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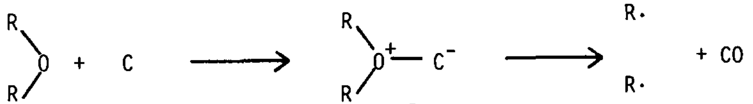
THE CLEAVAGE OF 2,5-DIHYDRO-2-FURANYLCARBENE

Phillip C. Martino and Philip B. Shevlin*

Department of Chemistry, Auburn University, Alabama 36849

ABSTRACT: Atomic carbon reacts with 2,5-dihydrofuran to effect deoxygenation and by C-H insertion to give 2,5-dihydro-2-furanylcarbene which subsequently cleaves to two molecules of acetylene and formaldehyde.

Atomic carbon is an electrophilic species which generally attacks organic molecules at the point of highest electron density.[1] Oxygenated compounds are often attacked on the oxygen to generate an initial ylid, 1. Subsequent decomposition of ylid 1 often yields carbon monoxide and a pair of radicals (eq 1). An interesting exception occurs in the reaction of carbon atoms with furan. Since there is no electron density on oxygen in the highest occupied molecular orbital (HOMO) of furan, attack occurs on the π bond as shown in eq 2.[2]



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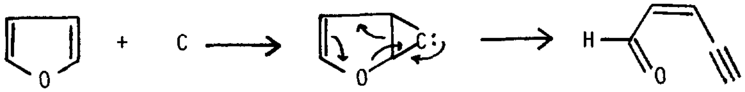
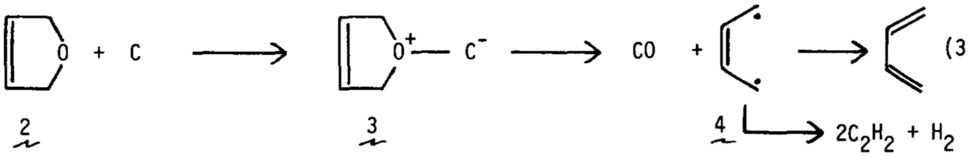
(1)



(2)

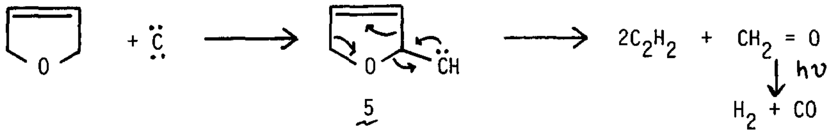
The reaction of arc generated carbon with 2,5-dihydrofuran, 2, has been reported to produce ylid 3 which subsequently deoxygenates as shown in eq 3.[3] An interesting feature of the process shown in eq 3 is the postulated cleavage of biradical 4 to hydrogen and two molecules of acetylene. Although the deoxygenation of 2 is extremely exothermic and would presumably provide enough energy



(3)

for the cleavage of 4 to occur, such a reaction is without precedent in the literature.

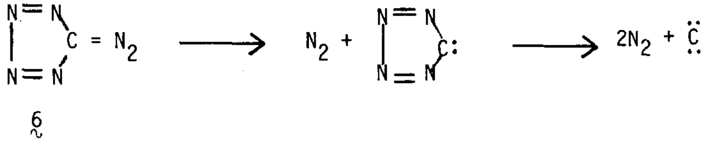
An alternative mechanism for the formation of hydrogen, acetylene and some of the carbon monoxide is an initial insertion into an allylic C-H bond to generate carbene 5. Subsequent cleavage



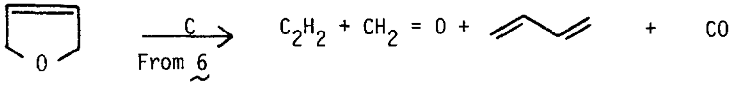
(4)

of 5 could yield two molecules of acetylene and formaldehyde as shown in eq. 4. Since the carbon arc is known to be a good source of uv light, it is reasonable to assume that the formaldehyde could photolyse to carbon monoxide and hydrogen; a process which has been reported.[4]

In order to test the possibility shown in eq 4, we have generated atomic carbon by the thermolysis of 5-diazotetrazole, 6,[5] and have reacted it with 2. Since this method of generating atomic carbon involves no possible source of uv light, the process shown in eq 4 should lead to isolable amounts of formaldehyde.



