

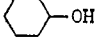

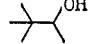
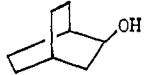
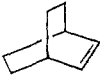


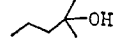
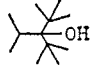

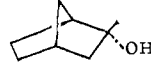
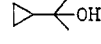

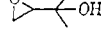



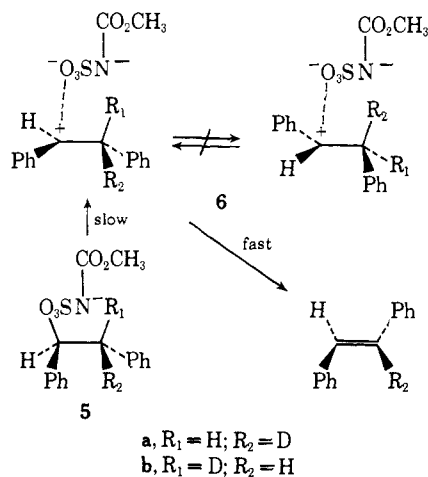


Table I. Fragmentation of *sec*- and *tert*-ROSO<sub>2</sub>N<sup>-</sup>CO<sub>2</sub>CH<sub>3</sub>X<sup>+</sup>

Precursor	Product(s) <sup>a</sup> (ratio) <sup>b</sup>	Temp, °C
		40 <sup>c,e</sup>
		50 <sup>d,f</sup>
		60 <sup>d,g</sup>
	(1) (3) (1.5)	70 <sup>d,h</sup>
		60 <sup>c,g</sup>
		30 <sup>c,e</sup>
		30 <sup>c,e</sup>
		50 <sup>c,i</sup>
		30 <sup>c,g</sup>
		30 <sup>c,e</sup>
		55 <sup>c,e</sup>

<sup>a</sup> Isolated in 70–90% yield and characterized by comparison with authentic samples or by nuclear magnetic resonance and mass spectroscopy. <sup>b</sup> Determined by gas chromatography. <sup>c</sup> Triethylammonium counterion. <sup>d</sup> Sodium counterion. <sup>e</sup> Neat. <sup>f</sup> Tetrahydrofuran. <sup>g</sup> Benzene. <sup>h</sup> Triglyme. <sup>i</sup> Acetonitrile.

the rotational interconversion of the erythro- and threo-derived ion pairs (**6a,b**). The observed stereospecificity remains invariant in dimethylformamide

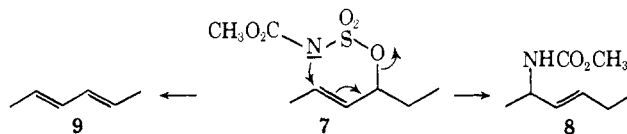


solution and indicates the higher basicity of this gegenion compared with the structurally related tosylate ion in polar solvents.<sup>6</sup> This singular characteristic should contribute to the synthetic potential of this leaving group in elimination reactions in a wide variety of systems.

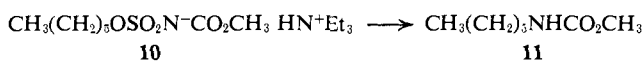
(5) Although proton transfer to nitrogen of the gegenion is possible the involvement of oxygen may be favored thermodynamically and statistically. A referee has suggested that in the case studied proton transfer from the triethylammonium cation to the departing anion resulting in the formation of a simple ion pair may be involved in the slow step.

(6) The correlation of solvent basicity with the alteration of stereochemistry in E<sub>1</sub> reactions of tosylates has been reported: P. S. Skell and W. L. Hall, *J. Amer. Chem. Soc.*, **85**, 2851 (1963).

When the reaction is applied to an allylic alcohol either elimination or an S<sub>N</sub>i' rearrangement ensues depending on the experimental conditions. For example, the thermal decomposition (80°) of sodium 4-hex-2-enyl *N*-carbomethoxysulfamate (**7**) as a solid provides after protonation >90% yield of the rearranged urethane, **8**, while the diene **9** is obtained in 70% yield from reaction in triglyme solution.



With primary alkyl *N*-carbomethoxysulfamate salts the S<sub>N</sub>2 (or S<sub>N</sub>i) pathway becomes more important providing an expedient synthetic route for the conversion of primary alcohols to urethanes (or further to primary amines).<sup>1,7</sup> Illustrative in this case is triethylammonium *n*-hexyl-*N*-carbomethoxysulfamate (**10**) which heated to 95° provides >90% yield of the urethane (**11**).



We are continuing to explore the synthetic application of this new leaving group.

**Acknowledgments.** We sincerely wish to thank the National Institutes of Health for a research grant (GM-

(7) Analogous conversions of methyl, ethyl, and benzyl *N,N*-dialkylsulfamates have been reported: W. Traube, H. Zander, and H. Gaffron, *Ber.*, **57**, 1045 (1924).

12672) and the National Science Foundation for an undergraduate research fellowship (to H. R. P.).

\* To whom correspondence should be addressed.

Edward M. Burgess,\* Harold R. Penton, Jr., E. A. Taylor  
Georgia Institute of Technology, School of Chemistry  
Atlanta, Georgia 30332  
Received April 27, 1970

### Preparation of the Pentagonal Pyramidal Carborane, 2,3,4,5-Tetracarba-nido-hexaborane(6)

Sir:

We wish to report the synthesis of 2,3,4,5-tetracarba-nido-hexaborane(6), I (Figure 1), from 1,2-tetramethylenediborane(6). The conversion was accomplished at 550° using a high-vacuum system which permits a rapid flow of gaseous reactant<sup>1,2</sup> through the hot zone at low pressures. In addition to the carborane, C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>, in low yield, a number of other carboranes are also produced. The experimental details of this reaction and the nature of the side products will appear in a longer dissertation at a later date.

