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FORMATION OF CYCLOBUTA[b]PYRIDINE AND CYCLOBUTA[c]PYRIDINE BY THE PYROLYSIS OF PROPARGYL 4-PYRIDYL ETHER

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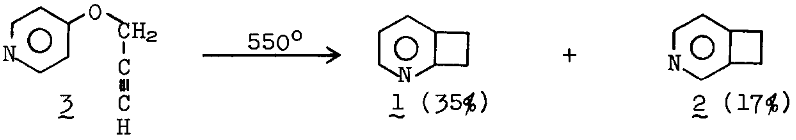
The flash vacuum pyrolysis (FVP) of aryl propargyl ethers provides a convenient route to substituted 2-indanones and 1,2-dihydrobenzocyclobutenes.[1,2] In this communication we wish to report that the pyridine analogs of 1,2-dihydrobenzocyclobutene, cyclobuta[b]pyridine (1) and cyclobuta[c]pyridine (2) can be obtained by the FVP of propargyl 4-pyridyl ether (3). The parent

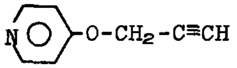
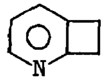
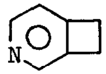
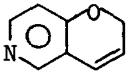


compounds 1 and 2 have been reported only recently[3] and the number of known compounds that possess these ring systems is quite small.[4] Compounds 1 and 2 are of special interest since they are nitrogen analogs of 1,2-dihydrobenzocyclobutenes, a class of compounds which is of importance in the synthesis of both theoretically interesting molecules and natural products.[5]

The above reaction is also of interest since it establishes that the pyridine ring behaves in a fashion similar to that of the benzene ring in the pyrolysis of aryl propargyl ethers. Moreover, the production of both isomers 1 and 2 raises some interesting questions concerning the mechanism of this reaction since the pyrolysis of a 4-substituted phenyl propargyl ether gives rise to only one substituted 1,2-dihydrobenzocyclobutene, not two.[2]

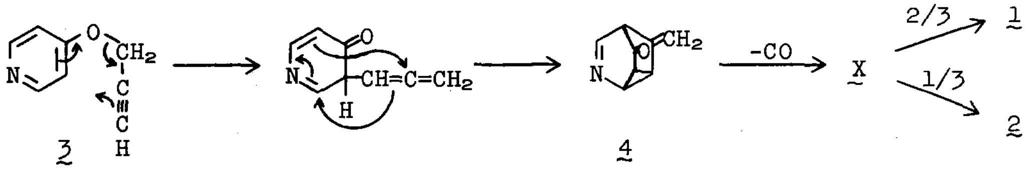
In the Table are presented the yields of the products from the pyrolysis of 3[6,7] at temperatures from 400-650°.[10] At 550° no starting material is recovered and the major products are pyridines 1 and 2 obtained in the ratio of 2.1:1.0. Even at a temperature of 400° where much starting material is recovered the ratio of 1 to 2 produced is 1.7. The average ratio for the 4

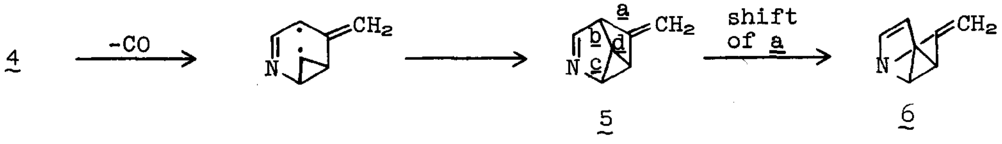
TABLE Products from the Pyrolysis of Propargyl 4-Pyridyl Ether (3)

Compound	Yield, %[a] 400°	500°	550°	650°
 (3)	62.4 ± 4.0	4.9 ± 2.5	-	-
 (1)	8.7 ± 2.6	30.6 ± 1.0	34.7 ± 4.1	30.1 ± 5.5
 (2)	5.1 ± 0.5	16.8 ± 2.4	16.9 ± 2.5	14.6 ± 2.3
	7.1 ± 2.5	9.4 ± 1.9	4.7 ± 0.4	trace
TOTAL	83.3	61.7	56.3	44.7

