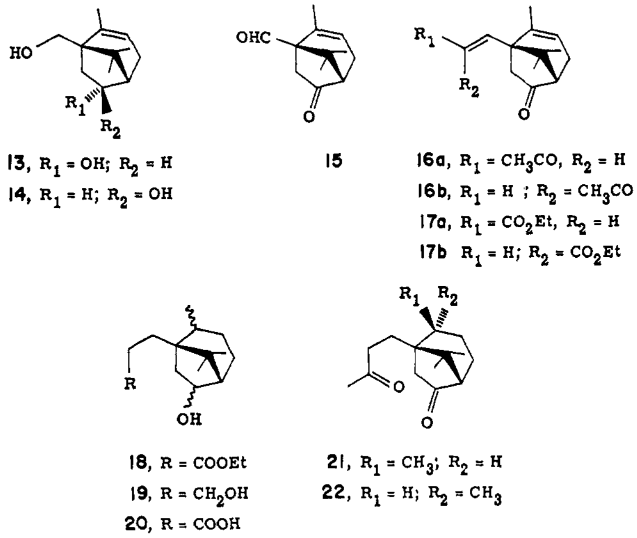
boron trifluoride etherate (2% in 1,2-dichloroethane, 85 min)[17] on **8**.

Lithium aluminum hydride reduction of the keto ester **6** in ether solution provided an inseparable mixture of the epimeric alcohols **13** and **14** (82% yield) in a ratio of 55:45[18] (Chart II). Oxidation of this mixture with dipyridinechromium trioxide in methylene chloride[19] rendered the aldehyde **15** as colorless plates, mp 120° (dec) after sublimation (69% yield). Attempts to condense **15** with acetone or with sodium diethylphosphonoacetonate over extended periods failed to provide even traces of the desired diketones **16a** or **16b**. However, the condensation of **15** with 1 equiv of sodium triethylphosphonoacetate, using essentially a procedure described by Wadsworth and Emmons[20] (benzene solvent, 4-hr reflux) led to a mixture of the *E* and *Z* unsaturated esters **17a** and **17b** (52% yield), which was easily resolved by preparative gas chromatography (ratio **17a**:**17b** = 10:1 to 14:1). A side product was the ketone **9** (2%) which probably was formed by thermal homolytic decarbonylation of **15**. Hydrogenation of an ethanol solution of a 10:1 mixture of **17a** and **17b** in the presence of W-5 Raney nickel[21] produced a mixture of epimeric hydroxy esters **18** (50–93%)[22] and diols **19** (5–40%).[22] The free acids **20** were separated readily from the diols **19** after saponification of the esters **18** with 10% methanolic potassium hydroxide. Treatment of **20** with 3 molar equiv of ethereal methyllithium at 26–27° for 16 hr provided a mixture of epimeric ketols which were converted directly to the diketones **21** and **22** (43% yield; ratio **21**:**22** = 9:1) on treatment with standard chromate solution in acetone.[23] The epimer **21** was crystallized from petroleum ether as colorless plates, mp 62–63.5°, while the epimer **22** was obtained only as an oil by adsorption chromatography on silica gel. The epimer **21** was cyclized to epipatchoulenone (**2b**) in 92% yield by the action of potassium *tert*-butoxide in *tert*-butyl alcohol (26–27°, 30 min). The ketone **2b** was recrystallized from petroleum ether as colorless plates, mp 75.5–77.5° [ir (CCl_4) 1713, 1668 cm^{-1}; nmr ($CDCl_3$) τ 8.03 (broad s), 8.84 (d, J = 6.5 Hz), 8.88 (s); mass spectrum (70 eV) base and parent ion peak, *m/e* 218].

Chart II



13, R_1 = OH; R_2 = H
14, R_1 = H; R_2 = OH
15
16a, R_1 = CH_3CO, R_2 = H
16b, R_1 = H ; R_2 = CH_3CO
17a, R_1 = CO_2Et, R_2 = H
17b R_1 = H; R_2 = CO_2Et
18, R = COOEt
19, R = CH_2OH
20, R = COOH
21, R_1 = CH_3; R_2 = H
22, R_1 = H; R_2 = CH_3

Similar treatment of **22** with potassium *tert*-butoxide afforded *dl*-patchoulenone (**2a**) (colorless plates, mp 37–38°) in 70% yield. The infrared and nmr spectra of our specimen of *dl*-**2a** were identical in all major respects with the infrared[24,25] and nmr[25] spectra of natural patchoulenone. The high-resolution mass spectrum showed a parent ion peak of *m/e* 218 and a base peak of *m/e* 91.

