. Response factors were determined for each of the products using *n*-decane or *n*-undecane as internal standards. Analyses were performed by adding a stoichiometric amount of organic halide to a 2-mL volumetric flask capped with a septum and containing a known amount of organophosphide in THF. GLC measurements were initiated immediately after adding the internal standard and diluting to the mark. Representative preparative scale reactions are given below.

Potassium Dimethylphosphide. Following a modification of the preparation of sodium dimethylphosphide,[8] 5.7 g of tetramethylbiphosphine[2i] (47 mmol) and 6.6 g of potassium (0.17 g-atom) in 150 mL of THF were stirred for 10 h under reflux to produce a deep red solution. After cooling and filtration through Celite, the volume was