SYNLETT Spotlight

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

Iron Phthalocyanine

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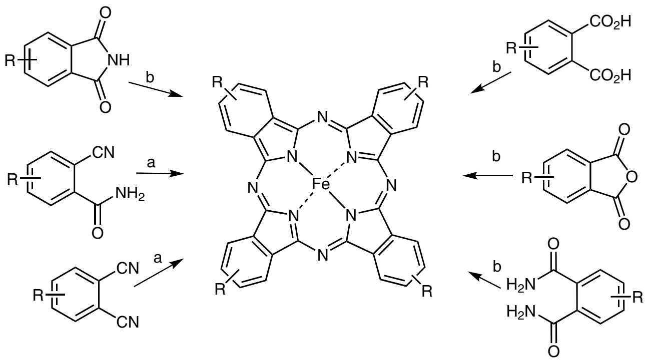
Introduction

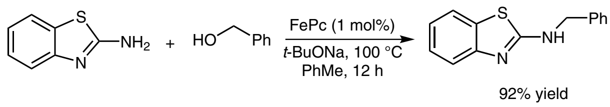
Iron phthalocyanine (FePc) complexes are structurally related to porphyrin complexes; phthalocyanines have been used as alternative catalysts because they are cheaper and more stable to degradation. FePc is widely used in a variety of catalytic transformations,[1] including N-alkylation,[2] C–H amination,[3] C–C bond formation,[4] preparation of esters[5] and oximes,[6] reduction,[7] oxidation,[8,9] and radical reactions.[10] Although FePc is particularly studied as a catalyst for *organic* reactions, this particular reagent is also described in many other applications. For example, FePc complexes are efficient catalyst for the charge/discharge process in lithium–oxygen large-capacity batteries.[11] The following literature data indicate that FePc displays a strong bibliographic background in a wide variety of reactions and is currently considering as an active and 'hot' research topic. On overview of typical iron phthalocyanine syntheses is shown in Scheme 1.



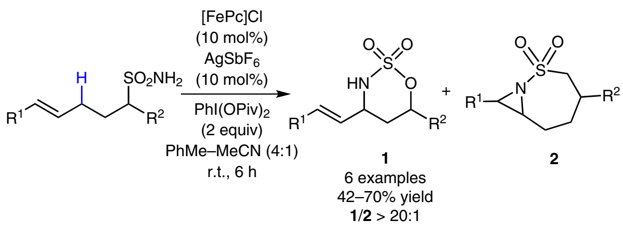
Scheme 1 Preparation of FePc complexes from cyclotetramerization of common precursors. *Reagents and conditions*: (a) iron salt, Δ; (b) iron salt, urea, catalyst, Δ.

Abstracts

(A) FePc has been reported as an efficient and versatile catalyst for the N-alkylation of amine-substituted heterocycles with alcohols. The one-pot syntheses of *ortho*-amino-substituted benzimidazoles, benzothiazoles, and benzoxazoles are achieved by using FePc in combination with a base. The best reaction conditions were found to be *t*-BuONa in toluene.[2]



(B) Intramolecular C–H amination is catalyzed by FePc in the presence of $AgSbF_6$ under mild reaction conditions. Allylic C–H amination is preferred over aziridination. Interestingly, this very selective amination is due to the difference in reactivity, closely paralleling C–H bond dissociation energies (allylic > benzylic > ethereal > tertiary > secondary C–H bonds). C–H aminations are particularly important reactions because may biologically active moleculs are amines.[3]



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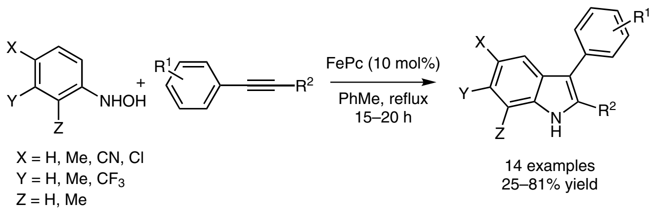
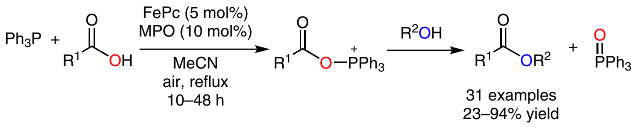
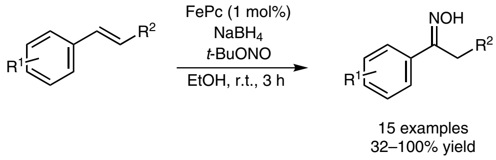
(C) Lamar and Nicholas developed an efficient method for the direct synthesis of 3-arylindoles catalyzed by FePc. 3-Arylindoles are produced in moderate to excellent yields via annulation of aryl hydroxylamines with alkynes in the presence of FePc in refluxing toluene.[4]



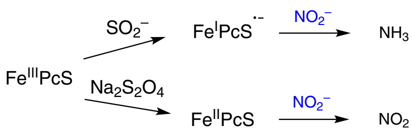
(D) The preparation of various esters from a wide range of alcohols and carboxylic acids is achieved through the aerobic activation of Ph_3P catalyzed by FePc. The reaction is accelerated in the presence of pyridine *N*-oxide derivatives such as 4-methoxypyridine *N*-oxide (MPO). It is noteworthy that the only phthalocyanine derivative able to catalyze this reaction is the iron complex thanks to the ability of FePc to use O_2 for the activation of Ph_3P.[5]



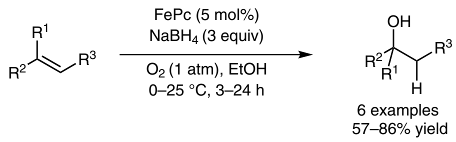
(E) Beller and co-workers reported the first iron-catalyzed synthesis of oximes from olefins. The treatment of substituted styrenes with *tert*-butyl nitrite and $NaBH_4$ in the presence of FePc affords oximes in moderate to high yields.[6]



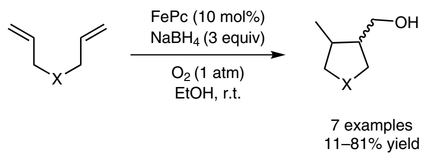
(F) Iron tetrasulfophthalocyanine (FePcS) catalyzes the reduction of nitrite (NO_2^-) by dithionite or sulfoxylate in aqueous alkaline solution. Interestingly, different products can be obtained depending on the choice of the reductant. Using dithionite, NO_2^- is reduced to N_2O, while the use of sulfoxylate as reductant lead to ammonia as the product.[7]



(G) Boger and co-workers extended the initial work of Kasuga on the oxidation of styrenes[8] to the first oxidation of unactivated alkenes by a FePc–$NaBH_4$–O_2 system. The oxidation of a range of alkenes to the corresponding alcohols is achieved by using a catalytic amount of FePc. In this system, O_2 acts as metal oxidant and as a radical trap.[9]



(H) The radical cyclization of 1,6-dienes to give functionalized cyclic compounds is catalyzed by FePc in the presence of $NaBH_4$ and O_2 in EtOH at room temperature. The reaction gives five-membered carbo- or heterocyclic compounds with a hydroxyl group.[10]



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