and boron hydrides[4] has been hampered to some extent by the expense and difficulty of obtaining sufficient material. Decaborane(14) has been prepared in industrial facilities by the controlled thermolysis of diborane(6) or mixtures of diborane(6), tetraborane(10), and various diluent gases.[5] Much smaller amounts of $B_{10}H_{14}$ have been prepared by several routes including the thermal decomposition, in the presence of I_2, of decaborane(16),[6] the reaction of certain silver salts with LiB_5H_8,[7] and the reaction of diborane(6) with $B_5H_8^-$ ion.[8] All of the latter reactions require pentaborane(9).[9-12] Decaborane(14) can also be prepared by the pyrolysis of $B_9H_{13}S(CH_3)_2$[13] and in trace quantities by the reaction of $NaB_{11}H_{14} \cdot 3C_4O_2H_8$ with HCl;[14] however, both materials were originally derived from $B_{10}H_{14}$;[15,16] so these routes presently offer no synthetic utility. Thus, in the known procedures for the preparation of $B_{10}H_{14}$, hazardous boron hydrides derived from the pyrolysis of diborane were necessary starting materials and relatively elaborate apparatus and procedures were required which precluded the methods for general laboratory use.

We report here a new, facile, relatively low-cost synthesis of $B_{10}H_{14}$ from $NaBH_4$ which can be performed in standard laboratory apparatus and thus make $B_{10}H_{14}$ generally available for the first time.

An efficient one-step synthesis of $B_{11}H_{14}^-$ ion from $NaBH_4$ and $BF_3 \cdot O(C_2H_5)_2$ in diglyme at ~105 °C has been discovered and will be described in detail.[17] The major neutral product obtained from the oxidation of an aqueous solution of the $B_{11}H_{14}^-$ ion prepared in this way was found to be $B_{10}H_{14}$.[18] For example, in a 2000-mL, 3-neck flask assembled as previously described,[17] 300 mL of dry diglyme and 60.0 g (1.59 mol) of $NaBH_4$ were heated to 105 °C (under N_2 with mechanical stirring) followed by the addition of 250 mL (2.04 mol) of 98% $BF_3 \cdot O(C_2H_5)_2$ over 6 h. The mixture was heated 1 additional h and then cooied to 20 °C. The flask was fitted with a concentrator head and water (800 mL) was added slowly to the mixture (gas evolution).[19] The reaction mixture was heated (slowly to allow for gas evolution[19]) to distil the water/diglyme azeotrope and additional water (400 mL) was added until a total of 1243 mL of distillate was collected (pot temperature 112 °C maximum). After the solution was cooled to 10 °C, 500 mL of 2,3-dimethylbutane and 275 mL of cold 50% aqueous H_2SO_4 solution were added. With vigorous stirring, a solution of 159 g (0.53 mol) of $Na_2Cr_2O_7 \cdot 2H_2O$ in 70 mL of water was added (total volume 133 mL, 45 mL/h) with sufficient cooling to maintain the pot temperature at 30 ± 5 °C.[19] The stirring was stopped and the organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated to ~150 mL. The solution was cooled to -15 °C overnight and filtered to yield 5.88 g (0.048 mol, 30.3% conversion based upon the $NaBH_4$ charged) of $B_{10}H_{14}$ (mp 97-98 °C). The liquor was stripped to dryness and 1.94 g (0.016 mol, 10% conversion) of additional $B_{10}H_{14}$ was obtained from the residue by sublimation. The infrared, ^{11}B NMR, and mass spectra were identical with those of authentic $B_{10}H_{14}$.[4,20-22]

Studies concerning the scale-up of this procedure, the use of additional oxidizing agents including $KMnO_4$ and H_2O_2, and the use of solutions of $B_{10}H_{14}$ directly in the formation of various derivatives of $B_{10}H_{14}$ including carboranes are in progress and will be reported elsewhere.