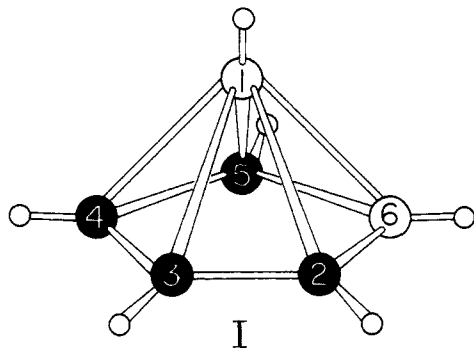


Figure 1. Ball and stick model of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>.

The evidence used to establish the formula and structure of this parent four-carbon two-boron carborane is outlined.

(a) The mass spectrum of the product purified by repeated vacuum fractional distillation exhibits a sharp cutoff at  $m/e$  76 (calcd for <sup>12</sup>C<sub>4</sub><sup>11</sup>B<sub>2</sub>H<sub>6</sub>). When the parent envelope of peaks of the polyisotopic spectrum is subjected to a monoisotopic boron analysis a good fit is found for a compound consisting of two boron atoms.

(b) The <sup>11</sup>B nmr at 32.1 MHz exhibits two sharp doublets in an area ratio of 1:1 with chemical shifts (parts per million relative to boron trifluoride ethyl etherate) and coupling constants of +60.8 ppm (202 Hz) and -10.4 ppm (144 Hz). This is consistent with two B-H groups, with the high-field doublet assigned to one of these groups in an apical environment of a pyramid and the low-field doublet assigned to a basal position.<sup>3</sup>

(c) The proton nmr taken at both 100 and 220 MHz consist of two slightly broadened singlet resonances at

(1) H. G. Weiss, W. J. Lehmann, and I. Shapiro, *J. Amer. Chem. Soc.*, **84**, 3840 (1962).

(2) H. H. Lindner and T. Onak, *ibid.*, **88**, 1886 (1966).

(3) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

(relative to  $\tau$  10.00 ppm for TMS)  $\tau$  5.38 and 4.24 ppm of equal area which are assigned to the two different kinds of carbon-attached hydrogens of I, and also two equal-area 1:1:1:1 quartets at 6.08 ( $J = 141$  Hz) and 10.59 ppm ( $J = 205$  Hz) which are assigned to H-<sup>11</sup>B(6) and H-<sup>11</sup>B(1), respectively.<sup>4</sup> The area of each quartet is almost one-half of the area of each H-C singlet. The chemical shifts of all of the protons are reasonably within the range of values found for other pyramidal systems containing a different number of carbon and boron atoms in the series C<sub>*n*</sub>B<sub>6-*n*</sub>H<sub>10-*n*</sub> (*i.e.*,  $n = 0-3$ ).<sup>3</sup>

(d) The most informative portions of the infrared spectrum are consistent with the assigned structure, *i.e.*, bands at 2950 (C-H) and 2570 cm<sup>-1</sup> (B-H) and an absence of peaks in the B-H-B bridge regions.

In the pentagonal-pyramidal series of isoelectronic compounds C<sub>*n*</sub>B<sub>6-*n*</sub>H<sub>10-*n*</sub>, the parent and/or monomethyl derivatives of those with  $n = 0, 1, 2$ , or 3 have been previously prepared and reasonably well structurally characterized. The present work adds to the parent compounds in the series a compound in which  $n = 4$ . It should be pointed out, however, that the permethyl<sup>5</sup> and perphenyl<sup>6</sup> derivatives of C<sub>4</sub>B<sub>2</sub>H<sub>6</sub> have been previously reported and the structures tentatively, but inconclusively, assigned. The data we present, however, leave little doubt about the identification and structural characterization of the parent C<sub>4</sub>B<sub>2</sub>H<sub>6</sub>.

**Acknowledgment.** This project was supported, in part, by the Office of Naval Research. The Varian HA-100 nmr spectrometer was obtained through Grant No. GP-8347 from the National Science Foundation and the HR-220 at the California Institute of Technology was available through NSF Grant No. GP-8540.

(4) Smaller septets within each quartet are partially visible and are attributed to H-<sup>10</sup>B contributions.

(5) P. Binger, *Tetrahedron Lett.*, 2675 (1966).

(6) F. Joy, M. F. Lappert, and B. Prokai, *J. Organometal. Chem.*, **5**, 506 (1966); M. F. Lappert, "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 455.

(7) Address correspondence to this author.

Thomas P. Onak,<sup>7</sup> George T. F. Wong

Department of Chemistry, California State College  
Los Angeles, California 90032

Received June 4, 1970

### Solubilization of Alkali Metals in Tetrahydrofuran and Diethyl Ether by Use of a Cyclic Polyether

Sir:

We wish to report a new technique for dissolving alkali metals in solvents in which they are ordinarily either insoluble or only slightly soluble. This method may extend the range of solvents in which the properties of relatively stable solutions of solvated electrons and other species common to metal-amine solutions<sup>1,2</sup> can be studied. Of particular interest would be the ability to make extended comparisons with the properties of solvated electrons produced by pulse radiolysis.

The basis for this increased solubility is the ability of certain cyclic polyethers to complex alkali metal cations.<sup>3,4</sup> Noting that stabilization of the cations

(1) R. R. Dewald and J. L. Dye, *J. Phys. Chem.*, **68**, 121 (1964).

(2) M. Ottolenghi, K. Bar-Eli, and H. Linschitz, *J. Chem. Phys.*, **43**, 206 (1965).

(3) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

(4) C. J. Pedersen, *ibid.*, **92**, 386 (1970).