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ELECTROPHILIC ADDITION TO o-ArY-SUBSTITUTED PHENYLALKYNES. A HIGHLY SELECTIVE CYCLIZATION CONTROLLED BY HETEROATOMS

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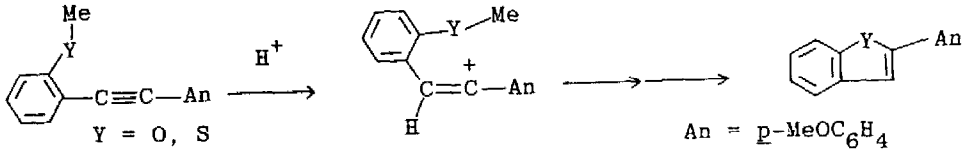
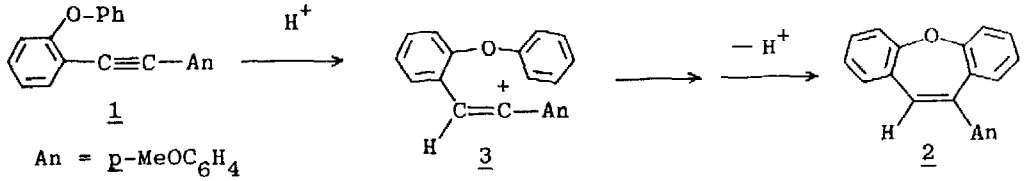
Summary: Treatment of o-(phenyloxy)phenylalkyne 1 with $HClO_4$ or HBF_4 gave dibenz(b,f)oxepin 2, whereas the sulfur analogue, o-(phenylthio)phenylalkyne 3, provided 1-phenyl-1-benzothiophenium salts 4.

Arylalkynes containing a functional group such as OR, SR, or NR_2 at the ortho position afford five-membered heterocycles by metal-induced intramolecular cyclization.[1,2] We also found the similar cyclization of o-methylheteroatom-substituted arylalkynes induced by proton, providing an efficient route to synthesize heterocycles.[3] This reaction proceeds



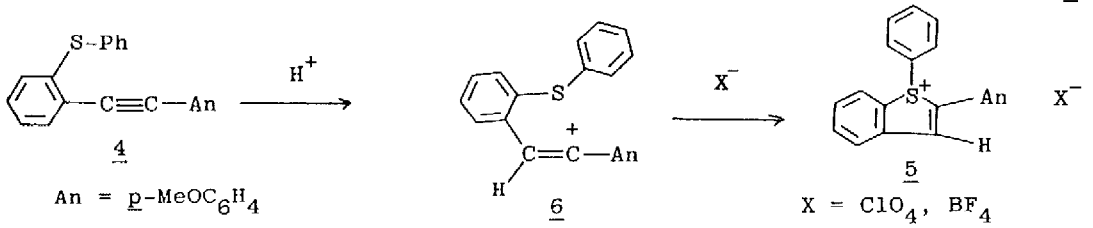
through a multistep sequence in which protonation of the triple bond is followed by nucleophilic attack of one of the lone pair of Y on the intermediate vinyl cation. This simple procedure provides a versatile synthesis of functionalized heterocycles. Then, we extended this intramolecular cyclization to o-ArY-substituted arylalkynes (Ar = phenyl; Y = O (1) or S (4)). Here we wish to report that five- and seven-membered heterocycles can be produced selectively by an electrophile-induced cyclization controlled by heteroatoms (oxygen and sulfur).

o-ArY-substituted phenylalkynes (1 and 4) were allowed to react with an acid. Treatment of 1-(p-methoxyphenyl)-2-(o-(phenyloxy)phenyl)ethyne (1) (1 mmol) with $HClO_4$ or HBF_4 (1.5 mmol) in acetic acid (3 ml)-CH_2Cl_2 (2 ml) at room temperature gave 5-(p-methoxyphenyl)dibenz(b,f)oxepin (2) in 74-80% isolated yield. This cyclization process is initiated by electrophilic addition of proton to the triple bond followed by intramolecular



electrophilic aromatic substitution of the resulting vinyl cation 3.

However, the corresponding sulfur analogue 4 behaved quite differently form 1. Similar treatment of 1-(p-methoxyphenyl)-2-(o-(phenylthio)phenyl)-ethyne (4) with $HClO_4$ or HBF_4 in acetic acid-CH_2Cl_2 afforded 1-phenyl-1-benzothiophenium perchlorate (5-ClO_4)[4] or tetrafluoroborate (5-BF_4)[4] in 65-69% isolated yield. No other products were detected. In the case of 4,



attack by sulfur atom on the resulting vinyl cation 6 is predominant probably because of a high nucleophilicity of sulfur atom and its large size, whereas in the case of 1 cyclization at the aryl ring is favored since the aryl ring is activated by electron-donating oxygen atom.

In summary, heteroatoms played a significant role on the cyclization of ArY-substituted systems 1 and 4. In addition to the methylheteroatom-substituted systems, these kinds of intramolecular cyclization provide a general synthetic method for heterocyclic compounds. We are now continuing to find the scope and limitations of this cyclization controlled by heteroatoms.

References

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2) R. C. Larock and L. W. Harrison, J. Am. Chem. Soc., 106, 4218 (1984).

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4) 2: mp 130-131 ℃; ^{1}H-NMR δ ($CDCl_3$) 3.82 (s, OMe), 6.83-7.47 (m, ArH); ^{13}C-NMR δ ($CDCl_3$) 55.28, 113.77, 120.78, 121.46, 124.51, 124.80, 127.22, 129.25, 129.39, 130.07, 130.12, 130.46, 130.86, 132.19, 134.91, 141.76, 153.91, 158.51, 159.38.

5-ClO_4: mp 189-193 ℃; ^{1}H-NMR δ ($CDCl_3$-DMSO-d_6) 3.81 (s, OMe), 6.91-8.21 (m, ArH); ^{13}C-NMR δ ($CDCl_3$-DMSO-d_6) 55.39, 115.18, 119.63, 123.89, 127.09, 127.62, 129.07, 130.01, 130.31, 131.24, 131.54, 133.42, 134.11, 134.91, 141.97, 142.73, 161.58.

5-BF_4: mp 177-187 ℃; ^{1}H-NMR δ ($CDCl_3$-DMSO-d_6) 3.80 (s, OMe), 6.91-8.21 (m, ArH); ^{13}C-NMR δ ($CDCl_3$-DMSO-d_6) 55.37, 115.18, 119.63, 123.86, 127.09, 127.61, 129.05, 130.01, 130.30, 131.25, 131.54, 133.41, 134.11, 134.91, 141.94, 142.71, 161.58.

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