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New Synthetic Reactions Based on the Onium Salts of Azaaromatic Compounds

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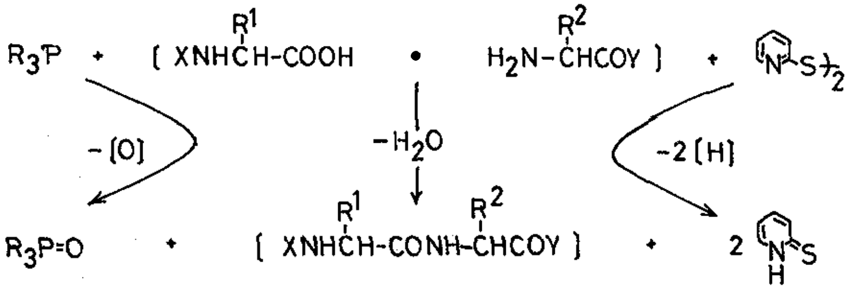
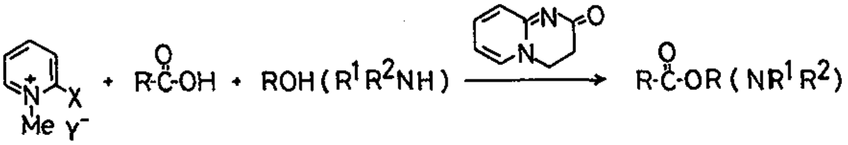
A potential example of reactions which complete in the absence of acids and/or bases, namely, under neutral and mild conditions was demonstrated in the oxidation-reduction condensation.

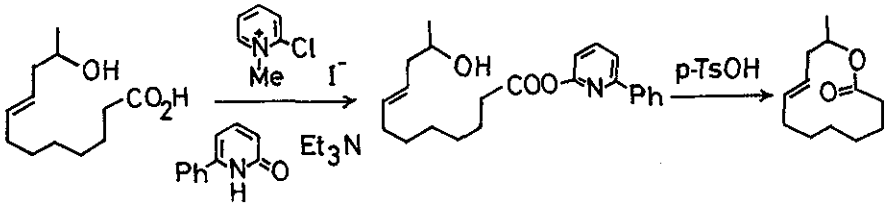


Carboxylic ester or amide formation from a carboxylic acid and an alcohol or an amine was also successfully achieved by using 2-halopyridinium salt. In this reaction, it is expected that all the reacting species gather together in the close proximity of the pyridinium salt to acquire advantage in entropy for the reaction and that the reaction may accordingly be realizable under neutralization condition and moreover mild conditions, especially when pyrimidine derivatives such as 3,4-dihydro-

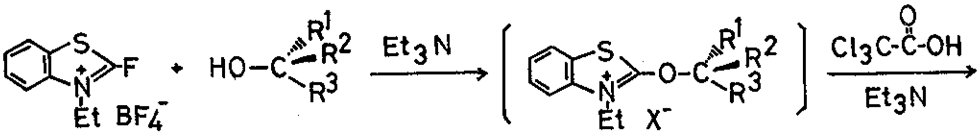
2H-pyrido[1,2-a]pyrimidin-2-one, are used as a hydrogen halide captor.

