

The Chemistry of the *N*-Methyl-3-dehydropyridinium Ylid

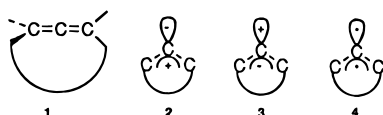
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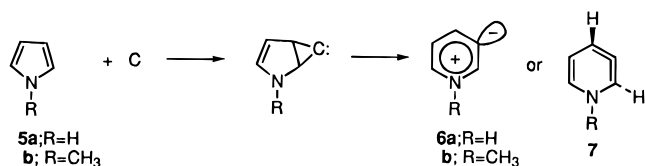
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**Abstract:** The reaction of atomic carbon with *N*-methylpyrrole, **5b**, at 77 K generates the *N*-methyl-3-dehydropyridinium ylid, **6b**, which can be trapped with added hydrogen halides or CO<sub>2</sub>. The addition of CO<sub>2</sub> is strong evidence for the ylid **6b** rather than cumulene **7**. Deuterium and <sup>13</sup>C labeling studies demonstrate that **6b** rapidly rearranges to the *N*-methyl-2-dehydropyridinium ylid, **13**, by an intermolecular mechanism. Ylid **13** can be trapped with added acids or with O<sub>2</sub> to form 1-methyl-2-pyridone.

One of the interesting ways in which to introduce strain into organic molecules is to place cumulative double bonds in small rings. It has long been recognized that there are several possible structures for these highly strained cyclic cumulenes.<sup>1</sup> In addition to a nonplanar allene, **1**, these include the zwitterionic species **2** or **3** and biradical **4** (either singlet or triplet). Although there is no doubt that the accessible 1,2-cycloalkadienes are



nonplanar allenes, it is of interest to design systems in which a planar zwitterionic species such as **2** may be stabilized. Our recently reported reaction of atomic carbon with pyrrole, **5a**, which appears to proceed via the novel dehydropyridinium ylid **6a**, is an example of such a system.<sup>2</sup> In this case, we propose that the aromaticity of the pyridinium ion favors the planar ylid **6** over the nonplanar cumulene **7**.<sup>3</sup>

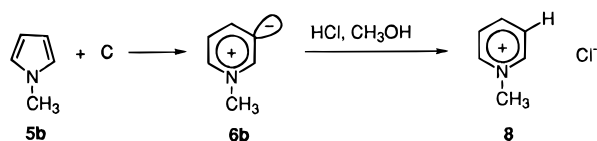


However the formation of **6a** in the presence of **5a** with its acidic hydrogen, limits the chemical reactivity which can be observed for **6** to intermolecular proton transfer to generate pyridine.<sup>2</sup> In order to further probe the reactivity of **6** and to gain additional chemical evidence for its structure, we now report an investigation of the *N*-methyl-3-dehydropyridinium ylid, **6b**, in which novel chemistry is observed.

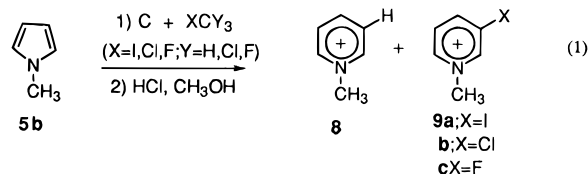
## Results and Discussion

Reactions were carried out in the standard carbon arc reactor in which atomic carbon is generated by striking an arc between two high purity graphite electrodes and condensed with substrate

at 77K.<sup>4,5</sup> The intermediacy of **6b** in the 77 K cocondensation of arc generated carbon with *N*-methylpyrrole, **5b**, is implied by the fact that addition of methanolic HCl to the cold condensate generates the *N*-methylpyridinium ion, **8**.



The absence of acidic protons in **5b** was expected to increase the lifetime of **6b** and permit the observation of additional reactions. In particular, reactions with electrophiles other than the proton were anticipated. In an attempt to observe such reactions and to probe the nucleophilicity of **6b**, methyl iodide was added to the 77 K matrix of C + **5b**. However upon subsequent addition of HCl, this reaction gave only **8** and none of the anticipated *N*-methyl-3-methylpyridinium ion. When an attempt was made to alkylate **6b** as it is formed by condensing C + **5b** + CH<sub>3</sub>I at 77K, the products were **8** and, quite surprisingly, the 3-iodo-*N*-methylpyridinium ion (**9a**, eq 1) in a 4:1 ratio. The condensation of other alkyl halides invariably results in the formation of 3-halo-*N*-methylpyridinium ions (eq 1).



