

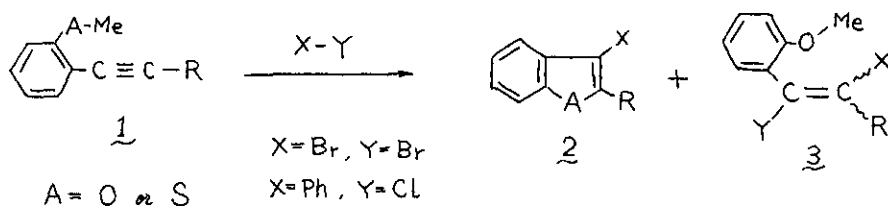
HETEROCYCLE SYNTHESIS BY ELECTROPHILIC ADDITION TO ACETYLENES

Shinjiro Kobayashi, Muneyuki Matsumoto, and Hiroshi Taniguchi

Department of Applied Chemistry, Faculty of Engineering, Kyushu University

Hakozaki, Higashi-ku, Fukuoka 812, Japan

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 benzenesulfonyl chloride to acetylenes (1) gave heterocycles (2) and 1,2-addition compounds (3). The ratio of 2 to 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 benzenesulfonyl 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 benzenesulfonyl 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 benzenesulfonyl chloride.

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