the pH range 6 ≤ pH ≤ 9, the difference in the water ^{17}O line widths of the two solutions is ~4 Hz, indicating that there is, at most, only a weak second coordination sphere interaction between H_2O and Ni–EDTA. Below pH 6 there is little change (<10%) in the width of the ^{17}O resonance of the Mg–EDTA solution but the ^{17}O line width of the Ni–EDTA solution increases to 350 Hz at pH 2. If the pH dependence of the ^{17}O relaxation is treated in terms of the formation of **1b**, then a p*K* value of 3.05 is obtained for reaction 1.[15] Although the ^{13}C shift data are not inconsistent with structure **1c**, the ^{17}O relaxation rates in the pH range 6–9 rule out a strong first coordination sphere interaction between Ni(II) and H_2O.

The protonation of **1a** is also accompanied by changes in the electronic absorption spectrum. Bhat and Krishnamurthy[7] used dilute solutions ($[Ni^{2+}] = 10^{-3}$–10^{-2} *M* and ionic strength $\mu = 1$) and obtained p*K* values of 2.73 and 3.12 for the protonation of Ni–EDTA from changes in the electronic spectrum at 980 and 380 nm, respectively. In our analysis of the pH dependence of the electronic spectra of 0.2 *M* ($\mu \cong 1$) and 0.5 *M* ($\mu \cong 2.5$) Ni–EDTA solutions, we obtain $pK = 3.1 \pm 0.05$ for both solutions at 985 and 785 nm.

In contrast to the solution behavior of the Ni–EDTA complex, ^{13}C and ^{17}O nmr studies in progress indicate that the Fe^{III}–EDTA complex is seven-coordinate in solution (has structure **1c**) and that, if the Co^{II}–EDTA complex has structure **1a**, it is stereochemically nonrigid.

Acknowledgments. We are indebted to Dr. B. B. McInteer and Mr. R. M. Potter of the Los Alamos Scientific Laboratory (LASL) for supplying the enriched ^{13}C and to Dr. D. G. Ott and Mr. Arthur Murray, also of LASL, for preparing the ^{13}C-enriched EDTA.

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[15] No ^{17}O contact shifts were observed for these solutions at 32° in the pH range 2–6, indicating that the rate of $^{17}OH_2$ exchange from the Ni(II) coordination sphere of **1b** is much smaller than the ^{17}O shift. At temperatures above 90°, a large ^{17}O shift is observable, consistent with the entry of the ^{17}O relaxation rate into the region of rapid H_2O exchange. Similar observations have been made for the relaxation and chemical shift of $^{17}OH_2$ by the $Ni(OH_2)_6^{2+}$ ion.[16]

[16] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

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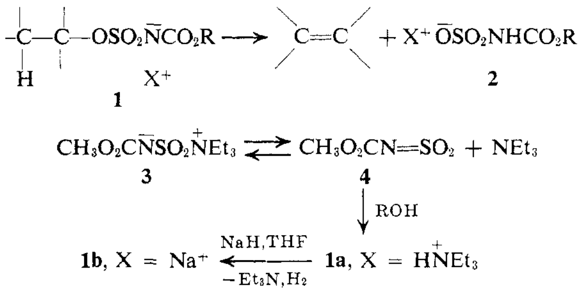
Synthetic Applications of *N*-Carboalkoxysulfamate Esters

Sir:

We have found a synthetically useful and facile method for the mild dehydration of secondary and tertiary alcohols to the corresponding olefins which employs an alcohol-derived new leaving group, trialkylammonium or sodium *N*-carboalkoxysulfamates (**1a,b**). Despite the charge initially associated with this leaving group, such derivatives appear to ionize at low temperatures in nonpolar solvents to provide tight ion pairs which undergo fast stereospecific proton transfer to give high yields of olefins and the corresponding salt of *N*-carboalkoxysulfamic acid (**2**). Similar studies with primary alcohols indicate that thermolysis of such derivatives provides urethanes in high yield by an SN2 (or SNi) pathway.[1]



$$-C-C-OSO_2\bar{N}CO_2R \longrightarrow C{=}C + X^+\,\bar{O}SO_2NHCO_2R$$

$$CH_3O_2C\bar{N}SO_2\overset{+}{N}Et_3 \rightleftharpoons CH_3O_2CN{=}SO_2 + NEt_3$$

