basic alumina for 16 hr led in high yield to **2** (mp 158–161°), identical with authentic **2** (mp 157–160°). Finally, reduction of **2** with an excess of lithium aluminum hydride in ether at −65° for 90 min[22] afforded 50% of **1** (mp 238–241°), identical with natural bufalin (mp 239–242°).

Acknowledgments. We are indebted to the Koninklijke Nederlansche Gist-en Spritusfabriek N.V. (Delft) for a generous supply of **4**, and to Professors K. Meyer (Basel), G. R. Pettit (Tempe), and T. Reichstein (Basel) for kindly providing samples of natural bufadienolides. We also thank Dr. J. Mathieu (Romainville) for valuable correspondence.

[22] See H. Kondo and S. Ohno, U. S. Patent 3,134,772 (*Chem. Abstr.*, **61**, 5736*f* (1964)).

[23] Author to whom inquiries may be addressed at the Chemistry Department, University College, London, W.C.1, England.

[24] Honorary NATO Fellow, 1964–1965; Imperial Chemical Industries Fellow, 1964–1966.

[25] Science Research Council Postdoctoral Fellow, 1966–1968.

F. Sondheimer,[23] W. McCrae,[24] W. G. Salmond[25]
University Chemical Laboratory
Cambridge, England
Received December 23, 1968

The Preparation of 2-Methoxypentaborane(9), a Novel Example of an Alkoxy Polyborane

Sir:

We have recently found that 1-iodopentaborane(9), $1\text{-IB}_5\text{H}_8$, reacts with dimethyl ether to produce 2-methoxypentaborane(9), $2\text{-(CH}_3\text{O)B}_5\text{H}_8$, in moderate yield. The only other examples of neutral alkoxypolyboranes have the general formula $\text{ROB}_{10}\text{H}_{13}$ and are prepared by a complex reaction between $\text{NaB}_{10}\text{H}_{13}$ and a solution of I_2 in various ethers.[1] The position of attachment of the alkoxy group is not known, but has been discussed.[2] A previous study of the reaction of $1\text{-BrB}_5\text{H}_8$ with dimethyl ether resulted in the preparation of $2\text{-BrB}_5\text{H}_8$ and $1\text{-CH}_3\text{B}_5\text{H}_8$, but no tractable alkoxy derivatives of B_5H_9 were observed.[3]

In a typical preparation of $2\text{-(CH}_3\text{O)B}_5\text{H}_8$, 1.317 g (6.97 mmoles) of $1\text{-IB}_5\text{H}_8$ was allowed to react with 20.7 mmoles of liquid $\text{(CH}_3)_2\text{O}$ for 15 hr at −12°. High-vacuum fractional distillation of the pale yellow reaction mixture yielded 0.161 g (1.73 mmoles, 25%) of $2\text{-(CH}_3\text{O)B}_5\text{H}_8$. There was 4.9 mmoles of $\text{(CH}_3)_2\text{O}$ consumed. Substantial quantities of B_5H_9, $\text{B(OCH}_3)_3$, and CH_3I, a relatively small amount of $\text{HB(OCH}_3)_2$, and traces of H_2 were also produced in the reaction. A side product of low volatility has prevented quantitative estimation of the $1\text{-IB}_5\text{H}_8$ recovered from the reaction.

This new B_5H_9 derivative is a colorless liquid which freezes as a glass at −196°. Upon warming the glass begins to flow and then crystallizes. The melting point is in the vicinity of −100°. Representative vapor pressures are 4.4 ± 0.2 mm at 0° and 15.5 ± 0.2 mm at 20°. Moderately rapid decomposition occurs in the liquid phase such that the vapor pressures are of qualitative value only. In the gas phase at low pressure (~7 mm) no decomposition can be observed after 12 hr at ambient temperature (infrared).