Although we were first tempted to attribute the formation of **9a** to a halogen abstraction by a biradical form of **6b**,<sup>6</sup> we were forced to revise our ideas when the use of CF<sub>3</sub>Cl and FCCl<sub>3</sub> incorporated both fluorine and chlorine into the 3-position of the *N*-methylpyridinium ion. In the case of CF<sub>3</sub>Cl, the **9b**:**9c** ratio was 1:1.5, while it was 6.8:1 in the case of FCCl<sub>3</sub>. Since abstraction of fluorine by biradicaloid **6b** is unlikely, we feel that the 3-halo-*N*-methylpyridinium ions result from halometh-

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, May 1, 1997.

(1) Johnson, R. A. *Chem. Rev.* **1989**, *89*, 1111.

(2) Emanuel, C. J.; Shevlin, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 5991.

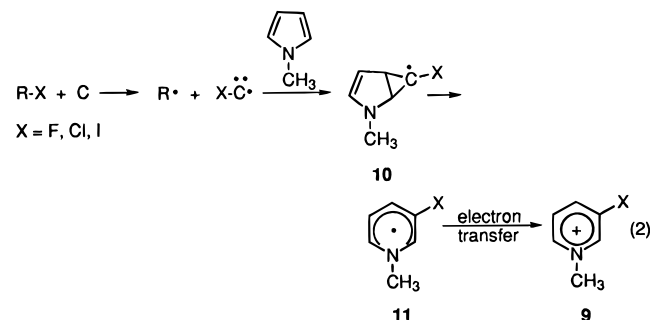
(3) Although we have not yet carried out detailed calculations of the energy surfaces involved in these reactions, we note that geometry optimization at the MP2/6-31G\* level demonstrates that planar **6a** and **6b** are energy minima. All attempts to find energy minima for cumulenes **7** gave **6** instead.

(4) For reviews of the chemistry of atomic carbon, see: (a) Skell, P. S.; Havel J.; McGlinchey, M. J. *Acc. Chem. Res.* **1973**, *6*, 97. (b) MacKay, C. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. II, pp 1–42. (c) Shevlin, P. B. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. I, pp 1–36.

(5) Skell, P. S.; Wescott, L. D., Jr.; Golstein, J. P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829.

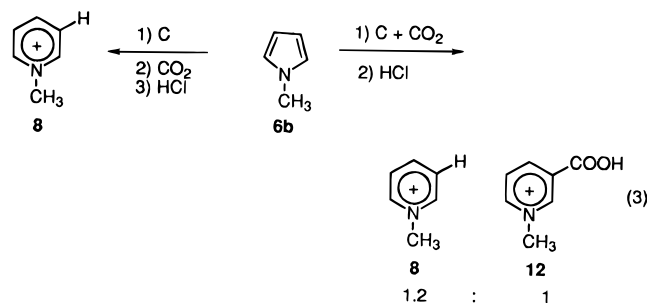
(6) For a discussion of the various electronic states possible in cyclic cumulenes see ref 1.

ylidynes formed directly in the reaction of atomic carbon with the alkyl halide as shown in eq 2. We have reported the rapid addition of CF and CCl to double bonds to generate  $\alpha$ -halocyclopropyl radicals,<sup>7ab</sup> and work in our laboratory indicates that CI is generated and reacts in the same manner.<sup>7c</sup> In this



case the exothermicity of the addition reaction to form  $\alpha$ -halocyclopropyl radical **10** drives the ring opening to **11** which subsequently generates **9** in an electron transfer. In an analogous reaction, we have observed the reaction of CF with cyclopentadiene to give fluorobenzene and with pyrrole to generate 3-fluoropyridine.<sup>7d</sup> Although the above observations nicely rationalize the formation of **9**, they do not fully explain the failure of **6b** to undergo alkylation.