The triethylammonium *N*-carbomethoxysulfamates employed in this investigation were prepared by the interaction of the alcohol and the readily available methyl(carboxysulfamoyl)triethylammonium hydroxide inner salt (**3**) neat or in hydrocarbon solution at 30° or below. The electrophilic species responsible for the observed exothermic reaction even in the case of hindered tertiary alcohols may be methyl *N*-sulfonylcarbamate (**4**).[2]

The *tert*-alkyl sulfamate esters and their salts are sufficiently liable at room temperature as to preclude isolation and characterization. In many cases it was found to be operationally convenient to exchange the triethylammonium for a sodium cation in the more stable primary or secondary sulfamate ester salts and this could be readily accomplished by treatment of **1a** with sodium hydride in THF at 30°. Table I summarizes the results of our product investigation on the thermal decomposition of these *sec*- and *tert*-*N*-carbomethoxysulfamate salts.

A kinetic study of the solvolytic elimination reaction of 1,2-diphenylethyl-*N*-carbomethoxysulfamate triethylammonium salt in ethanol to give only *trans*-stilbene provided a first-order rate constant at 35° of $2.66 \pm 0.03 \times 10^{-6}$ sec^{-1} with $\Delta H = 21.7$ kcal/mol and $\Delta S = -3.3$ eu.[3] As a probe into the stereochemical requirements we examined the behavior of the corresponding *erythro*- and *threo*-2-deuterio-1,2-diphenylethyl-*N*-carbomethoxysulfamate salts[4] (**5a,b**) in benzene at 50°. The former provided only *trans*-stilbene containing 97% deuterium while the latter gave only protio-*trans*-stilbene as determined by mass spectral analysis and this result remains invariant in substituting dimethylformamide as the solvent.

A small β-hydrogen isotope effect was kinetically observed with $k_H/k_D = 1.05 \pm 0.02$ and 1.08 ± 0.03 for the erythro and threo isomers, respectively, in ethanol at 35°. These kinetic and stereochemical results are consistent with an initial rate-limiting formation of an ion pair followed by a fast cis β proton transfer[5] to the departing anion at a rate greater than

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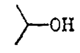
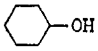
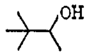
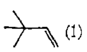
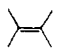
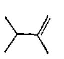
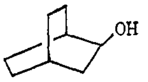
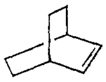
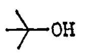
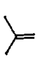
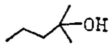
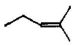
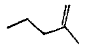
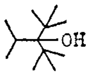
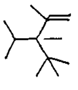
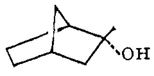
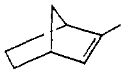
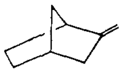
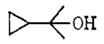
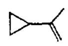
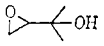
[1] An elegant method for the conversion of alcohols that yields moderately stable carbonium ions to amines *via* the SNi rearrangement of *N,N*-dialkylsulfamate esters has been published: E. H. White and C. A. Elliger, *J. Amer. Chem. Soc.*, **87**, 5261 (1965).

[2] G. M. Atkins, Jr., and E. M. Burgess, *ibid.*, **90**, 4744 (1968).

[3] Product development was followed spectrophotometrically at 295 nm and good first-order kinetics were displayed to 60% reaction.

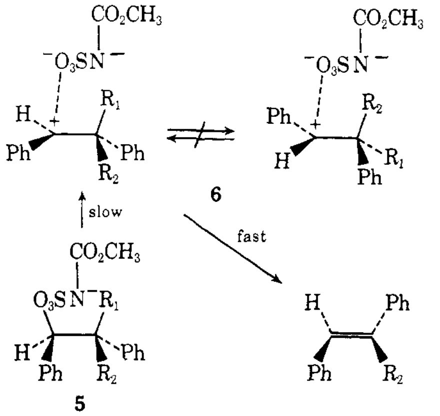
[4] The precursor deuteriated alcohols were prepared by the procedure of D. Y. Curtin and D. B. Kellom, *J. Amer. Chem. Soc.*, **75**, 6011 (1953).