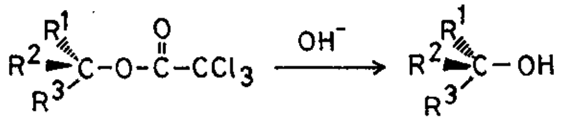


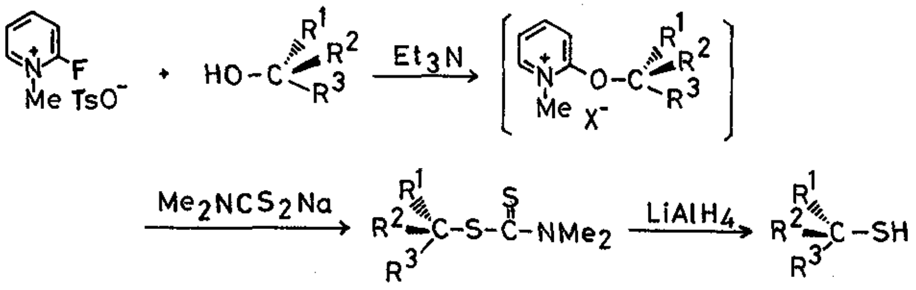
These reagents further provided the excellent method for acylamide formation in the total synthesis of variotin and were also successfully applied further macrolide formation, such as recifeiolide.



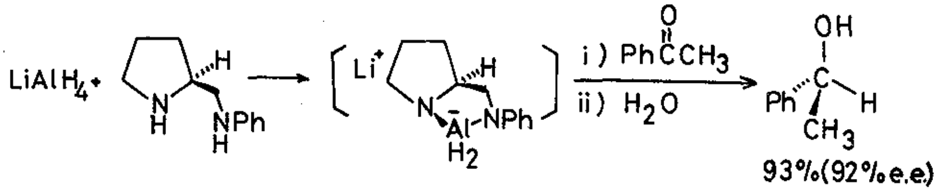
A series of alkylation reactions utilizing the onium salts of 2-alkoxyazaaromatics, readily prepared from alcohols and the onium salts of 2-haloazaaromatics, were developed. For example, the convenient methods for sulfide formation, interconversion of enantiomeric alcohols, preparation of optically active thiols and amines, and stereoselective preparation of halides were explored. This reaction is one of the best methods to prepare optically active thiols and amines, and interconversion of alcohols because of high optical purity and excellent yield of the products.



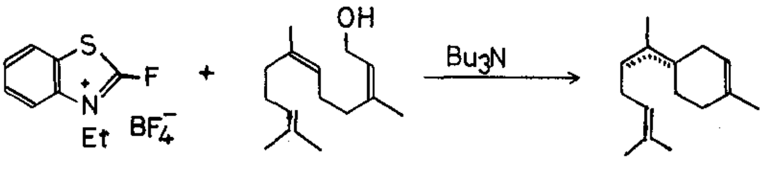




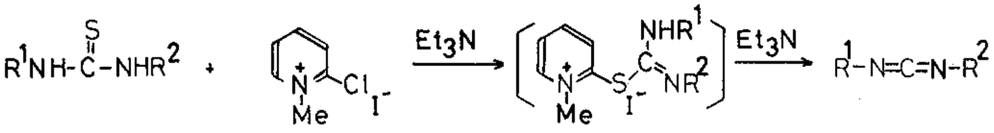
In connection with this problem, highly optically pure alcohols were prepared from prochiral carbonyl compounds by asymmetric reduction with $LiAlH_4$ and simple ligand easily prepared from readily available (S)-proline.

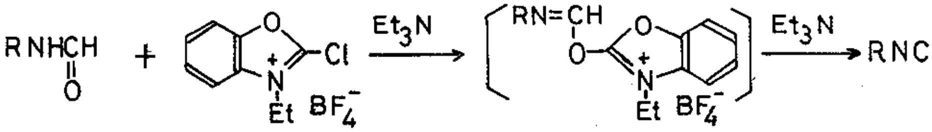


Further, biogenetic-like cyclization of polyenic alchols was accomplished using the onium salts of 2-fluoroazaaromatics under very mild conditions, and cyclized products were obtained from nerol or trans,cis-farnesol in much higher yields as compared with conventional acid-catalyzed method.



In addition to the above mentioned reactions of formally intermolecular dehydrations, intramolecular dehydration reactions of forming nitriles, isothiocyanates, carbodiimides and isonitriles by the use of onium salts of 2-haloazaaromatics were also explored.





By the use of the onium salts of azaaromatics, the improved methods for the Beckmann and pinacol rearrangements, which proceeded under very mild conditions, were developed.