In our search for nucleophilic reactions of **6b**, we next turned to carbon dioxide, an electrophile not expected to generate another highly energetic species upon reaction with carbon. Cocondensation of **5b** + C + CO<sub>2</sub> at 77 K followed by addition of methanolic HCl generates **8** and *N*-methylpyridinium 3-carboxylic acid **12**<sup>8</sup> in a 1.2:1 ratio (eq 3). The observation of **12**

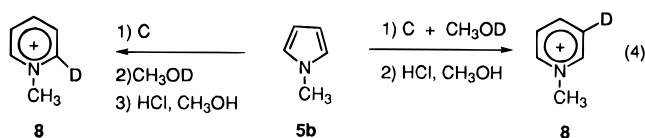


provides strong chemical evidence in favor of ylid structure **6** rather than cumulene **7** which would not be expected to react with CO<sub>2</sub>. However, **12** is not generated when CO<sub>2</sub> is added to the 77 K matrix formed upon reaction of C with **5b** (eq 3).

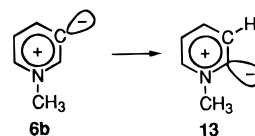
In order to attempt to understand why **6b** could seemingly be trapped by methanolic HCl added to the low temperature matrix of C + **5b** after reaction but not by carbon dioxide added to this same matrix, we have used CH<sub>3</sub>OD as the trapping agent. Surprisingly, addition of CH<sub>3</sub>OD to the low temperature matrix after reaction results in the formation of **8** whose <sup>2</sup>H NMR spectrum shows deuterium only in the 2-position. However when the CH<sub>3</sub>OD is added during the condensation, the deuterium is found exclusively at the 3-position in **8** (eq 4). A third experiment, in which a layer of CH<sub>3</sub>OD is first condensed followed by cocondensation of C + **5b** and the process repeated many times, leads to **8** with D in both the 2- and 3-positions in a 3:1 ratio.

(7) (a) LaFrancois, C. J.; Shevlin, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 9405. (b) Szyrbicka, R.; Rahman, M. M.; D'Aunoy, M. E.; Shevlin, P. B. *J. Am. Chem. Soc.* **1990**, *112*, 6712. (c) LaFrancois, C., J. Ph. D. Thesis, Auburn University, 1996. (d) Szyrbicka, R. Ph. D. Thesis, Auburn University, 1992.

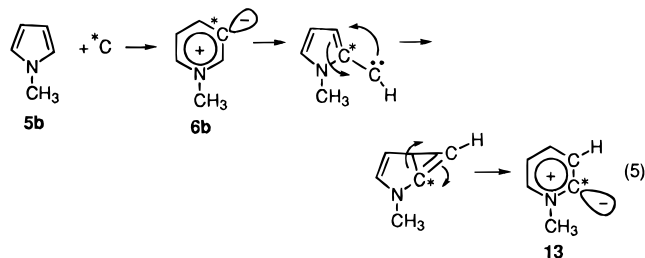
(8) Späth, B. *Chem. Ber.* **1944**, *77*, 362.



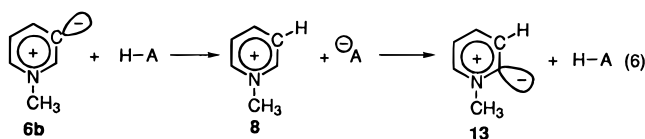
These interesting results suggest that initially formed **6b** rearranges to the 2-dehydropyridinium ylid **13** in a reaction in which the thermodynamic driving force may be the fact that the negative charge moves closer to the electronegative nitrogen. There are a number of mechanistic possibilities for this interesting rearrangement. An intramolecular rearrangement by a simple 1,2-hydrogen migration seems unlikely to occur on a 77 K surface. Rearrangements such as this in which a group migrates to an adjacent filled orbital generally have a high barrier due to the fact that the four-electron system requires that an



electron pair occupy a high energy (usually) antibonding orbital. However, this rearrangement could proceed by an intramolecular skeletal rearrangement of the type that occur in the phenyl<sup>9</sup> and pyridyl<sup>10</sup> carbene rearrangements. Equation 5 demonstrates that this skeletal rearrangement would reveal itself upon addition of <sup>13</sup>C atoms to **5b**. Thus, <sup>13</sup>C enriched carbon vapor was reacted with **5b** and methanolic HCl added to the low temperature matrix. However, this reaction gave **8** with 87% of its excess <sup>13</sup>C in the 3-position ruling out the intramolecular rearrangement in eq 5 as a major process.