The mass spectrum of $2\text{-MeOB}_5\text{H}_8$, obtained using AEI MS-9 and CEC 21-103 spectrometers, is consistent with that expected for an alkoxypentaborane(9). The cutoff at *m/e* 94 corresponds to the parent ion $^{12}\text{CH}_3{}^{16}\text{O}^{11}\text{B}_5\text{H}_8{}^+$: calcd *m/e* 94.12754; found 94.12751 ± 0.00010 (estimated error range). The most intense peak in the spectrum at *m/e* 43 corresponds to $^{12}\text{CH}_3{}^{16}\text{O}^{11}\text{BH}^+$; calcd *m/e* 43.03552; found 43.03549 ± 0.00010.

The ^{11}B nmr spectrum of $2\text{-(CH}_3\text{O)B}_5\text{H}_8$ (at 32.1 MHz) is very similar in appearance to that of $2\text{-FB}_5\text{H}_8$.[4] The chemical shifts (δ in parts per million from $\text{BF}_3\text{O(C}_2\text{H}_5)_2$ ± 0.2), coupling constants (*J* in Hz ± 5), and relative areas are given in Table I. The extreme separation between the B(2) and B(4) resonances suggests that $2\text{-(CH}_3\text{O)B}_5\text{H}_8$ is more closely related, electronically, to $2\text{-FB}_5\text{H}_8$ than to any other known B(2)-substituted B_5H_9 derivative.

Table I

	δ	*J*	Area (rel)
B(2)-OCH_3	−14.1		1.00
B(3, 5)-H	+16.8	158	1.99
B(4)-H	+31.5	160	0.99
B(1)-H	+55.0	170	1.04

The ^1H nmr spectra of $2\text{-(CH}_3\text{O)B}_5\text{H}_8$ (at 60 and 100 MHz) show the presence of two bridge hydrogen regions, as does the spectrum of $2\text{-FB}_5\text{H}_8$.[4] Overlap of other areas of the spectra makes assignments for $\text{H-B}_{3,5}$, H-B_4, and H-B_1 ambiguous, but the general appearance is similar to that of $2\text{-FB}_5\text{H}_8$. The methoxy resonance of $2\text{-(CH}_3\text{O)B}_5\text{H}_8$ at −3.56 ppm is substantially shifted from that of $\text{(MeO)}_3\text{B}$ at −3.09 ppm.

The gas-phase infrared spectrum of $2\text{-(CH}_3\text{O)B}_5\text{H}_8$ contains major bands (cm^{-1} ± 10) at 3005 (w), 2960 (w), 2870 (w), 2600 (s), 1985 (w, br), 1850 (w, br), 1475 (m), 1315 (s, br), 1005 (m), 950 (w), 875 (m), 825 (w). The two broad bands at 1985 and 1850 cm^{-1} are tentatively attributed to the two types of bridge hydrogens indicated in the ^1H nmr spectra. The band at 1475 cm^{-1} is attributed to the methoxy methyl deformation, and the band at 1005 cm^{-1} is probably due to a C–O stretch.

Boron trichloride reacts with $2\text{-(CH}_3\text{O)B}_5\text{H}_8$ to form what appears to be a 1:1 complex. Solutions of the complex in CS_2 and BCl_3 exhibit ^{11}B nmr spectra similar to those expected for a mixture of $2\text{-ClB}_5\text{H}_8$ and ROBCl_2 (which appears to undergo rapid exchange with excess BCl_3). Subsequent isolation of $2\text{-ClB}_5\text{H}_8$, however, is not possible unless the mixture is heated to ~50°. Further studies of this behavior are in progress.

Acknowledgments. Support of this research by the National Science Foundation is gratefully acknowledged. We wish to thank Bill Stebbings for the exact *m/e* mass spectral determinations.

---

[1] M. F. Hawthorne and J. J. Miller, *J. Am. Chem. Soc.*, **82**, 500 (1960).

[2] R. E. Williams, *Inorg. Chem.*, **4**, 1504 (1965).

[3] A. B. Burg and J. S. Sandhu, *J. Am. Chem. Soc.*, **87**, 3787 (1965).

[4] A. B. Burg, *ibid.*, **90**, 1407 (1968).

Donald F. Gaines
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706
Received November 30, 1968