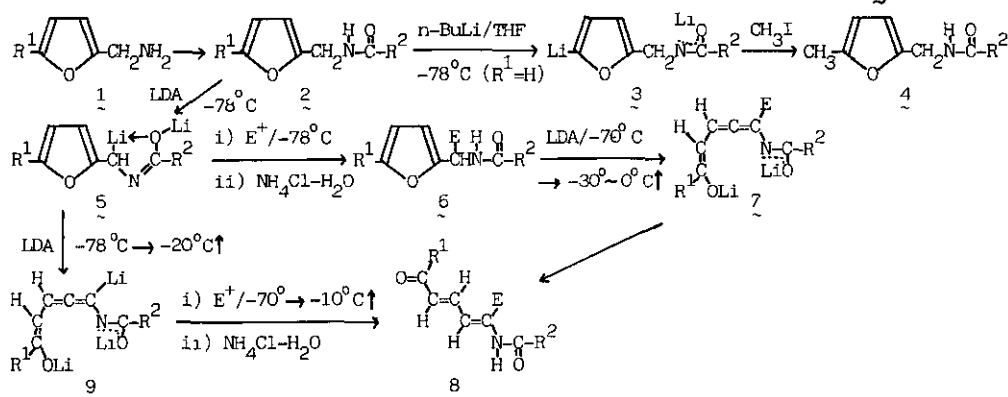


FORMATION AND REACTIVITY OF DILITHIATED N-ACYLFURFURYLAMINES

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Formation and reactivity of dilithiated N-acylfurfurylamines were investigated. N-Furfurylbenzamide **2** ($R^2 = C_6H_5$), obtained by benzylation of furfurylamine (**1**), was lithiated predominantly at 5-position of the furan ring with n-butyllithium (n-BuLi) / THF / $-78^\circ C$ 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 regio-selective 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 $-78^\circ C$ to $-30^\circ C \sim -10^\circ C$ 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** ($E = \text{alkyl}$) was also prepared by one-pot reaction from **2**, namely, which was lithiated with 3.2 eq. mol. of LDA / $-78^\circ C$ and was allowed to warm to $-30^\circ C$ 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.