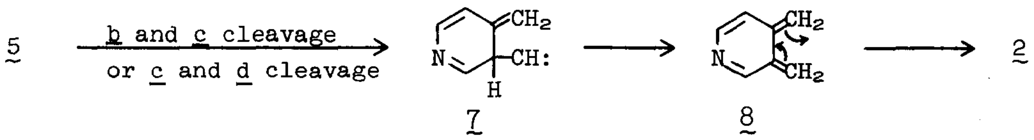
[a] Yields based on 2 or more determinations

sets of data obtained over the temperature range of 400-650° is 1.9 ± 0.2. No isomerization of 1 to 2 was detected when pyridine 1 was resubmitted to the pyrolysis conditions at 550°; only 1 was recovered. The following mechanism, which is similar to that proposed for the formation of 2-indanones from aryl propargyl ethers,[1] accounts for these results. The symbol X represents an intermediate or set of intermediates which scrambles the position of the nitrogen atom. A reasonable possibility is that 4 loses CO, probably by a diradical mechanism, to form 5. Intermediate 5 could rearrange to 6 by a [1,3] sigmatropic shift involving bond a. This shift would most likely





proceed through a diradical since the constraints of the bicyclic system demand a suprafacial shift which is symmetry-forbidden.[11] Intermediate 5 by cleavage of bonds b and c or c and d could give carbene 7 which could



form 2 via 8. The corresponding bond cleavages of 6 would lead to a similar sequence resulting in the formation of 1. Intermediates 5 and 6 could undergo other rearrangements that would form other intermediates that could go on to 1 or 2. Without further information the number of conceivable routes to form 1 and 2 is quite large and at this time we favor no unique pathway. The main point is that these azatricyclic intermediates do offer reasonable mechanisms for scrambling the position of the nitrogen atom. A more definite route must await the results of additional experiments.

It should be noted that the ratio of 1 to 2 is essentially constant over a 250° temperature range and its value is almost equal to an integer value. These facts suggest that the value of two is a statistical factor. However this temperature independent ratio of two could result from two pathways having the same temperature dependence and relative rates that differ by a factor of two.

It is not clear why the intermediate tricyclic ketone tends to lose CO more readily in the pyridine system than in the benzene system. Presumably the relative stabilities of the intermediate diradicals account for this. The lack of scrambling of the benzene ring positions in the formation of the 1,2-dihydrobenzocyclobutenes from the phenyl ethers could mean that the CO is lost from an intermediate that follows the tricyclic ketone or that the intermediate tricyclic hydrocarbon formed by the loss of CO from the ketone opens up immediately before scrambling can occur.

The minor pyrolysis product, 2*H*-pyrano[3,2-c]pyridine[12] can be accounted for by the mechanism proposed for the conversion of aryl propargyl ethers to benzopyrans in the liquid phase.[13]

In conclusion, the FVP of propargyl 4-pyridyl ether is a good source of cyclobuta[b]pyridine and cyclobuta[c]pyridine and the mechanism of this reaction must involve extensive scrambling of the pyridine atoms which is not the case with the benzene system.[2]

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References and Notes:

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6. Compound **3**: mp 77.0-77.5°, NMR ($CDCl_3$) δ7.70 (AA'BB' pattern, ν_a~8.50, ν_b~6.90, 4H), 4.71 (d, *J* = 2.5 Hz, 2H), 2.60 (t, *J* = 2.5 Hz, 1H); ir($CHCl_3$) 3310, 3020, 2980, 2130, 1595, 1578, 1505, 1288, 1030 cm^{-1}; exact mass calcd for C_8H_6NO(P-1): 132.0449; found: 132.0450.
7. Ether **3** was prepared from 4-nitropyridine oxide following the procedure of Hertog and Combe[8] with the exception that sodium 2-propyn-1-olate in 2-propyn-1-ol[9] was used instead of sodium hydroxide and the alcohol. Also, the product of the first step was the pyridine oxide-hydrochloric acid adduct, not the free pyridine oxide.
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10. The pyrolysis conditions and work up were the same as those described in footnote 2 of reference 2. All yields were determined by PMR analysis and the products were isolated by GLPC. The PMR spectra of the products agreed with those reported.
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