Mechanism of the Reaction of Atomic Carbon with Pyrrole. Evidence for the Intermediacy of a Novel Dehydropyridinium Ylide

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In view of the fact that atomic carbon is a precursor to a wide spectrum of fascinating clusters[1] and a variety of energetic intermediates,[2] it is important to understand the reactivity of this interesting species. We report here an investigation of the reaction of carbon atoms with pyrrole **1**, in which we demonstrate that carbon attacks at the HOMO to produce pyridine in a reaction which proceeds via the intermediacy of a unique dehydropyridinium ylide. We have proposed that atomic carbon, an electron deficient species, attacks substrate at the point of highest electron density in the HOMO.[3] This proposal leads to the rather surprising conclusion that atomic carbon, although extremely energetic, should be rather discriminating in its initial point of attack on substrate. That carbon does exhibit such behavior is exemplified by its reaction with tetrahydrofuran and furan in which the former is deoxygenated to ethylene and CO while the latter adds carbon to a double bond leading ultimately to 4-pentyn-2-enal.[3]

In order to further test our postulated proclivity for attack by carbon at the point of highest electron density in the HOMO, we have investigated the reaction of carbon with pyrrole, **1**, a reaction which we have previously observed to produce pyridine.[4] Since the heteroaromatic **1**, like furan, has no electron density on the most electronegative atom in the HOMO,[5] we expect initial attack to occur elsewhere in the molecule. Reaction of arc-generated carbon with **1** was carried out by cocondensing the two species at 77 K in a conventional carbon arc reaction.[6] Examination of the volatile products by ^1H and ^{13}C NMR spectroscopy revealed that the only detectable product was pyridine, certainly the most stable species on the C_5H_5N energy surface. Scheme 1, in which the attacking carbon is labeled with an asterisk and X = H or D, illustrates four possible mechanisms for pyridine formation. Attack at N could produce ylide **2**, which could rearrange to carbenes **3** and/or **4**, leading to a pyridine in which the attacking carbon and X are both at the 2-position. C–H insertion at C_2 would give carbene **5**, which upon ring expansion yields 1-azacyclohexa-2,3,5-triene, **6**, labeled at the 2-position by attacking carbon. Like, C–H insertion at C_3 yields carbene **7**, which, upon ring expansion, also yields **6**, now labeled at the 4-position. Attack of carbon at the double bond should yield bicyclic carbene **8**, which is expected to ring open to **6** labeled at the 3-position with the attacking carbon. A [1,5] sigmatropic migration of the H (or D) on N in **6** would subsequently yield pyridine labeled in the 3-position with X. The three mechanistic pathways leading to **6** in Scheme 1 can, in principle, be distinguished, as the attacking carbon will end up on three different carbons in the product pyridine.

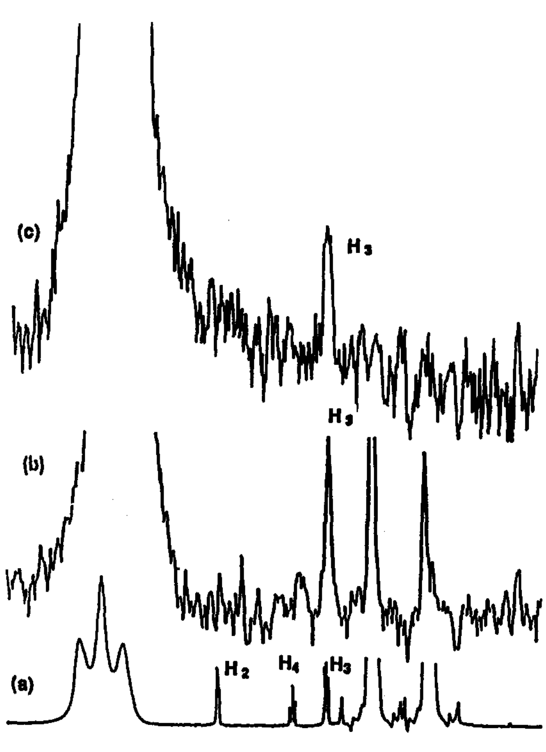
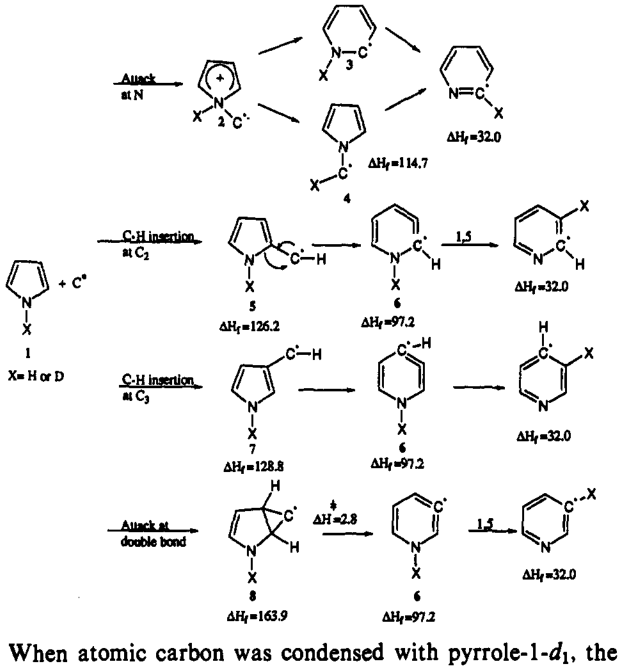