Table I. Fragmentation of *sec*- and *tert*-$ROSO_2N^{-}CO_2CH_3X^{+}$

Precursor	Product(s)[a] (ratio)[b]	Temp, °C
		$40^{c,e}$
		$50^{d,f}$
	 (1)  (3)  (1.2)	$60^{d,g}$
	(1) (3) (1.5)	$70^{d,h}$
		$60^{c,g}$
		$30^{c,e}$
	 (2.4)  (1)	$30^{c,e}$
		$50^{c,i}$
	 (1)  (1)	$30^{c,g}$
		$30^{c,e}$
		$55^{c,e}$

[a] Isolated in 70–90% yield and characterized by comparison with authentic samples or by nuclear magnetic resonance and mass spectroscopy. [b] Determined by gas chromatography. [c] Triethylammonium counterion. [d] Sodium counterion. [e] Neat. [f] Tetrahydrofuran. [g] Benzene. [h] Triglyme. [i] 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.[6] *This singular characteristic should contribute to the synthetic potential of this leaving group in elimination reactions in a wide variety of systems.*

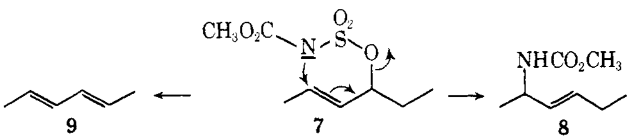


6

5

a, $R_1 = H$; $R_2 = D$
b, $R_1 = D$; $R_2 = H$

When the reaction is applied to an allylic alcohol either elimination or an S$_N$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.



9 **7** **8**

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

$$\underset{\mathbf{10}}{CH_3(CH_2)_5OSO_2N^{-}CO_2CH_3\ HN^{+}Et_3} \longrightarrow \underset{\mathbf{11}}{CH_3(CH_2)_5NHCO_2CH_3}$$

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-

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(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$_1$ reactions of tosylates has been reported: P. S. Skell and W. L. Hall, *J. Amer. Chem. Soc.*, **85**, 2851 (1963).

(7) Analogous conversions of methy, 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.).

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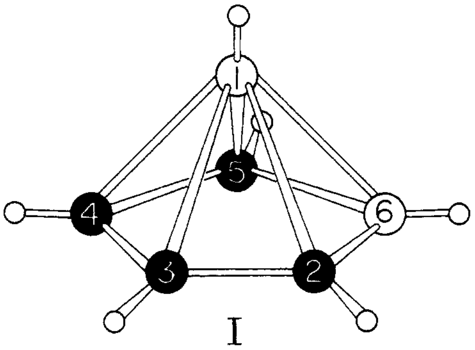
Preparation of the Pentagonal Pyramidal Carborane, 2,3,4,5-Tetracarba-*nido*-hexaborane(6)

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[1,2] through the hot zone at low pressures. In addition to the carborane, $C_4B_2H_6$, 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.



I

Figure 1. Ball and stick model of $C_4B_2H_6$.

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 $^{12}C_4{}^{11}B_2H_6$). 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 ^{11}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.[3]

(c) The proton nmr taken at both 100 and 220 MHz consist of two slightly broadened singlet resonances at (relative to τ 10.00 ppm for TMS) τ 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–^{11}B(6) and H–^{11}B(1), respectively.[4] 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 $C_nB_{6-n}H_{10-n}$ (*i.e.*, n = 0–3).[3]

(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^{-1} (B–H) and an absence of peaks in the B–H–B bridge regions.

In the pentagonal-pyramidal series of isoelectronic compounds $C_nB_{6-n}H_{10-n}$, 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[5] and perphenyl[6] derivatives of $C_4B_2H_6$ 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 $C_4B_2H_6$.

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.

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[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.

[4] Smaller septets within each quartet are partially visible and are attributed to H–^{10}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.

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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[1,2] 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.[3,4] Noting that stabilization of the cations

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[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).