

Figure 2. Mössbauer spectrum of iron(III) sulfide at 4.2 K (bar indicates error).

were carried out at 4.2 K with an external magnetic field applied collinear with the  $\gamma$ -ray direction. This resulted in a broadening of the outer Mössbauer lines, indicating the presence of magnetic moments at the iron ions aligned in opposite directions. Thus, it can be inferred that iron(III) sulfide is ordered antiferromagnetically at 4.2 K.

Mössbauer measurements at elevated temperature also have been made, the details of which will be published in future work. Suffice it to say here that an irreversible transformation to other products begins to occur at 20 °C in vacuo. Although the decomposition is slow considerable doubt is thus cast on the reliability of the previous synthetic procedures, all of which would appear to have been carried out at temperatures near that where  $\text{Fe}_2\text{S}_3$  decomposes.

The infrared spectrum<sup>17</sup> of iron(III) sulfide exhibits bands at 795 (sh), 485 (br), 390, and 320  $\text{cm}^{-1}$ . The spectrum clearly is different from that of  $\text{FeS}_2$  and other iron sulfide minerals.<sup>18</sup>

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- (11) In a typical preparation 500 mL of 0.0483 M  $\text{FeCl}_3$  was treated with 500 mL of 0.0737 M  $\text{Na}_2\text{S}$  at  $-2$  °C under an atmosphere of  $\text{N}_2$ . The black air-sensitive precipitate that formed was permitted to settle and then was filtered (with extreme difficulty). The product was washed with ice water until the filtrate gave a negative test for chloride, and it then was washed with cold 25:75  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ . The filtrate contained no detectable iron(III), iron(II), or  $\text{S}^{2-}$ . After the temperature of the gelatinous precipitate was reduced to ca.  $-5$  °C, the sample was placed over  $\text{P}_4\text{O}_{10}$  in an evacuated chamber and pumped, the temperature remaining at  $-5$  °C until the precipitate turned to a black, dry powder ( $\sim 4$  weeks). The last traces of water are difficult to remove, and the compound may contain water of hydration. A portion of the powder was decomposed with nitric acid at room temperature. The resulting solution gave negative tests for  $\text{Na}^+$  and  $\text{Cl}^-$ .
- (12) Mössbauer measurements were made using a  $^{57}\text{Co}:\text{Pd}$  source with an initial activity of 25 mCi. The spectrometer was calibrated with standard iron foils, and the center shift values reported are with respect to metallic iron.
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## Carbon-Carbon Bond Formation at $\text{C}_4'$ of a Nucleoside. Synthesis and Utilization of a Uridine 4',5'-Enamine<sup>1</sup>

Sir:

The search for methods allowing substituent incorporation at  $\text{C}_4'$  of nucleosides began with the isolation and structure identification of nucleocidin (**1**), a powerful, but toxic, anti-trypanosomal agent with a fluorine in this unique position on the carbohydrate ring.<sup>2-5</sup> Synthetic methods have thus far been developed which allow incorporation of fluorine,<sup>6-8</sup> various alkoxyl groups,<sup>1,9-11</sup> and hydroxymethyl.<sup>12-14</sup> The challenge of devising a reasonably versatile method for carbon-carbon bond formation at  $\text{C}_4'$ , however, is still at hand. We wish to report that alkylation of a nucleoside 4',5'-enamine with allylic halides provides a solution to this problem.

Our work in the area of nucleoside 4',5'-enol acetates<sup>15</sup> and their conversion to certain 4'-substituted compounds<sup>1</sup> prompted us to examine the feasibility of utilizing a 4',5'-enamine as a vehicle for introduction of a carbon-carbon bond via enamine alkylation. To date no literature reports exist for the formation of a nucleoside enamine, although recently a carbohydrate enamine was reported.<sup>16</sup> Treatment of 2',3'-

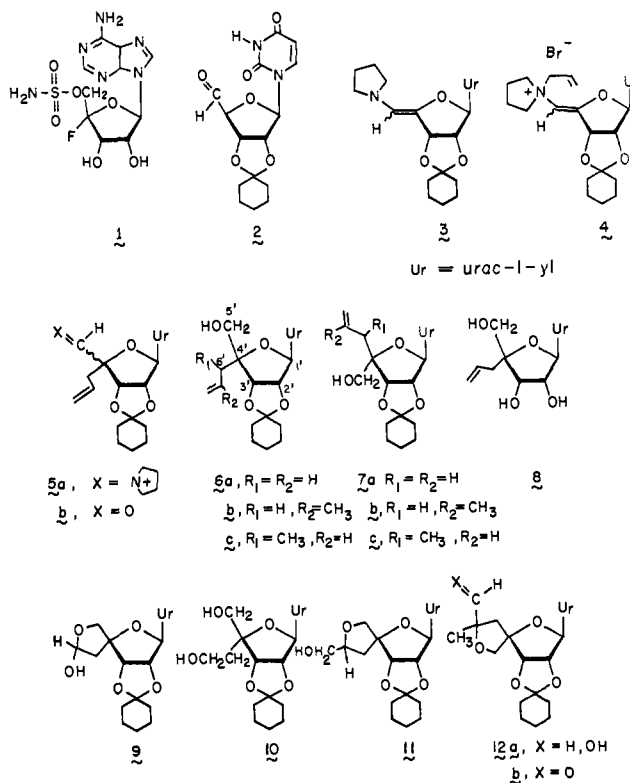


Table I.  $^{13}\text{C}$  Chemical Shifts of Selected Compounds<sup>a</sup>

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>