SYNLETT Spotlight

Iron Phthalocyanine

Compiled by Cédric Colomban

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

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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 esters⁵ 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 AgSbF₆ 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 > etheral > tertiary > secondary C–H bonds). C–H aminations are particularly important reactions because many biologically active molecules are amines.³

(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 Ph₃P 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 O₂ for the activation of Ph₃P.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 NaBH₄ in the presence of FePc affords oximes in moderate to high yields.⁶

(F) Iron tetrasulfophthalocyanine (FePcS) catalyzes the reduction of nitrite (NO₂[−]) by dithionite or sulfoxylate in aqueous alkaline solution. Interestingly, different products can be obtained depending on the choice of the reductant. Using dithionite, NO₂[−] is reduced to N₂O, while the use of sulfoxylate as reductant leads to ammonia as the product.⁷

(G) Boger and co-workers extended the initial work of Kasuga on the oxidation of styrenes⁸ to the first oxidation of unactivated alkenes by a FePc–NaBH₄–O₂ system. The oxidation of a range of alkenes to the corresponding alcohols is achieved by using a catalytic amount of FePc. In this system, O₂ 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 NaBH₄ and O₂ in EtOH at room temperature. The reaction gives five-membered carbo- or heterocyclic compounds with a hydroxyl group.¹⁰

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