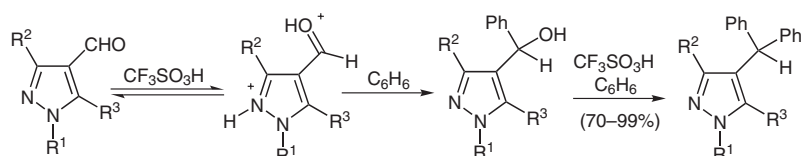


Superacid-Promoted Reactions of Pyrazolecarboxaldehydes and the Role of Dicationic Electrophiles



Significance: Treatment of pyrazolecarboxaldehydes with super acids leads to the formation of dicationic species which are highly reactive for electrophilic diarylation even with weakly nucleophilic arenes. Thus a variety of substituted pyrazolecarboxaldehydes condense with benzene to provide side-chain substituted products. The mechanism involving a dicationic intermediate is supported by low temperature ¹³C NMR studies.

Comment: Friedel–Crafts type electrophilic reactions of aromatics with benzaldehyde derivatives are a classical method for hydroxyarylation and has been used in large-scale industrial synthesis, e.g. DDT. (J. March *Advanced Organic Chemistry*, 5th ed.; Wiley: New York, **2001**, p 719). This work builds on the arguably poorly appreciated fact that protonated N-heterocycles can enhance the reactivity of adjacent electrophilic centers such as aldehydes for hydroxyarylation and further arylation. Strong acid-catalyzed intramolecular Friedel–Crafts reactions are also reported for some substituted pyrazoles.