Acknowledgments. We gratefully acknowledge Professor William von E. Doering for his vital suggestion to attempt the acid-catalyzed transformation of **4** to **6** and fruitful discussions with Professors Ernest Wenkert and E. C. Taylor.

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(17) These and related studies of the addition of diazo ketones to olefins and the mechanism of product formation will be discussed elsewhere.

(18) Determined from the nmr spectrum.

(19) According to the procedure of J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

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(21) H. R. Billica and H. Adkins, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 176.

(22) The relative yields of hydroxy esters and diols varied with the period of storage of the W-5 Raney nickel.

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(24) Kindly sent to us by Professor Hiroshi Hikino, Pharmaceutical Institute, School of Medicine, Tohoku University, Sendai, Japan.

(25) B. Trivedi, O. Motl, V. Herout, and F. Sorm, *Collect. Czech. Chem. Commun.*, **29**, 1675 (1964).

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(S–B) 3-(Methylthio)propylborane, a Distillable Monoalkylborane

Sir:

Although a number of disubstituted derivatives of borane are well known, stable uncomplexed monomeric monosubstituted derivatives of borane are almost unknown. The only well-documented example is dimethylstibinoborane.[1] Brown has reported the preparation of monoalkylboranes with bulky alkyl groups, but these are actually dialkyldiboranes even in basic ethers and are not distillable without disproportionation and pyrolysis. He suggested their utility in synthesis, but no application was reported.[2a] Hawthorne demonstrated that a monoalkylborane complex (trimethylamine-*tert*-butylborane)[3a] is useful in preparing heterocyclic boron compounds from doubly unsaturated substances such as divinyl ether. However, the preparation of this complex is an involved multistep process,[3b,4] and elevated temperatures are required for its use in hydroborations. We had previously prepared an internally coordinated alkylborane (3-di-

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(1) A. B. Burg and L. R. Grant, *J. Amer. Chem. Soc.*, **81**, 1 (1959).

(2) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962: (a) Chapter 11; (b) p 64; (c) Chapter 12.

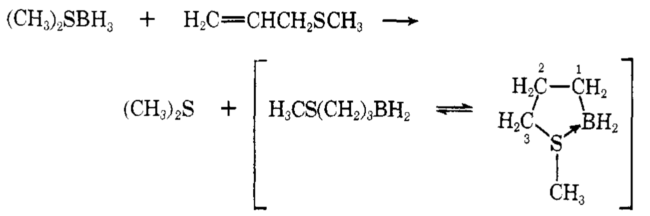
(3) (a) M. F. Hawthorne, *J. Amer. Chem. Soc.*, **83**, 2541 (1961); (b) *ibid.*, **81**, 5836 (1959).

(4) P. M. McCusker, E. C. Ashby, and H. S. Makowski, *ibid.*, **79**, 5179 (1957).

methylaminopropylborane)[5] but the product is too strongly coordinated for convenient hydroboration.

Brown also reported the hydroboration of allyl methyl sulfide with borane in diglyme in a 3:1 ratio followed by protonolysis with propionic acid to yield methyl *n*-propyl sulfide,[2b] but did not isolate any immediate hydroboration product.

We have prepared 3-(methylthio)propylborane (I) by the reaction of dimethyl sulfide–borane[6] with a small excess of allyl methyl sulfide dissolved in benzene.



I

The stability and distillable character of I are doubtless due to coordinate bonding of the sulfur to boron. However, the hydridic hydrogens are sufficiently reactive for hydroboration of carbon–carbon and carbon–nitrogen multiple bonds and reaction with alcohols.