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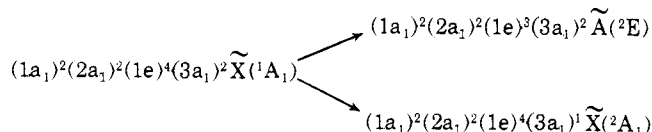*Received December 19, 1977*

An Experimental Determination of the Geometry and Electron Affinity of CH₃

Sir:

We have produced CH_3^- in the gas phase and by photoelectron spectroscopy have found the electron affinity (EA) of CH_3 to be 0.08 ± 0.03 eV (1.8 ± 0.7 kcal/mol). The vibronic structure connecting the methide ion and methyl radical shows the geometry of the carbanion to be pyramidal. Any inversion barrier present in the neutral is less than half the zero point energy; consequently CH_3 is quasi-planar.

In the years since the first direct observation[1] of CH_3, this radical has been studied by a number of techniques. Electron resonance spectroscopy,[2] gas phase infrared spectroscopy,[3] and complementary matrix isolation studies[4,5] all indicate a planar molecule. CH_3 has been studied by photoionization spectroscopy[6-8] which assigns planar geometries to both CH_3 and CH_3^+. CH_3^- has never been definitively observed in the gas phase. Numerous computational studies[9-14] report the ion to be pyramidal, but only one[10] predicts that CH_3^- will exist.

As detachment possibilities for the methide ion, consider the low-lying states of CH_3 produced in the process $CH_3^- + h\nu \rightarrow CH_3 + e^-$.

$$(1a_1)^2(2a_1)^2(1e)^3(3a_1)^2 \widetilde{A}(^2E)$$
$$(1a_1)^2(2a_1)^2(1e)^4(3a_1)^2 \widetilde{X}(^1A_1)$$
$$(1a_1)^2(2a_1)^2(1e)^4(3a_1)^1 \widetilde{X}(^2A_1)$$

Detachment of CH_3^- to the $\tilde{X}$ state of CH_3 is expected to be characterized by two features: (a) the EA of CH_3 should be very small and (b) a progression in ν_2 (the umbrella-like mode) should be evident.

We have extracted mass-selected negative ion beams with a charge to mass ratio of 15 from an electrical discharge in fresh CH_2CO. Our ion source operates at sample pressures of ~0.2 Torr and it is probable that the ketene decomposes via a surface reaction (on either the filament or on the anode
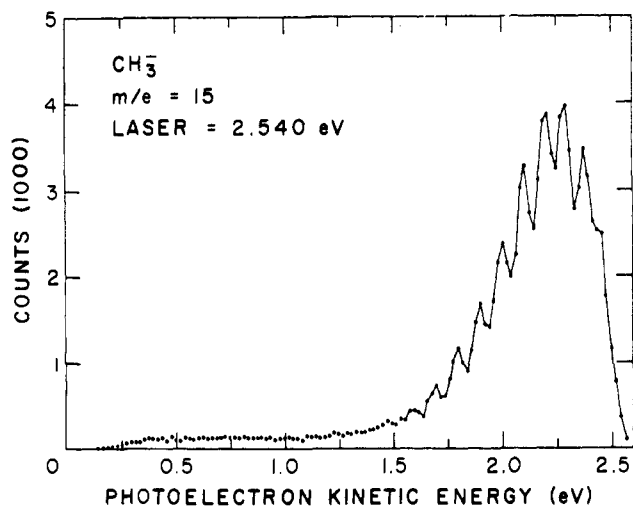
Figure 1. An experimental photoelectron spectrum of CH_3^-; the data points are spaced ~20 meV.
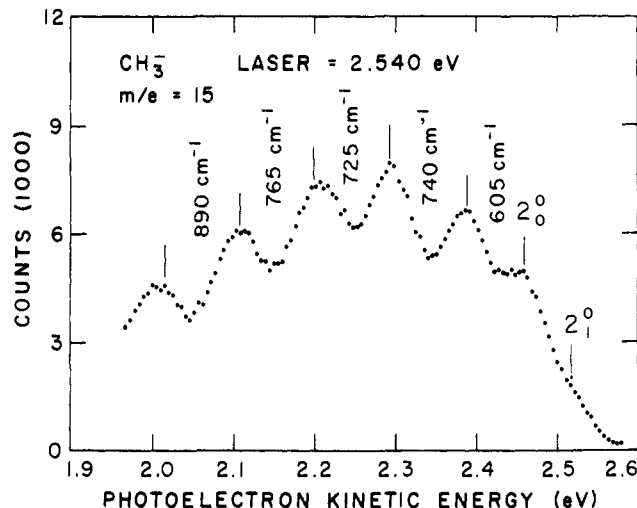

