SYNTHESIS OF FURANS AND BUTENOLIDES USING ACYLKETENE DITHIOACETALS

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Reaction of acylketene dithioacetals(1) with dimethylsulfonium methylide gave 2,2-dimethylthio-2,5-dihydrofurans(2) in high yields. Mild acidic hydrolysis or treatment with Florisil of 2 afforded in good yields 2-methylthiofurans(3), severer acidic hydrolysis of which led to the formation of butenolides(4). The 2-methylthiofurans(3) were converted to various substituted furans by following reactions: A: Alkylation of 5-position by treatment with butyllithium followed by addition of alkyl halide

B: Removal of the 2-methylthio group with Raney-Ni(W-7) deactivated by acetone

C: Substitution of the 2-methylthio group with nickel-catalyzed Grignard crosscoupling

The alkylation(A) of 3 followed by hydrolysis gave 5-alkylbutenolides(5).

Two naturally occurring, isomeric furans, perillene(6) and rosefuran(7) were synthesized by the above reactions from 1,1-dimethylthio-3-oxo-1-butene(1, R^1=Me, R^2=H) and 1-bromo-3-methyl-2-butene.