



## A novel metal promoter for the Sandmeyer reaction

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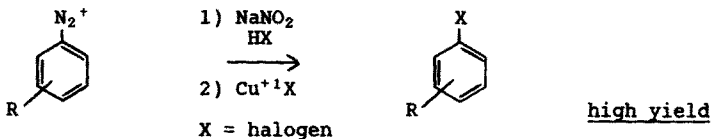
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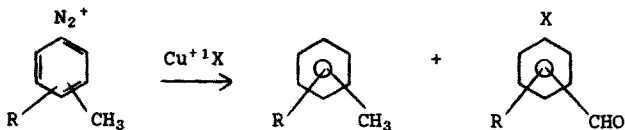
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The replacement of a diazonium group by halogen has been a long standing method in the organic literature. Such a process has achieved industrial importance. The reaction as developed by Sandmeyer typically uses a  $\text{Cu}^+$  catalyst with a diazonium ion usually generated from the corresponding amino compound. The reaction works very well on simple aromatic diazonium derivatives such as p-nitro, p-chloro, etc.



Complications start to arise when the R becomes methyl and when  $\text{N}_2^+$  is flanked by groups other than H. When R=methyl, the use of  $\text{Cu}^+$  metal promoters give rise to extensive oxidation products of  $\text{CH}_3$  to  $\text{CHO}$  along with reduction of the carbon-bearing  $\text{N}_2^+$ , i.e.,



We have confirmed that this detrimental side reaction is related to the presence of the  $\text{Cu}^+$  promoter.

The literature does not address this problem to a significant extent. Alternative methods use expensive alkyl nitrite esters to generate the diazonium ion in the absence of water. Such reagents are not cost effective in an industrial process. Our solution was quite simple. We used either  $\text{Fe}^{+2}$  halide or a 1:2 mixture of  $\text{Fe}^0$  with  $\text{Fe}^{+3}$  in the appropriate hydrogen halide aqueous solution. The stoichiometry of Fe salt was related to the individual system and was based on optimization studies. The temperature of the reaction can be varied as one typically varies a classical Sandmeyer reaction. The oxidation of pendant methyl groups was not evident in the system and conditions studied. Furthermore, the reaction, like a typical Sandmeyer, was applicable to a wide variety of functional groups present, i.e., R=Me, halogen, alkyl,  $\text{CF}_3$ ,  $\text{HSO}_3$  in any or multiple combinations.

It may be assumed that the actual promoter is  $\text{Fe}^{+2}$  but for economic reasons, the  $\text{Fe}^0/\text{Fe}^{+3}$  system might be more advantageous. Thus, one would presume that  $\text{Fe}^{+2}$  is generated in-situ. This metal promoter does not manifest the problems of side-chain oxidation associated with  $\text{Cu}^+$  metal promoters and also does not

suffer any decrease in yield as the literature suggests. Furthermore, we have found that an Fe metal system is better economically and environmentally since  $\text{Cu}^{+1}$  is more expensive and cannot be freely discharged into waste streams.

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