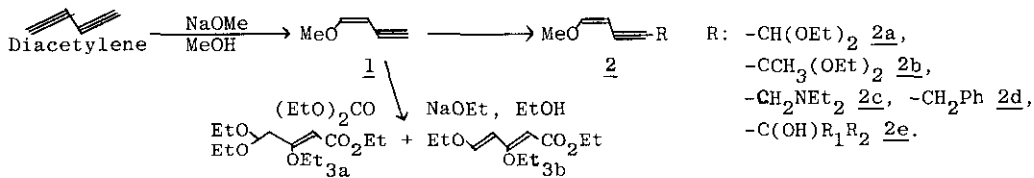


SYNTHESIS OF HETEROCYCLIC COMPOUNDS FROM DIACETYLENE AND ITS DERIVATIVES

Masaaki Takami, Yoichi Ninagawa and Yoshiaki Omura

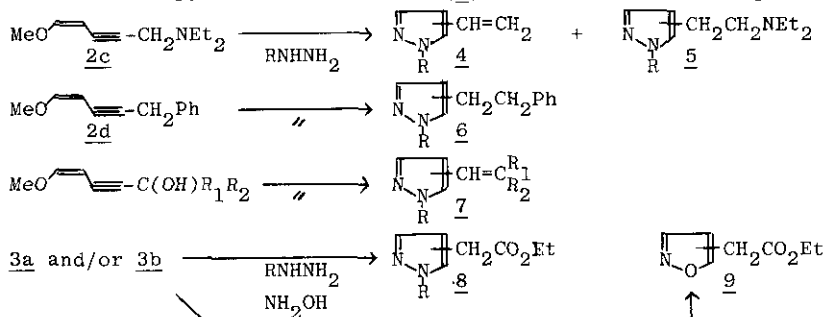
Kuraray Central Research Laboratories, Aoeyama, Sakazu, Kurashiki, Japan

The synthetic utilization of "Diacetylene" as a starting material has been examined in the synthesis of heterocyclic compounds. Diacetylene can be converted easily into 4-methoxy-3-butene-1-yne (1), and its alkylated homologs (2) can be derived from 1 with various alkylating reagents in moderate yields. The reaction of 1 with diethyl carbonate give a mixture of 3a and 3b (~50% yield). In the present work, the



heterocycles synthesis via alkylated homologs 2 and 3a, 3b were investigated.

When 2 was reacted with hydrazines in an acidic ethanol solution, a variety of 3- and 5-substituted pyrazoles were obtained, ig. vinylpyrazole (4) and 2-diethylaminoethylpyrazole (5) (total 80% yield), 2-phenylethylpyrazole (6) (74%), and substituted vinylpyrazole (7) (80%). Similarly in the reaction of 3a and 3b with hydrazines, ethyl ester of 3- and 5-pyrazole acetic acid (8) was obtained almost quantitatively.



Ethyl ester of isoxazole acetic acid (9) was yielded in the similar manner, when 3a and 3b were treated with hydroxylamine in an acidic media. On the other hand, in a basic media in the same reaction only 3-substituted pyrazoles were formed.

This synthesis via 4-methoxy-3-butene-1-yne derivatives 2, 3a and 3b is a useful method for preparation of heterocyclic compounds having functionalized methyl group.