HETEROCYCLE SYNTHESIS BY ELECROPHILIC ADDITION TO ACETYLENES

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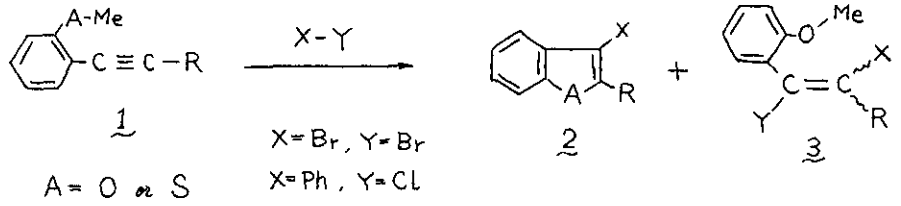
We studied on an application of electrophilic addition to acetylenes for synthesis of heterocycles, especially, 3-hetero atom-substituted benzofurans and benzothiophenes. The reaction of bromine or benzenesulfenyl chloride to acetylenes (1) gave heterocycles (2) and 1,2-addition compounds (3). The ratio of 2 to 3



1 2 3

depended both on the electrophiles and on the acetylenes. When R was p-methoxyphenyl group, the acetylenes examined here gave only 2. On the contrary, o-methoxyphenyl-1-propyne gave only 1,2-addition products (3) by both cases of bromine and benzenesulfenyl chloride. In case of R=C_6H_5 the reaction was influenced by the substituent on the triple bond. Benzothiophenes were exclusively formed, but benzofurans were given as the minor products. The reaction with benzenesulfenyl chloride gave the cyclized product more than the one with bromine did. The 1,2-addition products were mixtures of E- and Z-isomers in case of bromine, but stereospecifically E-isomers in case of benzenesulfenyl chloride.

Consequently, the reactions might be controlled by combination of electrophiles and substrates.