Figure 1. (a) ^1H NMR spectrum of the products of C + **1**; H_2, H_3, and H_4 are the pyridine protons. (b) ^2H NMR spectrum of the products of C + **1**-d_1. (c) ^2H NMR spectrum of the products of C + **1** + CH_3OD.

Scheme 1



When atomic carbon was condensed with pyrrole-1-d_1, the deuterium NMR spectrum (shown in Figure 1b) revealed that the only position in which deuterium could be detected in the pyridine the the C_3 position. This result rules out formation of pyridine by attack of carbon on nitrogen.

In order to distinguish between the remaining three modes of attack of C on pyridine, it was necessary to use ^{13}C-labeled carbon atoms. This was done by packing two graphite rods with ^{13}C carbon powder and striking an arc between them while condensing **1** at 77 K under the usual conditions. In this way, it was possible to generate carbon vapor partially labeled with ^{13}C. An examination of the ^{13}C NMR spectrum of the pyridine generated

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(1) For recent reviews, see: Billups, W. E., Ciufolini, M. A., Eds. *Buckminsterfullerenes*; VCH: New York, 1993.

(2) 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.

(3) Dyer, S. F.; Shevlin, P. B. *J. Am. Chem. Soc.* **1979**, *101*, 1303.

(4) Pan, O.-G. Ph.D. Dissertation, Auburn University.

(5) Jorgenson, W. L.; Salem, L. *The Organic Chemists Book of Orbitals*; Academic Press: New York, 1972; pp 231–233.

(6) The reactor is modeled after that described by Skell et al.; Skell, P. S.; Wescott, L. D., Jr.; Golstein, J. P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829.

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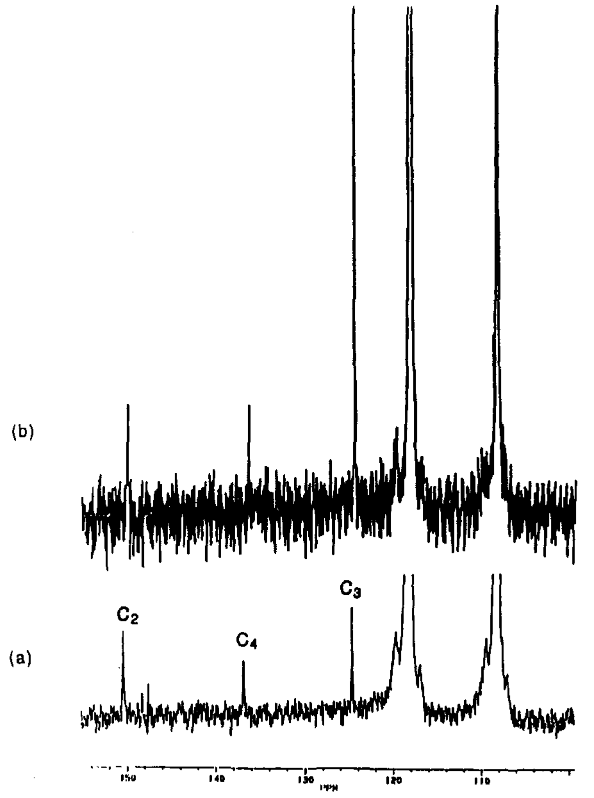
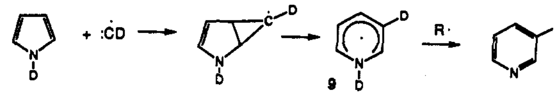


Figure 2. (a) ^{13}C NMR spectrum of the products of C + **1**; C_2, C_3, and C_4 are the pyridine carbons. (b) ^{13}C NMR spectrum of the products of ^{13}C + **1**.

in this reaction (Figure 2b) indicated an enrichment of carbon at the 3-position of the pyridine, as expected for attack by carbon on the double bond as shown in Scheme 1.