Figure 2. An experimental photoelectron spectrum of CH_3^-; the data points are ~5 meV apart. The 2_0^9 peak corresponds to the electron affinity of CH_3. See text.

plate). Mass identification is achieved by photodetachment[15] of neighboring peaks and is unambiguous. The proof that the anion at m/e 15 is CH_3^- comes from the fact that the observed photoelectron spectrum is consistent with that which we expect for CH_3^-, and not that of other species (e.g., NH^-, CHD^-) with m/e 15.

The experimental[16] method consists of crossing the mass-selected ion beam with an argon ion laser operating at 488 nm (2.540 eV). Photodetached electrons that enter the acceptance aperture of the hemispherical electrostatic monochrometer are energy analyzed and counted. Electron binding energies are obtained approximately by subtracting the measured electron kinetic energy from the laser photon energy. The absolute electron energy scale is determined by simultaneous photodetachment of CH_3^- and O^-, the latter EA[17] being well known.

A low resolution scan of the methide photoelectron spectrum is shown in Figure 1. The long progression with its 700-cm^{-1} spacing is assigned to transitions in ν_2 from $v'' = 0$ in the ion to $v' = 0, 1, 2, \ldots, 10$ in the radical (written as 2_0^n where $n = 0, 1, 2, \ldots$). The extent of this progression reveals a portion of the CH_3 surface never seen before and allows the construction of a potential curve ~7000 cm^{-1} above the zero point level. Figure 1 only shows detachment to the $\tilde{X}$ state of CH_3 and thus bounds the energy of the $^2E'$ state of the radical as $\Delta E(\tilde{A} - \tilde{X}) > 2.2$ eV.

Figure 2 shows the first part of the spectrum at higher resolution. The origin is at kinetic energy of 2.460 eV, giving an EA of 0.08 ± 0.03 eV. The splitting between the 2_0^0 and 2_0^1 peaks is 605 ± 40 cm^{-1} which compares with the infrared value[4] of 603 cm^{-1}. The high-energy side of the 2_0^0 band indicates a splitting between $v'' = 0$ and $v'' = 1$ in ν_2 to be 460 ± 40 cm^{-1} in CH_3^-.