Since both experimental evidence and experience appear to eliminate an intramolecular mechanism as the major pathway in the rearrangement of **6b** to **13**, we turned our attention to intermolecular mechanisms. Such mechanisms would most likely involve simple acid–base chemistry of the type illustrated in eq 6. In this case, the acid is probably the *N*-methylpyrrole,



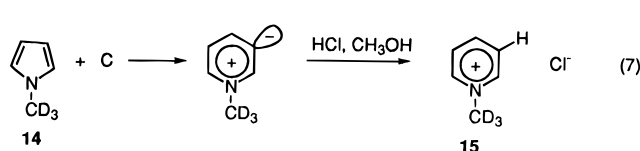
**5b**. An alternative in which two molecules of **6b** find each other on the low temperature matrix seems unlikely when one considers that highly reactive **6b** is generated in the presence of a large excess of **5b**.

If **5b** does participate in the rearrangement of **6b** to **13** via acid–base chemistry, this fact may be uncovered by appropriate “crossover” experiments using deuterium labeled **5b**. We have

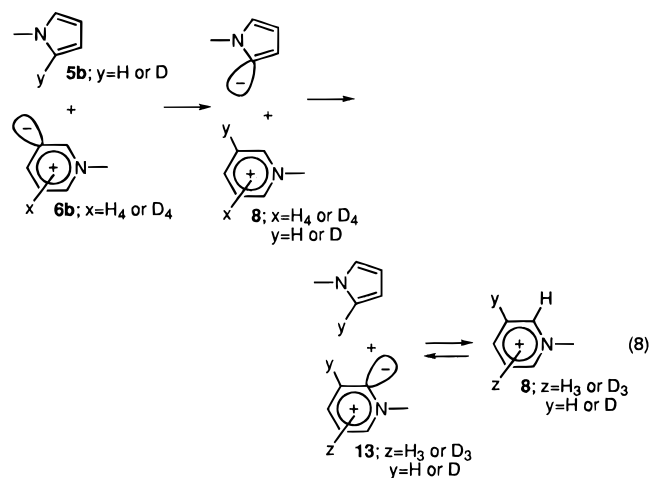
(9) Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M., Jr. *Tetrahedron* **1985**, *41*, 1479 and references therein.

(10) (a) Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 173. (b) Wentrup, C. *Reactive Molecules*; Wiley-Interscience: New York, 1984.

carried out two such experiments. In the first, *N*-trideuteromethylpyrrole, **14**, was reacted with C atoms, and methanolic HCl was subsequently added to generate *N*-trideuteromethylpyridinium ion, **15**, with only very minor traces of deuterium on the ring carbons (eq 7). Thus the methyl group in **5b** is not a significant source of acidic protons in the intermolecular rearrangement.



However a second experiment in which a 1.2:1 mixture of **5b** and **5b-1,2,3,4-d<sub>4</sub>** is reacted with C atoms reveals, after addition of methanolic HCl, **8-d<sub>0</sub>**, **8-d<sub>1</sub>**, **8-d<sub>3</sub>**, **8-d<sub>4</sub>**, and **8-d<sub>5</sub>** in a 6.8:3.5:1:5.1:2.2 ratio as determined by electrospray ms. If the rearrangement of **6b** to **13** were intramolecular, we would expect only **8-d<sub>0</sub>** and **8-d<sub>4</sub>** after addition of HCl. The fact that appreciable amounts of **8-d<sub>1</sub>**, **8-d<sub>3</sub>**, and **8-d<sub>5</sub>** are formed implicates an intermolecular mechanism involving acid–base equilibria in which **6b** is protonated by **5b** and a subsequent proton transfer generates **13** as shown in eq 8. The **8-d<sub>5</sub>** formed in this reaction results from a D transfer to **8-d<sub>4</sub>** which fails to undergo a second D transfer to give **13-d<sub>4</sub>** and remains as **8-d<sub>5</sub>** (eq 8). It is interesting that the acidic hydrogens which protonate **6b** are the vinyl hydrogens in **5b** rather than the supposedly more acidic methyl hydrogens.<sup>11</sup> However, it has been observed that the C<sub>2</sub>-position and not the methyl in **5b** is lithiated upon treatment with alkylolithiums.<sup>12</sup> In the present case, it appears that a kinetically controlled transfer of a vinylic proton in **5b** to **6b** occurs on the matrix at low temperature.



