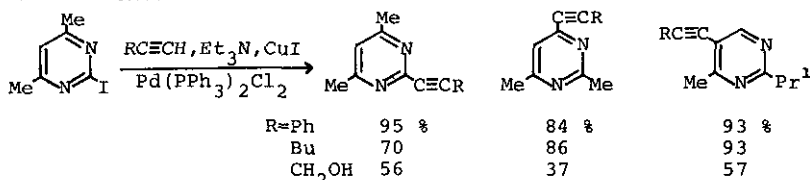


CROSS-COUPLING REACTIONS OF HALOPYRIMIDINES WITH TERMINAL
ACETYLENES AND OLEFINS LEADING TO FUSED PYRIMIDINE RING

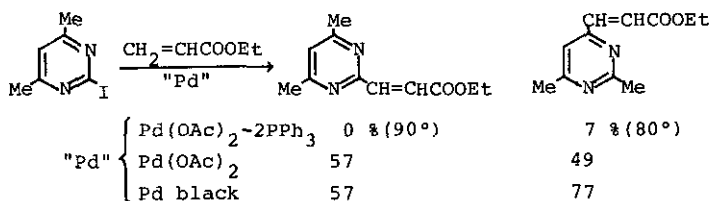
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Prior to the present work, pyrimidines containing an unsaturated carbon chain formed relatively less explored family. Thus the syntheses and reactions of such compounds were investigated, and successful results were obtained.

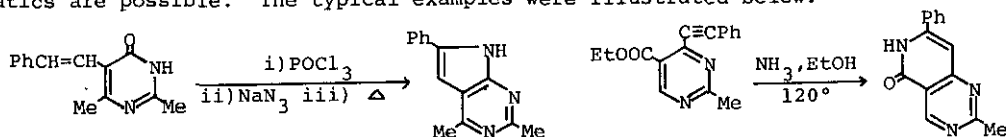
1) 2-, 4-, and 5-Halopyrimidines coupled with terminal acetylenes by the catalytic action of a $\text{PdCl}_2\text{-PPh}_3$ complex to give the corresponding alkynylpyrimidines without significant difference.



2) In the presence of the above catalyst, the cross-coupling reaction of 2- and 4-iodopyrimidines with olefins such as ethyl acrylate, acrylonitrile, and styrene was disturbed by the formation of by-products, whereas the reaction at the 5-position proceeded to give desired products in good yields. In the former case, the use of $\text{Pd}(\text{OAc})_2$ or Pd-black without PPh_3 produced satisfactory results as follows.



3) When an appropriate functional group was located in the neighborhood of the unsaturated substituents, the ring-closure reactions to various polyaza-heteroaromatics are possible. The typical examples were illustrated below.



4) In addition to the above reactions, the hydration of acetylenic pyrimidines was investigated to give acylmethylpyrimidines (pyrimidinyl- CH_2COR) as expected.