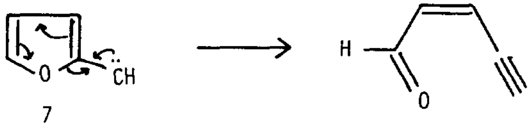
When 6 (9.8 x 10^{-2} mmole) was pyrolysed in an atomosphere of 2 (5.0 mmole), the products were carbon monoxide (5.2 x 10^{-4} mmole), 1,3-butadiene (5.7 x 10^{-4} mmole), acetylene (4.0 x 10^{-3} mmole) and formaldehyde (6.9 x 10^{-4} mmole). These results can be rationalized by assuming that



there are two pathways for the reaction of atomic carbon with 2. One pathway involves attack on oxygen to generate ylid 3 which loses carbon monoxide to generate 1,3-butadiene as shown in eq. 3. The formaldehyde and acetylene are best rationalized as arising from a competing C-H insertion to generate carbene 5 which cleaves as shown in eq. 4. In this case however, subsequent photolysis of the formaldehyde does not occur.[6]

In order to determine if this C-H insertion is unique to systems in which carbon atoms are generated by thermolysis of 6, we have carried out the reaction of arc generated carbon atoms with 2. This reaction was carried out by cocondensing carbon atoms with 2 at -196° in an apparatus similar to that described by Skell.[1b] Although the non-condensible gasses H_2 and CO were not determined in this investigation, the results indicate that C-H insertion competes with deoxygenation in this system as well. Thus, cocondensation of carbon (2.78 x 10^{-2} mmol) with 2 (7.15 x 10^{-2} mmol) produces 1,3-butadiene (9.4 x 10^{-5} mmol) formaldehyde (1.1 x 10^{-4} mmole) and acetylene (4.9 x 10^{-4} mmol). In this case, the ratio of acetylene to formaldehyde is larger than 2 as some acetylene results from hydrogen abstraction by C_2.

Since carbene 5 has not been generated by conventional methods, the cleavage shown in eq 4 has not been reported. However, a similar cleavage was observed by Schecter and Hoffman[7] when carbene 7 was generated by tosylhydrozone salt pyrolysis (eq 5). In this case, the presence of the additional double bond precludes fragmentation to small molecules. We are currently attempting to generate carbene 5 by conventional methods and observe its rearrangement.



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(5)

An examination of the eigenvectors of the HOMO of 2, calculated by the MNDO method[8] indicates that there is considerable electron density of the π-CH_2 orbitals.[9] We propose that an interaction between the occupied π-CH_2 orbitals and an empty p orbital on the attacking carbon lowers the energy of the transition state for C-H insertion causing this process to compete with attack on oxygen. The interaction between the HOMO of 2 and the carbon p orbital leading to C-H insertion is depicted in Figure 1. Figure 2 shows the interaction between the attacking carbon and 2 which leads to deoxygenation. It is interesting that we can find no products corresponding to attack of the carbon atom on the carbon-carbon double bond. This seems surprising

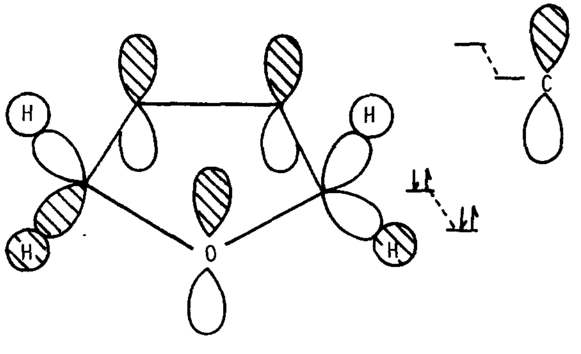

Figure 1

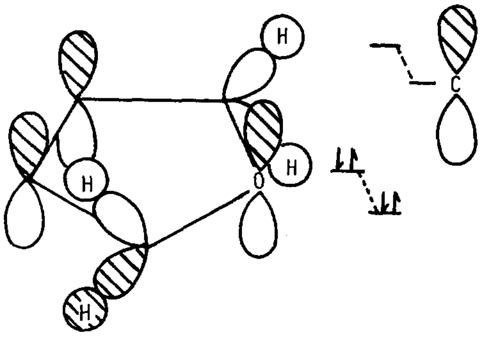

Figure 2

when one considers that there is a considerable contribution of this π orbital to the HOMO of **2** (Figures 1 and 2). However, frontier MO theory predicts that the magnitude of the coefficients of the HOMO and the overlap between the orbitals of **2** and those of attacking carbon will determine the position of attack.[10] It is possible that the overlap between the π-CH_2 orbitals and the empty p orbital on carbon is more effective than that between the double bond π-orbitals and the orbitals of the attacking carbon.

Acknowledgment: Finanical support by the National Science Foundation under grant no CHE-8103034 is gratefully acknowledged.

References and Notes:

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6. The fact that the yield of acetylene is more than twice that of formaldehyde indicates that there are other reactions which form this molecule. Appreciable yields of C_2H_2 are always observed in the reactions of atomic carbon.[1] This is especially true of gas phase reactions in which excess energy is not dissipated.[5]
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