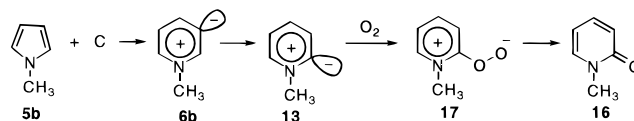
It is now clear that attempts to observe the chemistry of **6b** are complicated by its rapid intermolecular rearrangement to **13**. Only electrophiles added during the formation of **6b** whose rate of trapping is competitive with rearrangement, such as CO<sub>2</sub> and acids, may be used as traps. The fact that **13** can be protonated to a pyridinium ion but fails to undergo nucleophilic addition to alkyl halides or carbon dioxide may reflect the enhanced stability of **13** over **6b**. In this connection, we note that decarboxylation of *N*-methylpyridinium 2-carboxylic acid is 500 times faster than that of **12** at 196°.<sup>13</sup>

(11) DePuy, C. H.; Kass, S. H.; Bean, G. P. *J. Org. Chem.* **1988**, *53*, 1427.

(12) (a) Shirley, D. A.; Gross, B. H.; Roussel, P. A. *J. Org. Chem.* **1955**, *20*, 225. (b) Chadwick, D. J.; Cliffe, I. A. *J. Chem. Soc., Perkin Trans. I* **1979**, 2845.

(13) Hake, P.; Mantecón, J. *J. Am. Chem. Soc.* **1964**, *86*, 5230.

Although we cannot trap **13**, with CO<sub>2</sub>, we have found that it can be trapped as 1-methyl-2-pyridone, **16**, by addition of oxygen to the matrix resulting from the reaction of C + **5b**. Although the mechanistic details of this trapping reaction are not clear, it seems likely that it proceeds *via* stabilized carbonyl oxide, **17**.



## Conclusions

These investigations provide interesting examples of the ability of atomic carbon to channel its high energy into the production of novel reactive intermediates. In particular, we have demonstrated the generation of highly reactive 3-dehydropyridinium ylids whose chemistry indicates an ylid rather than a cumulene structure. These 3-dehydropyridinium ylids are rather elusive species which, if not trapped immediately, will undergo an intermolecular rearrangement to the 2-dehydropyridinium ylid. The reaction conditions, which permit these species to be generated at low temperatures in the absence of complicating factors such as counter ions and strong acids and bases, allow mechanistic studies which would not be possible with these intermediates generated by other methods.

## Experimental Section

**General Methods.** Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. NMR spectra were recorded on a Bruker 250 MHz spectrometer. Mass spectra were determined on a TRIOS 2000 mass spectrometer operating in the electrospray mode. HPLC was performed using a Shimadzu 10-A instrument.

**General Procedure for the Reaction of Carbon Vapor with Substrate.** The carbon arc reactor was modeled after that described by Skell and co-workers.<sup>5</sup> Carbon was vaporized by striking an intermittent arc between two graphite rods attached to water-cooled brass electrodes and condensed on the walls of the reactor at 77 K at  $5 \times 10^{-2}$  Torr. The quantities of carbon given below are calculated from the loss of weight of the electrodes. Since most of the carbon is lost in macroscopic pieces, yields based on carbon are not meaningful. Carbon was either cocondensed with degassed substrate or condensed on a layer of substrate. In the latter case, a number of condensation cycles were generally run. At the conclusion of the reaction, the liquid nitrogen bath was removed, and the reactor was allowed to warm to room temperature. The reactants and some volatile products were pumped to a trap at 77 K. The residue in the reactor bottom was first extracted twice with 20 mL of CH<sub>2</sub>Cl<sub>2</sub> containing several drops of concentrated HCl and further extracted three times with 20 mL of MeOH containing several drops of concentrated HCl. The combined CH<sub>2</sub>Cl<sub>2</sub> extracts were generally found to contain mainly starting material. The combined MeOH extract was filtered, the solvent was evaporated, and the residue was analyzed by NMR (<sup>1</sup>H, <sup>2</sup>H, and <sup>13</sup>C as appropriate) and electrospray ms. With the exception of 3-iodo-*N*-methylpyridinium chloride, **9a**, all products were identified by comparing their spectra with those of authentic samples synthesized by literature procedures.<sup>14</sup>

**The Reaction of C with *N*-Methylpyrrole, **5b**.** Carbon (1.3 g, 108.3 mmol) and **5b** (3.00 g, 37.0 mmol) were cocondensed at 77K. The MeOH–HCl extract contained *N*-methylpyridinium chloride, **8** (0.19 mmol as determined by <sup>1</sup>H NMR). **8**: <sup>1</sup>H NMR (250 MHz, D<sub>2</sub>O) δ 4.27 (s, 3H), 7.92 (bt, *J* = 7.5 Hz, 2H), 8.41 (t, *J* = 7.8 Hz, 1H),

(14) Zoltewicz, J. A.; Cross, R. E. *J. Chem. Soc., Perkin Trans. II* **1974**, 1363.

