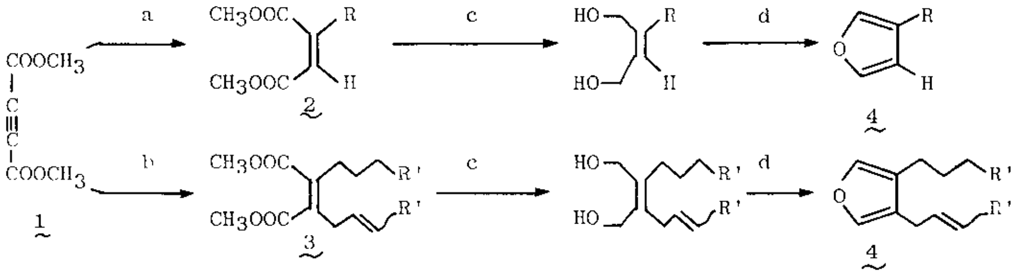
A NEW SYNTHETIC METHOD OF β-SUBSTITUTED FURANS

Kenji ITOH and Hisao NISHIYAMA

Department of Materials Science, Toyohashi University of

Technology, Tempaku-cho, Toyohashi, Aichi 440, Japan

New synthetic method of β-substituted furans employing dimethyl acetylenedicarboxylate (DMAD) as a furan equivalent is presented. β-Substituents of furan skeletons are introduced at the first step by the stereoselective syn addition of organometallic species to DMAD(1). Stereoselective monoalkylation of 1 was achieved by means of the dimethyl sulfide complexes of fairly wide range of alkyl, vinyl, or allylcopper reagents in THF at -78° to give corresponding 2-substituted maleates, 2, in 71-90% yields. Two molecules of 1-alkenes were found to induce regio- and stereoselective syn addition to DMAD in the presence of the particular Pd(0) catalyst at 40° to yield 2-(2-alkenyl)-3-alkylmaleates, 3; R'=C_2H_5(76%), R'=n-C_3H_7(68%), R'-n-C_4H_9(83%), and R'=n-C_5H_{11}(75%).



a. 1. $RCu(Me_2S)\cdot MgBr_2$, -78°, THF. 2. aq. NH_4Cl, -78°, then room temp.

b. R'-CH_2-CH=CH_2 and catalytic amount of Pd(maleic anhydride)$_2$(norbornene) in $CHCl_3$ at 40°, DMAD was added slowly.

c. LiAl(n-Bu)(i-Bu)(H), 0°, toluene. d. PCC or MnO_2, room temp, CH_2Cl_2

2-Substituted or 2,3-disubstituted maleic acid esters, 2 and 3, could be transformed to corresponding 3-mono- or 3,4-disubstituted furans, 4, in two steps, reduction with LiAl(n-Bu)(i-Bu)$_2$(H) at 0° to 1,4-butenediols(86-95%), followed by their oxidation with pyridinium chlorochromate(PCC) or manganese dioxide in dichloromethane at room temperature to 4 in 79-91% yields.