A yield of 27 g (71% theory) was obtained from the reaction of 39 ml (0.374 mol) of dimethyl sulfide–borane added dropwise to 50 ml (0.489 mol) of allyl methyl sulfide in 100 ml of benzene, keeping the temperature below 30°. After stirring overnight, the benzene and excess reactants were distilled off (1 atm), and the product was isolated by distillation through a Vigreaux column at 44° and 1 Torr. *Anal.* Calcd for BC_4H_7S: B, 10.78; C, 47.06; H, 10.78; hydridic H, 1.96; S, 31.37. Found: B, 10.9; C, 46.8; H, 10.82; hydridic H, 1.99; S, 31.07; mol wt (freezing point depression in benzene), 98; FW, 102; density, 0.932 g/ml; refractive index, 1.5005 at 25° (leading to an atomic refractivity of 2.4 for quaternary boron, in good agreement with the value obtained with a similar nitrogen compound).[5] The infrared spectrum had a BH stretching band at 2380 cm^{-1} with a shoulder at 2360 cm^{-1}, indicating the presence of a BH_2 group. Absence of absorption in the 1500–2100-cm^{-1} region indicated absence of bridging hydrogen.[2c] The ^1H nmr spectrum of the neat liquid showed a high-field triplet at δ 0.78 which we attributed to the C-1 methylene protons, a singlet at δ 2.07 superimposed on a pentet at δ 1.90 attributed to the methyl and C-2 methylene protons, respectively, and a triplet at δ 2.33 attributed to the C-3 methylene protons. Integration of the areas corresponded to this assignment; J_{HH} = 6 Hz. Quadrupole relaxation of the boron atom minimizes the signal from hydrogen on boron and prevents appreciable coupling to the C-1 methylene protons.

When I was left in the atmosphere, a white solid was slowly formed, presumably dihydroxy(3-methylthiopropyl)borane. This melted at 48–50°. Its infrared

$$RBH_2 + 2HOH \longrightarrow RB(OH)_2 + 2H_2$$

spectrum showed no BH. Its nmr spectrum in acetone was similar to that of I, with a high-field triplet at δ 0.62, a mid-field quintet at δ 1.50, a singlet at δ 1.88, and a triplet at δ 2.67.

The utility of I as an alkyl hydroborating agent was investigated on a millimolar scale by a procedure parallel to that of Brown and Subba Rao.[7] A solution of I (2.0 mmol) in 10 ml of benzene was allowed to react with the organic compound for 30 min. The reaction was then quenched with 1 ml of methanol. In a blank run, 4.0 mmol of hydrogen was evolved.

$$RBH_2 + 2CH_3OH \longrightarrow RB(OCH_3)_2 + 2H_2$$

After use of 4 mmol of cyclohexene as the organic substrate, 2 mmol of hydrogen was evolved upon addition of methanol, indicating steric hindrance to reaction of the second equivalent of cyclohexene. With borane, only 2 equiv of cyclohexene react.[2c]

After reaction with 2.0 mmol of butenenitrile, no hydrogen was evolved upon addition of methanol. Evidently both the C=C and C≡N bonds consumed hydridic hydrogen.

During reaction with 2.0 mmol of 3-butyn-1-ol, 1.84 mmol of hydrogen was evolved. None was evolved during the addition of methanol, indicating that both the hydroxyl and C≡C groups had reacted with the borane.

Acknowledgments. We thank Mr. W. V. Hough of Callery Chemical Co. for providing the dimethyl sulfide–borane and Mr. A. E. Weber for the boron and hydridic hydrogen analysis of I. Other analyses were by Galbraith Laboratories. This work was sponsored by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-872-65.

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[7] H. C. Brown and B. C. Subba Rao, *ibid.*, **22**, 1135 (1957).

Direct Observation of the Addition Products of the Reaction of Borane with Diborane and of the Reaction of Borane with Pentaborane(9)[1]

Sir:

The unstable species borane, BH_3, has long been postulated as an active intermediate in the reactions of boron hydrides; consequently, its reactions are of great interest. We have recently developed a fast-flow system with mass spectrometric analysis that has allowed the preparation of kinetically useful quantities of BH_3, and thus have been able to directly observe the reactions of BH_3.[2] This system has been used to study the self-association of borane to form diborane,[3] the reaction of borane with electron-pair

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[1] Supported by the National Science Foundation under Grant No. GP 10199.

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