(15) The deuterated *N*-methylpyrroles were prepared using the procedure for the unlabeled compound: Santaniello, E.; Farachi, C.; Ponti, F. *Synthesis* **1979**, 617.

8.66 (d,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (62.5 MHz,  $\text{D}_2\text{O}$ )  $\delta$  48.50, 127.97, 145.00, 145.27; ES-MS ( $\text{E}^+$ )  $m/z$  (rel intensity), 94.3(100), 95.3(8.9).

**The Reaction of C with *N*-Methylpyrrole, 5b, and  $\text{CH}_3\text{I}$ .** Carbon (1.2 g, 100 mmol), **5b** (3.66 g, 47.5 mmol), and  $\text{CH}_3\text{I}$  (6.6 g 46.5 mmol) were cocondensed at 77 K. The MeOH-HCl extract contained **8** and 3-iodo-*N*-methylpyridinium chloride, **9a**, in a 4:1 ratio as determined by  $^1\text{H}$  NMR. The 3-iodo-*N*-methylpyridinium chloride ( $1.6 \times 10^{-5}$  m) was separated from **8** by RP-HPLC. **9a**:  $^1\text{H}$  NMR (250 MHz,  $\text{D}_2\text{O}$ )  $\delta$  4.22 (s, 3H), 7.68 (dd,  $J = 6.2$  Hz, 8.4 Hz, 1H), 8.75 (d,  $J = 8.4$  Hz, 1H), 8.69 (d,  $J = 6.2$  Hz, 1H), 9.06 (s, 1H);  $^{13}\text{C}$  NMR (62.5 MHz,  $\text{D}_2\text{O}$ )  $\delta$  49.3, 128.3, 138.0, 144.2, 151.1, 153.8; ES-MS ( $\text{E}^+$ )  $m/z$  (rel intensity), 220.1(100), 221.1(7.7), ES-MS ( $\text{E}^-$ )  $m/z$ , 127.

**The Reaction of C with 5b and  $\text{CH}_3\text{Cl}$ .** Carbon (1.0 g, 83.3 mmol), **5b** (2.31 g, 28.2 mmol) and  $\text{CH}_3\text{Cl}$  (2.0 g, 38.9 mmol) were cocondensed at 77 K. The MeOH-HCl extract contained **8** and 3-chloro-*N*-methylpyridinium chloride, **9b**, in a 3.3:1 ratio as determined by  $^1\text{H}$  NMR. **9b**:  $^1\text{H}$  NMR (250 MHz,  $\text{D}_2\text{O}$ )  $\delta$  4.29 (s, 3H), 7.96 (dd,  $J = 8.2$ , 6 Hz, 1H), 8.48 (dt,  $J = 8.2$ , 0.6 Hz, 1H), 8.68 (d,  $J = 6$  Hz, 1H), 8.94 (s, 1H);  $^{13}\text{C}$  NMR (62.5 MHz,  $\text{D}_2\text{O}$ )  $\delta$  48.6, 128.18, 134.71, 143.36, 141.244, 144.9; ES-MS ( $\text{E}^+$ )  $m/z$  (rel intensity), 128.3 (100), 129.3 (8.6), 130.3 (44.7).

**The Reaction of C with 5b and  $\text{CFCl}_3$ .** Carbon (1.1 g, 91.7 mmol), **5b** (2.4 g, 29.6 mmol), and  $\text{CFCl}_3$  (50.0 mmol) were cocondensed at 77 K. The MeOH-HCl extract contained **8**, **9b**, and 3-fluoro-*N*-methylpyridinium chloride, **9c**, in a 2.8:6.8:1 ratio as determined by  $^1\text{H}$  NMR. **9c**:  $^1\text{H}$  NMR (250 MHz,  $\text{D}_2\text{O}$ )  $\delta$  4.32 (s, 3H), 7.97-8.04 (m, 1H), 8.32 (bt,  $J = 5.5$  Hz, 1H), 8.62 (d,  $J = 6.3$  Hz, 1H), 8.94 (bs, 1H);  $^{13}\text{C}$  (62.5 MHz,  $\text{D}_2\text{O}$ )  $\delta$  48.7, 129.2 (d,  $J = 8$  Hz), 132.85 (d,  $J = 19$  Hz), 135.15 (dt,  $J = 18$  Hz), 142.19 (bs), 160.1 (d,  $J = 250$  Hz); ES-MS ( $\text{E}^+$ )  $m/z$  (rel intensity), 112.3 (100), 113.3(9.0).

