

SYNLETT Spotlight 87

Formic Acid and its Salts

Compiled by Sivapackiam Jothilingam



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Sivapackiam Jothilingam was born in T. Ramanathapuram, Tamilnadu, India in 1976. After completing his undergraduate degree (BSc) and post-graduate degree (MSc) in Chemistry at Ayya Nadar Janaki Ammal College, Sivakasi, India, he joined the research group of Dr. H. Surya Prakash Rao (Pondicherry University) to pursue a PhD. His primary research interests focus on the synthesis and characterization of new heterocyclic compounds and development of environmentally benign procedures for their synthesis.

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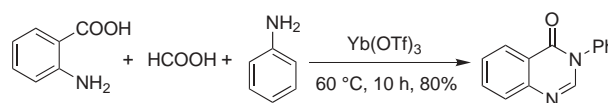
Introduction

Formic acid and its ammonium salts have been applied to synthetic chemistry for reduction of organic compounds and as a source of one carbon atom.¹ Recently formic acid based reagents are utilized for many synthetic transformations such as debenzoylation,² formal hydration³ and reduction of α,β -unsaturated carbonyl compounds,⁴ cyclic enones,⁵ and nitro compounds.⁶ Some alkali metal salts of

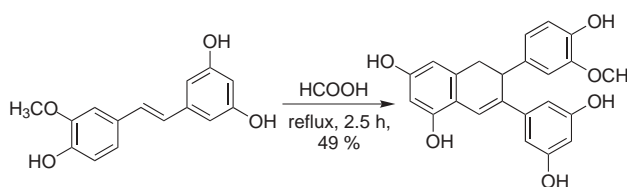
formic acid were used for a variety of functional group transformations. For example, the lithium formate was used for the conversion of halide to carboxylic acid⁷ and the potassium formate was used for reductive amination of aldehydes and ketones.⁸ Recently formic acid and its salts found use in various microwave-mediated organic reactions.⁹

Abstracts

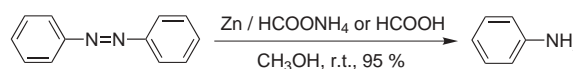
(A) Wang et al. reported a facile three-component condensation for the synthesis of quinazolin-4(3*H*)-ones.¹⁰ In this synthesis several quinazolin-4(3*H*)-ones were generated in good yield by the ytterbium complex mediated, solvent-free, one-pot reaction of anthranilic acid, formic acid, and amines.



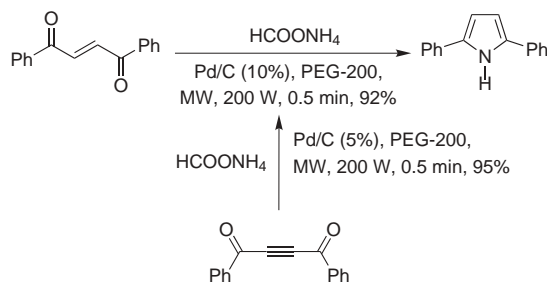
(B) Lin et al. discovered formic acid catalyzed dimerization of stilbenes to tetralin derivatives.¹¹ In this reaction the stereo defined tetralin derivatives were obtained by formic acid mediated dimerization of some stilbenes having activated aromatic rings.



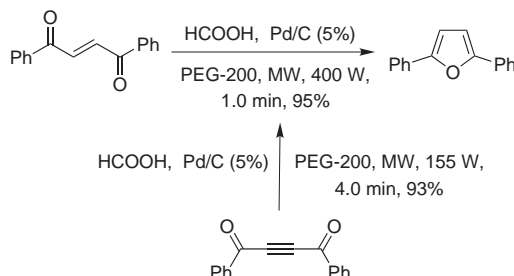
(C) Gowda et al. reported the zinc dust catalyzed reductive cleavage of azo-compounds to corresponding amines using ammonium formate or formic acid.¹² In this reaction the azo-compounds were cleaved to amine by ammonium formate or formic acid in the presence of a catalytic amount of zinc dust in methanol. Furthermore, during course of the reaction sensitive functional groups like OH, CH₃, OCH₃, COOH, COCH₃, etc. were not affected.



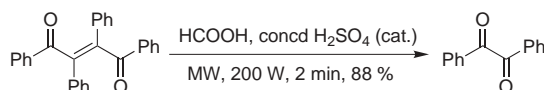
(D) Recently, our group reported the utilization of ammonium formate for the generation of 2,5-diphenylpyrrole from the corresponding 2-butene-1,4-dione and 2-butyne-1,4-dione.^{9a,d} In this one-pot microwave-mediated 'green chemistry' reaction, ammonium formate was used as the source of hydrogen and ammonia for the synthesis of pyrrole derivatives.



(E) We also reported the utilization of formic acid for the generation of 2,5-diphenylfuran from the corresponding 2-butene-1,4-dione and 2-butyne-1,4-dione.^{9b} In this facile one-pot microwave-mediated reaction, formic acid was used as the source of hydrogen and the acid catalyst for the generation of furan derivatives.



(F) Furthermore, unprecedented oxidation properties of formic acid were found in the conversion of 1,2,3,4-tetraphenyl-2-butene-1,4-dione to benzil.^{9c} In this facile transformation conducted under microwave conditions, formic acid behaves as an oxidizing agent in contrast to its well-known behavior as a reducing agent or an acid catalyst.



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