FORMATION AND REACTIVITY OF DILITHIATED N-ACYLFURFURYLAMINES

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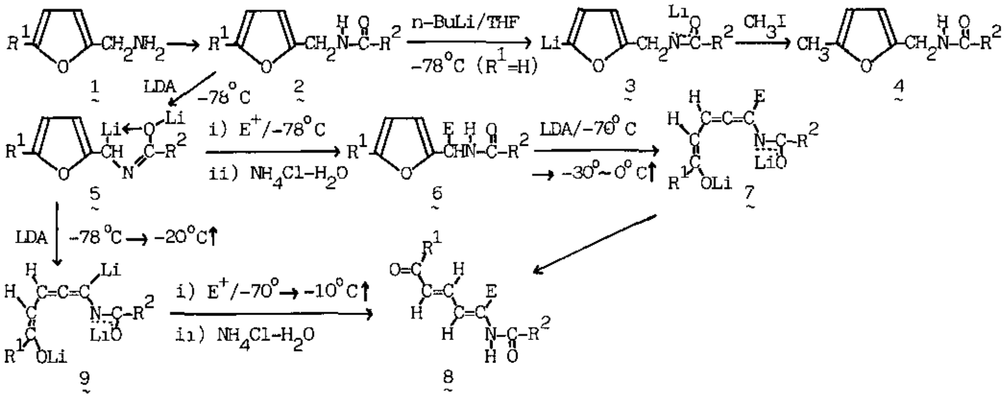
Formation and reactivity of dilithiated N-acylfurfurylamines were investigated. N-Furfurylbenzamide 2($R^2=C_6H_5$), obtained by benzoylation of furfurylamine(1), was lithiated *predominantly* at 5-position of the furan ring with n-butyllithium(n-BuLi) /THF/-78°C and was allowed to react with methyl iodide to give 5-methylated N-furfurylbenzamide(4). While instead of n-BuLi as a base, lithium diisopropylamide(LDA) was used for the reaction, N-furfurylbenzamide(2) underwent efficient and regioselective lithiation at the furfuryl position, followed by reaction with various electrophiles to give α-substituted N-furfurylbenzamide derivatives(6) in good yields.



On the other hand, dilithiated N-furfurylbenzamide(5) underwent a facile opening reaction of furan ring when warmed ambiently from -78° C to -30° C ~ -10° C followed by quenching with aq.sat.NH_4Cl solution to furnish all-trans 2,4-pentadienal derivatives (8)($R^2=C_6H_5$). 5-Alkylated 8 (E= alkyl) was also prepared by one-pot reaction from 2, namely, which was lithiated with 3.2 eq. mol. of LDA/-78° C and was allowed to warm to -30° C to yield ring-opened trianion(9), followed by reaction with alkyl halides to give 8.

The lithiation and ring-opening reaction of carbamate derivatives($-NHCO_2R$) and urea-type derivatives($-NHCON(R)_2$) as other acyl-derivatives with the same conditions as mentioned above, proceeded analogously as in the case of benzamide derivatives.