A set of potential curves for both CH_3 and CH_3^- is shown in Figure 3. We have taken computed values[12] (the points in Figure 3) and fit them to smooth curves. These potentials in Figure 3 were then displaced in energy to produce a (0,0) splitting of 0.08 eV, our experimental value. Using the fitted potentials for CH_3 and CH_3^-, energy levels shown in Figure 3 were obtained by solving the one-dimensional Schrödinger equation[18] which models ν_2 in XY_3 molecules. The computed vibrational levels in Figure 3 predict a photoelectron spectrum all of whose peak locations are indistinguishable from our experimental values (error ±40 cm^{-1}) of Figure 2. This agreement is obtained for a CH_3 geometry which is planar; addition of even a small barrier (~50 cm^{-1}) will markedly change that quality of fit, but the full range of surface possibilities has not
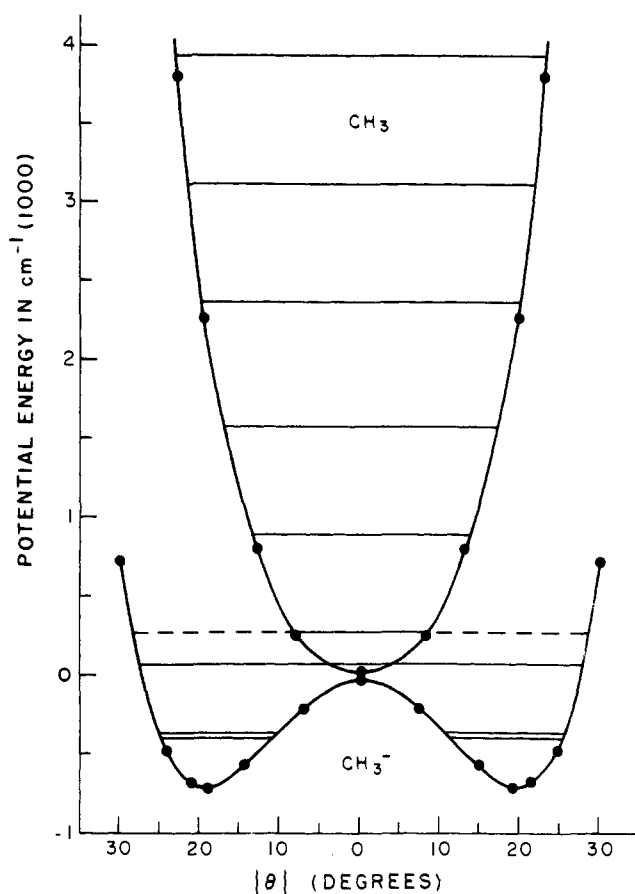

Figure 3. A set of computed potential curves for CH_3^- and CH_3. See text for details.

yet been carefully explored. At this stage, we agree with Dyke et al.[6] that CH_3 is "essentially planar"; any barrier to inversion is certainly no more than half the zero point energy (150 cm^{-1}). A more rigorous bound on this barrier, as well as an experimentally derived potential for both the ion and radical, will result from a detailed analysis of the Franck–Condon factors of the (CH_3, CH_3^-) and (CD_3, CD_3^-) spectra.

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Chiral [16O, 17O, 18O]Phosphate Monoesters. 1. Asymmetric Synthesis and Stereochemical Analysis of [1(R)-16O, 17O, 18O]Phospho-(S)-propane-1,2-diol

Sir:

To discover the stereochemical consequences of phosphoryl transfer reactions involving phosphate monoesters, we have devised *a general method for establishing whether retention or inversion at phosphorus occurs in these processes*. To make a phosphate monoester chiral at phosphorus, we use the three stable isotopes of oxygen, ^{16}O, ^{17}O, and ^{18}O. We report here the synthesis of [1(R)-16O, 17O, 18O]phospho-(S)-propane-1,2-diol (3) by a general route, and an independent evaluation of the configuration of the phosphoryl group in this compound.


Synthesis. The synthesis of **3** is outlined in Scheme I. Reaction of [17O]-POCl₃[1] with (−)-ephedrine gave two epimeric chloro adducts **1**,[2] which reacted with 2-benzyl-(S)-propane-1,2-diol[3] to give the two phosphoramidate diesters **2** in 9:1 ratio. This reaction goes with retention at phosphorus.[2] The predominant isomer (shown in Scheme I) was isolated in 70% yield (based on POCl₃) after chromatography on silica gel. The phosphoramidate **2** was ring opened in $H_2{}^{18}O$ by an in-line pathway.[2,4] The resulting diester was debenzylated by catalytic hydrogenolysis[5] to give **3** in 70% yield (based on **2**). The route