**The Reaction of C with 5b and  $\text{CClF}_3$ .** Carbon (1.4 g, 116.7 mmol), **5b** (2.6 gram, 32.1 mmol), and  $\text{CClF}_3$  (50.0 mmol) were cocondensed at 77 K. The MeOH-HCl extract contained **8**, **9b**, and **9c** in a 2:1:1.5 ratio as determined by  $^1\text{H}$  NMR.

**Reaction of 5b with  $\text{CO}_2$ .** Carbon (0.75 g, 62.5 mmol), **5b** (1.7 g, 21 mmol), and  $\text{CO}_2$  (7.8 g, 236 mmol) were cocondensed at 77 K. The MeOH-HCl extract contained **8** and 1-methyl-3-pyridinium carboxylate, **12**, in a 1.2:1 ratio as determined by  $^1\text{H}$  NMR. **12**:  $^1\text{H}$  NMR (250 MHz,  $\text{D}_2\text{O}$ )  $\delta$  4.35 (s, 3H), 8.06 (t,  $J = 7$  Hz, 1H), 8.94-8.85 (bm, 2H), 9.28 (s, 1H);  $^{13}\text{C}$  NMR (62.5 MHz,  $\text{D}_2\text{O}$ )  $\delta$  48.9, 128.3, 134.7, 145.5, 146.6, 147.3, 166.5; ES-MS  $m/e$  (rel intensity) 138.3 (100), 139.3 (12).

**Reaction of  $^{13}\text{C}$  Enriched Carbon Vapor with 5b.** A  $0.125 \times 1$  in. hole was drilled in a 0.25 in. diameter high purity graphite rod. The hole in this 3.0 g rod was filled with 0.129 g amorphous carbon-13 (99.4%  $^{13}\text{C}$ ). The rod was placed in the reactor and resistively heated under vacuum at a current of 100 A by keeping it in touch with an unlabeled graphite rod for 2 min. The heating cycle was repeated five times. The rod was placed in the reactor, and an arc was struck between it and an unlabeled rod. Enriched carbon vapor (1.01 g, 86.2 mmol) was reacted with 0.8 g (9.8 mmol) **5b** as described above. The  $^{13}\text{C}$  NMR spectrum of **8** showed peaks at  $\delta = 48.5$  (Me), 127.97 ( $\text{C}_3$ ), 145 ( $\text{C}_4$ ), 145.27 ( $\text{C}_2$ ) in a 1:30.7:2.1:3.8 intensity ratio. ES-MS  $m/e$  (rel intensity) 94.3 (100), 95.3 (24). The spectrum of unlabeled **8** showed these same peaks in a 1:5.6:2.3:2.0 intensity ratio. We assume that no

$^{13}\text{C}$  is incorporated into the methyl of **8** and conclude that 87% of the excess  $^{13}\text{C}$  is on  $\text{C}_3$  with 12.5% on  $\text{C}_2$  and 0.5% on  $\text{C}_1$ .

**The Reaction of C with 5b and  $\text{CH}_3\text{OD}$ .** Carbon (0.75 g, 62.5 mmol), **5b** (1.7 g, 21 mmol), and  $\text{CH}_3\text{OD}$  (7.8 g, 236 mmol) were cocondensed at 77 K. To the cold condensate was added 2 mL of 1 N HCl-30 mL of MeOH. Analysis of **8** by  $^2\text{H}$  NMR revealed deuterium only in the 3 position,  $^1\text{H}$  NMR showed  $\text{H}_2:\text{H}_3:\text{H}_4$  in a 2.0:1.5:1 ratio. ES-MS  $m/e$  (rel intensity) 94.3 (31), 95.3 (100), 96.3 (17).

