THE REFORMATSKY REACTIONS OF N-ARYL-2(1H)-PYRIMIDINONES

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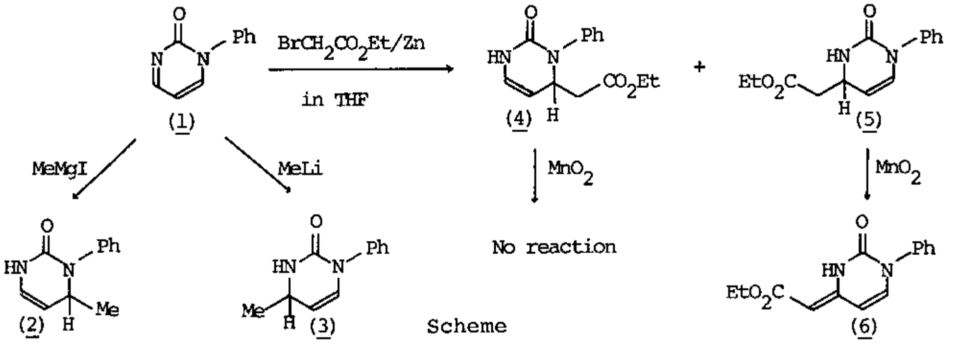
We have investigated the properties and reactions of N-substituted 2(1H)-pyrimidinones and their derivatives. Recently it was reported that 1-phenyl-2(1H)-pyrimidinone (1) was treated with methylmagnesium iodide to give only 3,6-dihydro-6-methyl-1-phenyl-2(1H)-pyrimidinone (2), while methyl-lithium selectively afforded 3,4-dihydro-4-methyl-1-phenyl-2(1H)-pyrimidinone (3). As a part of an extensive study on organometallic compounds, we investigated the reaction of N-aryl-2(1H)-pyrimidinones with α-haloesters in the presence of zinc metal (Reformatsky reaction).

1-Phenyl-2(1H)-pyrimidinone (1) was allowed to react with ethyl α-bromoacetate in the presence of zinc in THF under warming at 60 °C for 3 hr. The two products were assigned to be 3,6-dihydro-6-ethoxycarbonylmethyl-1-phenyl-2(1H)-pyrimidinone (4) and 3,4-dihydro-4-ethoxycarbonylmethyl-1-phenyl-2(1H)-pyrimidinone (5). The total yield of compounds 4 and 5 is 67%, and the ratio is 22 : 78, respectively. (Scheme) Further, compound 5 was easily oxidized to afford not 2(1H)-pyrimidinone but the exo-methylene compound 6 in 85% yield. (Scheme)



Scheme

In conclusion, N-aryl-2(1H)-pyrimidinones react with α-haloesters in the presence of zinc to give mainly 3,4-dihydro-2(1H)-pyrimidinones similar to alkyllithiums. Furthermore, 3,4-dihydro-2(1H)-pyrimidinones are converted into the exo-methylene derivatives in high yields.