

STIMULATION BY Sn^{+2} OR ASCORBIC ACID ON DIAZONIUM SALTS REACTIONS

Carlo GALLI

Centro di Studio sui Meccanismi di Reazione del Consiglio Nazionale
delle Ricerche, c/o Istituto di Chimica Organica dell'Università,
00185 Rome, Italy

Abstract: Use of a mild reducing agent and ligand transfer for the transformation of diazonium salts into aryl halides provides an alternative to the Sandmeyer procedure.

The Sandmeyer reaction of diazonium salts is a well known method to obtain aryl halides.¹ It makes use as promoting agent of Cu(I) halides which, due to their lability, have often to be prepared separately to ensure better results.²

The present procedure instead provides an easy way to stimulate the reaction employing as reducing species SnCl_2 or ascorbic acid³ in the presence of Cu(II) salts. There is no need for a specific cupric halide since also $\text{Cu}(\text{NO}_3)_2$ along with an excess of the proper halide is able to carry on the substitution. The halide exchanges with NO_3^- for the ligand sphere of Cu(II) which possibly acts as a ligand transfer agent.⁴

The reducing species (the bielectronic Sn^{+2} or the mono-electronic ascorbic acid) has to be supplied in equivalent ratio either as solid or in a concentrated aqueous solution.

Inspection of the Table shows that the yields are comparable with those obtained under typical Sandmeyer conditions and that Sn^{+2} seems more powerful than ascorbic acid, in agreement with their redox potentials.⁵

According to the Sandmeyer procedure for the synthesis of aryl bromides, the diazonium salt had to be added into a boiling solution of CuBr. This step, responsible sometimes for a lowering of the yield due to the formation of byproducts, is circumvented by the milder method at hand since the reaction occurs readily also at room temperature (see footnote b on the Table).

While Sn^{+2} , commonly available as its chloride salt, is employed only for the aryl chlorides synthesis, ascorbic acid can also be used for the synthesis of

Table. Results for the Sn^{+2} or Ascorbic Acid Stimulated Reaction of Aryl Diazonium Salts in Water^a

Substituent on the starting compd. (ArN_2^+)	H	p-Cl	p-NO ₂	p-CH ₃	3,4,5-trimethyl
% ArBr formed under ascorbic acid stimul.	72	76			22 ^b
% ArCl formed under Sn^{+2} stimulation	78	70 ^c	33	80	

a) After 30 min at room temperature, using 1 mol ascorbic acid or 0.5 mol Sn^{+2} with 1.5 mol $\text{Cu}(\text{NO}_3)_2$ and excess halide ion for 1 mol substrate (always phenyl derivatives). b) Obtained in 11% yield according to the Sandmeyer conditions. c) Stimulation by ascorbic acid gave 25% yield of ArCl.

aryl bromides, which are obtained in higher yields.

Little amounts ($\geq 2\%$) of reduction or coupling products (i.e., benzene and biphenyl from aniline) are obtained and hence the presence of a radical pathway can be inferred.¹

While a detailed mechanistic discussion is deferred to a future paper, the present procedure can be regarded as a convenient alternative to the classical Sandmeyer conditions.

References and Notes

1. W.A. Waters, "Chemistry of Free Radicals", 2nd Edn., Oxford University press, London, 1948.
2. J.K. Kochi, J.Amer.Chem.Soc., 79, 2942 (1957); H. Zollinger, Acc.Chem.Res., 6, 335 (1973).
3. For a Fe^{+2} stimulated procedure see: Y. Nakatani, Tetrahedron Lett., 4455 (1970).
4. J.K. Kochi, Tetrahedron, 18, 483 (1962).
5. $\text{Sn}^{+4} + 2e \rightarrow \text{Sn}^{+2}$ ($E_0 = 0.16$ V), while that of ascorbic acid being in the range 0.4-0.9 V depending on the pH of the solution: E. Pellizzetti, D. Meisel, W.A. Mulac, and P. Neta, J.Amer.Chem.Soc., 101, 6954 (1979).

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