Scheme I. Synthesis of [1(R)-16O, 17O, 18O]phospho-(S)-propane-1,2-diol.
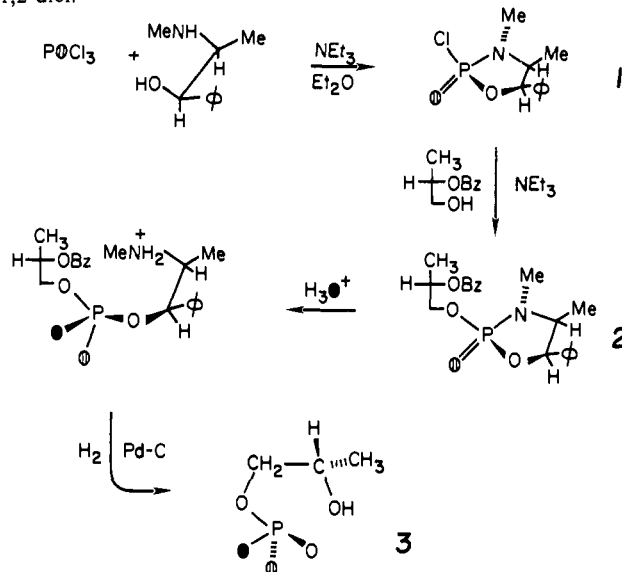
Scheme II. Sets of 1,2-cyclic phosphates derived by "in-line" ring closure of 1(R)-phospho-(S)-propanediol (3) and of 1(S)-phospho-(S)-propanediol (4).

1-R- phospho-S-propanediol

1-S-phospho-S-propanediol
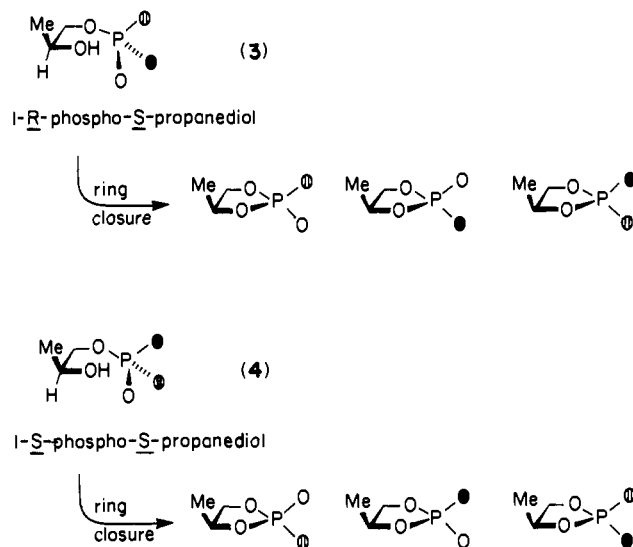
shown in Scheme I should be a general one for the preparation of chiral phosphate esters from appropriately protected precursors.[6]

Stereochemical Analysis. It is very unlikely that any physical technique would be capable of discriminating between the (R) and (S)-[16O, 17O, 18O]phosphate monoesters themselves, and so the following path was adopted. The ester **3** is cyclized to the 1,2-cyclic phosphate,[7] losing ^{16}O, ^{17}O, or ^{18}O equally,[8] producing an equimolar mixture of *three* species. Since the carbon skeleton is also chiral (at C-2), these three cyclic phosphates are epimers (at phosphorus) of the three species that would derive from a phosphoryl group of the opposite configuration. Scheme II shows these relationships. Methylation[9] of the cyclic phosphate occurs on either of the exocyclic oxygens, and gives the two ('syn' and 'anti') diastereoisomeric cyclic methyl esters that can be separated chromatographically.[10] Scheme III illustrates the three isotopic variants of the 'syn' cyclic triester derived from an (R)-phosphoryl group, alongside the corresponding set that derives from an (S)-phospho compound. These two sets of cyclic triesters give identical mass spectra,[8] with parent peaks at 153, 154, and 155 (corresponding to the species containing $^{17}O + ^{16}O$, $^{16}O + ^{18}O$,