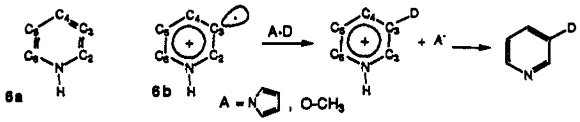
A qualitative investigation of the C_6H_5N energy surface in these reactions with the AM1[7] semiempirical method supports the experimental conclusions. Scheme 1 shows AM1 energies (in kilocalories/mole) of relevant intermediates on the C_6H_5N energy surface. It is interesting that AM1 does not calculate symmetric ylide **2** to be an energy minimum. Instead the attacking carbon has moved 60° out of the C_2–N_1–C_5 plane to give an intermediate in which it is close to equidistant from each of these atoms. In any case, this intermediate is calculated to be of higher energy than any of the others and would not be expected to lie on the reaction path. Carbenes **5** and **7** are calculated to lie at lower energy than bicyclic carbene **8** with its considerable ring strain. However, AM1 calculates a barrier of only 2.8 kcal/mol for rearrangement of **8** to azacyclohexatriene **6**, the lowest energy of the reactive intermediates in this system.

These experimental and computational results are in accord in demonstrating that carbon attacks **1** at the double bond to give azacyclohexatriene, **6**. However, the mechanism of rearrangement of **6** to pyridne is more problematical. An examination of the geometry calculated for **6** reveals that the H on N is in the plane of the ring 3.3 Å from C_3, rendering the [1,5] shift difficult.[8] Hence, we have considered two intermolecular routes to pyridine in this system. The first involves an initial D abstruction by C to generate CD, which adds to **1** to give, after ring opening, radical **9** (eq 1). However, we were able to exclude this mechanism by reacting carbon with **1** in the presence of toluene-α-d_3 and observing that the pyridine produced did not contain deuterium. Since it would be expected that the abstractable deuterium atoms on toluene would allow the formation of CD leading to pyridine-3-d_1, the mechanism in eq 1 is ruled out.



(1)

An examination of geometry and charges calculated for **6** provides a clue to its reactivity. Since the hydrogen atoms on C_2 and C_4 lie in the plane of the ring (H–C_2–C_4–H dihedral angle = 0.91°) and C_3 has a calculated charge of –1.12, **6** is best represented as pyridinium ylide **6b** rather than as allene **6a**. Reoptimization of the geometry of **6** with no symmetry constraints using Gaussian 92[9] at the MP2/631-G* level gives similar results with a H–C_2–C_4–H dihedral angle of 0.79° and a calculated charge of –1.08 on C_3. Hence, it is expected that **6b** will be readily protonated to yield the pyridinium ion providing the intermolecular route to pyridine-3-d_1 shown in eq. 2. That this



(2)

is actually the case has been demonstrated by cocondensing **1** and CH_3OD with carbon at 77 K and observing the production of pyridine-3-d_1 (Figure 1c).

The planarity of **6** may be contrasted with that of 1,2-cyclohexadiene, which has been shown to be nonplanar,[10] and 1,2,4-cyclohexatriene,[11] which is calculated (AM1) to have a H–C–C–H dihedral angle across the allenic system of 38°.[12] Other geometric features of **6** indicating its heteroaromatic character are the AM1-calculated C_4–C_5 and C_5–C_6 bond distances, which are both 1.40 Å (MP2/631-G* calculates 1.40 and 1.38 Å). In contrast AM1 calculates 1,2,4-cyclohexatriene to have C_3–C_4 and C_4–C_5 bond distances of 1.47 and 1.35 Å.[12]

These results illustrate the propensity of carbon to bring about the formation of interesting reactive intermediates and lend further support to the notion that atomic carbon, despite its extremely high energy, exhibits a frontier molecular orbital directed selectivity in its reactions with organic substrates. In this case, the high energy of carbon atoms is channeled into the production of a novel dehydropyridinium ylide.

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[7] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[8] An AM1 search for the transition state for the rearrangement of **6** to pyridine locates a high-energy (ΔH_f = 158.9 kcal/mol) transition state that seems to be leading to a carbene (1-aza-1,3-cyclohexadien-4-ylidene) rather than to pyridine. Of course, the barrier for rearrangement of this carbene to pyridine is expected to be low.

[9] Gaussian 92, Revision F.3. M. J. Frisch, G. W. Trucks, M Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople. Gaussian, Inc., Pittsburgh, PA, 1992.

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[11] Christl, M.; Braun, M.; Mueller, G. Angew, Chem., *Int. Ed. Engl.* **1992**, *31*, 473.

[12] Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 476.