**The Reaction of C with 5b followed by  $\text{CH}_3\text{OD}$ .** Carbon (1.40 g 116.7 mmol), and **5b** (2.5 g, 21 mmol) were cocondensed at 77 K. To the cold condensate was added  $\text{CH}_3\text{OD}$  (8.8 g, 267 mmol). After warming to room temperature was added 2 mL of 1 N HCl-20 mL of  $\text{CH}_3\text{OH}$ . Analysis of **8** by  $^2\text{H}$  NMR revealed deuterium only in the 2 position.  $^1\text{H}$  NMR showed  $\text{H}_2:\text{H}_3:\text{H}_4$  in a 0.89:1.98:1 Ratio. ES-MS  $m/e$  (rel intensity) 94.3 (100), 95.3 (91), 96.3 (28).

**The Reaction of C with 5b and  $\text{CH}_3\text{OD}$  Layered on the Reactor Bottom.** A layer of  $\text{CH}_3\text{OD}$  was condensed on the cold reactor bottom. Carbon vapor and **5b** were then cocondensed in ten short bursts of the arc and the process was repeated until the supply of **5b** was exhausted. A total of 1.0 g (83.3 mmol) of carbon, 2.5 g (30.9 mmol) of **5b**, and 3 mL (80.7 mmol) of  $\text{CH}_3\text{OD}$  was added at 77 K. To the cold reactor bottom was added 30 mL of 1 N HCl. Analysis of **8** by  $^2\text{H}$  NMR revealed deuterium in the 2 and 3 positions in a 3:1 ratio.  $^1\text{H}$  NMR showed  $\text{H}_2:\text{H}_3:\text{H}_4$  in a 0.91:1.73:1 ratio. ES-MS  $m/e$  (rel intensity) 94.3 (100), 95.3 (91), 96.3 (28).

**Reaction of C with *N*-Trideteromethylpyrrole, 14.** Carbon (0.66 g, 55 mmol) and **14**<sup>15</sup> (1.1 g, 13 mmol) were cocondensed at 77 K. To the cold condensate was added 2 mL of 1 N HCl-20 mL of MeOH. Analysis of **8** by  $^2\text{H}$  NMR revealed deuterium only on the methyl group. ES-MS  $m/e$  (rel intensity) 97.3 (100), 98.3 (19.5).

**The Reaction of C with a Mixture of 5b and 5b-1,2,3,4-d<sub>4</sub>.** Carbon (0.26 g, 21.6 mmol), **5b** (0.35 g, 4.3 mmol), and **5b-1,2,3,4-d<sub>4</sub>**<sup>15</sup> (0.30 g, 3.5 mmol) were cocondensed at 77 K. To the cold condensate was added 1 mL of 12 N HCl-10 mL of MeOH. Analysis of **8** by  $^2\text{H}$  NMR revealed deuterium in the 2, 3, and 4 positions in a 1.88:1.77:1 ratio. The  $^1\text{H}$  NMR showed  $\text{H}_2:\text{H}_4:\text{H}_3$ : *N*-Me in a 0.36:0.367:0.188:1 ratio. ES-MS  $m/e$  (rel intensity) 94.3 (100), 95.3 (51.5), 96.3 (7.7), 97.3 (14.7), 98.3 (74.7), 99.3 (31.8).

**Reaction of 13 with  $\text{O}_2$ .** Carbon (0.65 g, 54.2 mmol) and **5b** (2.63 g, 32.5 mmol) were cocondensed at 77 K. To the cold condensate was added 5 Torr  $\text{O}_2$ . The ether extract of the reactor bottom was purified by flash silica gel column chromatography ( $\text{CH}_2\text{Cl}_2$ - $\text{Et}_2\text{O}$ -MeOH) and found to contain 1-methyl-2-pyridone, **16**, which was identified by comparison of its  $^1\text{H}$  NMR with that of an authentic sample. **16**:  $^1\text{H}$  NMR (250 MHz,  $\text{D}_2\text{O}$ )  $\delta$  3.55 (s, 3H), 6.18 (dt,  $J = 6.75$ , 1.34 Hz, 1H), 6.54 (dt,  $J = 8.75$ , 0.92 Hz, 1H), 7.31-7.38 (m, 2H);  $^{13}\text{C}$  NMR (62.5 MHz,  $\text{D}_2\text{O}$ )  $\delta$  37.56, 105.90, 120.58, 138.38, 139.56, 163.12.

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