

Table I.  $^{13}\text{C}$  Chemical Shifts of Selected Compounds<sup>a</sup>

Compd	C <sub>4'</sub>	C <sub>5'</sub>	C <sub>6'</sub>
6a	89.28	66.46	37.67
7a	88.31	64.37	39.71
6b	88.89	65.98	41.17
7b	89.06	63.87	42.60
6c	91.37, 91.03 <sup>b</sup>	64.57	40.93, 40.29 <sup>b</sup>
7c	88.55	62.58	41.95

<sup>a</sup> Parts per million downfield from internal Me<sub>4</sub>Si; in CDCl<sub>3</sub>. <sup>b</sup> Two signals are observed due to the new chiral center introduced at C<sub>6'</sub>.

O-cyclohexylideneuridine-5'-aldehyde (**2**)<sup>17,18</sup> with 1.15 equiv of pyrrolidine in 1:1 benzene-acetonitrile at 50 °C for 5 min, followed by solvent removal under reduced pressure, afforded the 4',5'-enamine **3**<sup>19</sup> in quantitative yield as a moisture-sensitive foam:  $^{13}\text{C}$  NMR  $\delta$  118.07 (d, C<sub>5'</sub>), 132.15 (s, C<sub>4'</sub>).<sup>20</sup> That **3** was a single isomer (of undetermined character as yet) was suggested by the absence of extra lines in the  $^{13}\text{C}$  NMR.

It is well known that  $\beta,\beta$ -disubstituted enamines of aldehydes generally alkylate on nitrogen rather than carbon. In simple cases, however, it is possible to achieve high yield C-alkylation by utilization of an allylic bromide, which, after initial N-alkylation, can migrate to carbon via a Claisen-type rearrangement.<sup>21</sup> Treatment of **3** (1.5 mmol) in 10 mL of dry CH<sub>3</sub>CN with 2.0 equiv of allyl bromide under nitrogen with slow warming to 80 °C (oil bath temperature) over 6 h afforded the isolable N-alkylated product (**4**). Continued heating at 80 °C for 16 h allowed smooth rearrangement to the 4'-allyl iminium salts (**5a**), which were not isolated but subjected to aqueous hydrolysis to afford a mixture of the  $\beta$ -D-ribo and  $\alpha$ -L-lyxo aldehydes **5b**.<sup>22</sup> These aldehydes can be purified and separated chromatographically (silica gel), or directly reduced with NaBH<sub>4</sub> (1.05 equiv) in 5 mL of absolute ethanol for 2 h at room temperature. Processing by addition of H<sub>2</sub>O, evaporation, and gravity filtration through silica gel (95:5 CHCl<sub>3</sub>-CH<sub>3</sub>OH) afforded a 2:1 mixture ( $\alpha$ -L-lyxo; $\beta$ -D-ribo) of the alcohols **6a** and **7a**. On a small scale (1–2 mmol), separation of the isomers was possible at this stage by thick layer chromatography (95:5 CHCl<sub>3</sub>-CH<sub>3</sub>OH, three elutions), while high-pressure liquid chromatography was employed on a larger scale. The overall yield from **2** to **6a** and **7a** is 57% after purification. Configurational assignments were made on the basis of  $^{13}\text{C}$  NMR, where the sensitivity of carbon to steric crowding by a vicinal oxygen can be employed. Carbon atoms cis to oxygen will be at higher field relative to those same carbons in the trans configuration.<sup>9,23</sup> Thus the 5'-hydroxymethyl carbon is shifted upfield 2.09 ppm in the  $\alpha$ -L-lyxo isomer, while the allylic methylene is shifted upfield 2.04 ppm in the  $\beta$ -D-ribo isomer (see Table I for the relevant chemical shifts for compounds **6a-c** and **7a-c**).

In similar fashion this sequence can be carried out employing methallyl bromide and crotyl bromide to afford similar isomeric mixtures of **6b** and **7b** (27% overall from **2**) and **6c** and **7c** (34% overall from **2**), respectively. Deprotection of **6a**, for example, with trifluoroacetic acid–water (9:1) at room temperature affords the free nucleosides **8** in 55% yield.

The unit of unsaturation introduced by this procedure provides a handle by which the hydrophobic/hydrophilic nature of the 4'-substituent can be manipulated. Several examples are presented to exemplify this. Catalytic hydrogenation of **6a** at 1 atm (10% Pd/C) readily produced the 4'-*n*-propyl derivative (66%). Treatment of **6a** with OsO<sub>4</sub>-NaIO<sub>4</sub> in aqueous THF<sup>24</sup> at 0 °C cleaved the double bond to afford an aldehyde which was isolated as the internal hemiacetal **9** (56%). Reduction of **9** with NaBH<sub>4</sub> in absolute ethanol gave the diol **10** (57%). Epoxidation of **6a** with *m*-chloroperoxybenzoic acid proved impossible under normal conditions, but did proceed utilizing forcing conditions (*m*-CPBA, ClCH<sub>2</sub>CH<sub>2</sub>Cl, a trace amount

of 2,6-di-*tert*-butyl-4-methylphenol, 70 °C).<sup>25</sup> The epoxide was, however, not stable under these conditions and was rapidly opened intramolecularly to the spirocyclic nucleoside **11** (61%). The methallyl compound **7b** underwent epoxidation–rearrangement under normal conditions to provide **12a** in 91% yield. That opening of the epoxide ring occurred to form the five-membered ring rather than the six-membered ring<sup>26</sup> was demonstrated by oxidation (pyridinium chlorochromate)<sup>27</sup> of **12a** to the aldehyde **12b**, whose identity was readily confirmed spectroscopically ( $^1\text{H}$  NMR,  $\delta$  9.5).

