

Synthesis of Substituted Benzenes from Phenylacetylenes  
Catalyzed by Iron meso-Tetraphenylporphyrins

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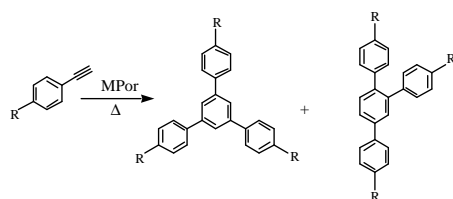
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Synthetic metalloporphyrins bearing electron-withdrawing substituents on the phenyl groups and/or on the beta-positions have been studied and used for a long time, as efficient catalysts for a large family of oxidation reactions of natural compounds and hydrocarbons.<sup>1-2</sup>

Such macrocycles are also able to catalyze the cyclopropane ring formation from olefins and diazocompounds<sup>3-4</sup>, Diels-Alder reactions<sup>5</sup> and recently in the literature appeared a new application of the porphyrins catalysis based on the olefination of the aldehydes.<sup>6</sup>



M= Fe

R= H, Br, Cl, OCH<sub>3</sub>, CH<sub>2</sub>OH

Figure 1

Here we want to report on a new application of the metalloporphyrin catalysis, the formation of benzene derivatives starting from substituted alkynes. In figure 1 is reported a simple reaction scheme.

Such reaction, named the Reppe's reaction, starting from monosubstituted acetylenes, usually gives the 1, 2, 4 substituted benzenes together with various amounts of the 1, 3, 5 and 1, 2, 3 isomers.<sup>7-8</sup>

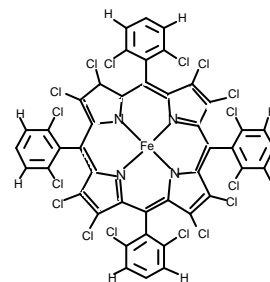
The mechanism of the formation of the 1, 2, 4 substituted isomer involves the consecutive presence of metallocyclopropene and metallocyclobutadiene compounds formed from the consecutive addition of three molecules of acetylene to the metal residue.<sup>9</sup>

However a simple trend in the formation of the products was tentatively proposed on the basis of the different metals and the steric interaction between the catalysts and the intermediates. Cobalt, rhodium, nickel, aluminum and other metal complexes were used as catalysts for such reaction, which can give also the cyclooctatetraene (COT) derivatives as by-products.

We will show the remarkable properties, in catalyzing the formation of benzene derivatives from substituted acetylenes, of Fe<sup>II</sup>(Cl<sub>8</sub>)TDCPP, where (Cl<sub>8</sub>)TDCPP is the dianion of 2, 3, 7, 8, 12, 13, 17, 18-octachloro-5, 10, 15, 20-tetrakis-(2', 6'-dichlorophenyl) porphyrin.

The reactions were performed, when possible, without solvents or in boiling dry toluene and under strictly anaerobic conditions. The catalyst was generated *in situ* by the cobaltocene chemical reduction of the iron(III) porphyrin chloride precursor.

This porphyrin catalyst precursor was synthesized by literature method<sup>10</sup> and its structure is reported in figure 2.



Fe(Cl<sub>8</sub>)TDCPP

Figure 2

The reaction yields are quite good, going from 60 to 86 %. The reaction products were isolated by column chromatography and analyzed by GC-MS and NMR spectra and all gave satisfactory elemental analysis.

About the reaction conditions, an interesting observation is related to the fact that, in our experiments, only Fe<sup>II</sup>(Cl<sub>16</sub>)TDCPP, bearing sixteen chlorine atoms on the macrocycle, is able to catalyze the reaction while other iron(II) porphyrins, like Fe<sup>II</sup>TPP or Fe<sup>II</sup>TDCPP systematically fail.

This experimental result, in our opinion, is related to the stabilization of the +2 oxidation state of the iron due to the presence of sixteen halogen atoms on the porphyrin skeleton.<sup>11</sup> In fact, running the experiments in the presence of oxygen, which maintains the iron to +3 oxidation state, the reaction does not occur.

This fact can be related to the difficulties of the acetylenic compounds to be coordinated on an electron-rich iron(II).

The reactions were also performed in the presence of stoichiometric amount of benzonitrile, giving pyridine derivatives as the final products, in moderate or good yields.

## References

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