The versatile nature of enamines portends their further use in the nucleoside/carbohydrate area for substituent incorporation in certain positions. Branched chain compounds of various kinds should be available through this type of methodology.

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## A Simplified Preparation of B<sub>10</sub>H<sub>14</sub> from NaBH<sub>4</sub>

Sir:

The study of reaction chemistry of decaborane(14) B<sub>10</sub>H<sub>14</sub>, and its derivatives, the large carboranes,<sup>1,2</sup> metallo-carboranes,<sup>3</sup>

and boron hydrides<sup>4</sup> 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.<sup>5</sup> Much smaller amounts of B<sub>10</sub>H<sub>14</sub> have been prepared by several routes including the thermal decomposition, in the presence of I<sub>2</sub>, of decaborane(16),<sup>6</sup> the reaction of certain silver salts with LiB<sub>5</sub>H<sub>8</sub>,<sup>7</sup> and the reaction of diborane(6) with B<sub>5</sub>H<sub>8</sub><sup>-</sup> ion.<sup>8</sup> All of the latter reactions require pentaborane(9).<sup>9-12</sup> Decaborane(14) can also be prepared by the pyrolysis of B<sub>9</sub>H<sub>13</sub>S(CH<sub>3</sub>)<sub>2</sub><sup>13</sup> and in trace quantities by the reaction of NaB<sub>11</sub>H<sub>14</sub>·3C<sub>4</sub>O<sub>2</sub>H<sub>8</sub> with HCl;<sup>14</sup> however, both materials were originally derived from B<sub>10</sub>H<sub>14</sub>,<sup>15,16</sup> so these routes presently offer no synthetic utility. Thus, in the known procedures for the preparation of B<sub>10</sub>H<sub>14</sub>, 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<sub>10</sub>H<sub>14</sub> from NaBH<sub>4</sub> which can be performed in standard laboratory apparatus and thus make B<sub>10</sub>H<sub>14</sub> generally available for the first time.

An efficient one-step synthesis of B<sub>11</sub>H<sub>14</sub><sup>-</sup> ion from NaBH<sub>4</sub> and BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> in diglyme at ~105 °C has been discovered and will be described in detail.<sup>17</sup> The major neutral product obtained from the oxidation of an aqueous solution of the B<sub>11</sub>H<sub>14</sub><sup>-</sup> ion prepared in this way was found to be B<sub>10</sub>H<sub>14</sub>.<sup>18</sup> For example, in a 2000-mL, 3-neck flask assembled as previously described,<sup>17</sup> 300 mL of dry diglyme and 60.0 g (1.59 mol) of NaBH<sub>4</sub> were heated to 105 °C (under N<sub>2</sub> with mechanical stirring) followed by the addition of 250 mL (2.04 mol) of 98% BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> over 6 h. The mixture was heated 1 additional h and then cooled to 20 °C. The flask was fitted with a concentrator head and water (800 mL) was added slowly to the mixture (gas evolution).<sup>19</sup> The reaction mixture was heated (slowly to allow for gas evolution<sup>19</sup>) to distill 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<sub>2</sub>SO<sub>4</sub> solution were added. With vigorous stirring, a solution of 159 g (0.53 mol) of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O 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.<sup>19</sup> The stirring was stopped and the organic layer was separated, dried over anhydrous MgSO<sub>4</sub> 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<sub>4</sub> charged) of B<sub>10</sub>H<sub>14</sub> (mp 97-98 °C). The liquor was stripped to dryness and 1.94 g (0.016 mol, 10% conversion) of additional B<sub>10</sub>H<sub>14</sub> was obtained from the residue by sublimation. The infrared, <sup>11</sup>B NMR, and mass spectra were identical with those of authentic B<sub>10</sub>H<sub>14</sub>.<sup>4,20-22</sup>

Studies concerning the scale-up of this procedure, the use of additional oxidizing agents including KMnO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>, and the use of solutions of B<sub>10</sub>H<sub>14</sub> directly in the formation of various derivatives of B<sub>10</sub>H<sub>14</sub> including carboranes are in progress and will be reported elsewhere.

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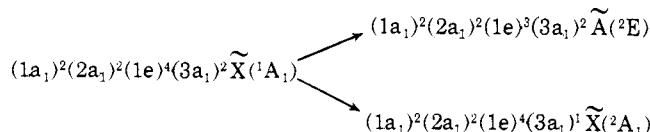
## An Experimental Determination of the Geometry and Electron Affinity of CH<sub>3</sub>

Sir:

We have produced CH<sub>3</sub><sup>-</sup> in the gas phase and by photoelectron spectroscopy have found the electron affinity (EA) of CH<sub>3</sub> 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<sub>3</sub> is quasi-planar.

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

As detachment possibilities for the methide ion, consider the low-lying states of CH<sub>3</sub> produced in the process CH<sub>3</sub><sup>-</sup> + hν → CH<sub>3</sub> + e<sup>-</sup>.



Detachment of CH<sub>3</sub><sup>-</sup> to the  $\tilde{X}$  state of CH<sub>3</sub> is expected to be characterized by two features: (a) the EA of CH<sub>3</sub> should be very small and (b) a progression in ν<sub>2</sub> (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<sub>2</sub>CO. 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