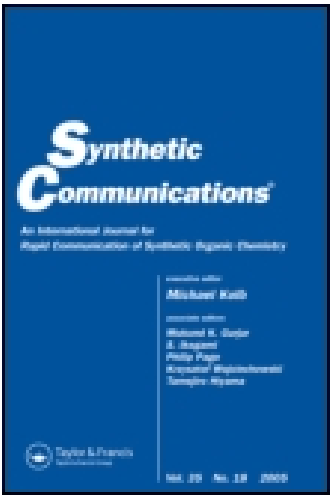

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Selective Reduction of Aryl Diazonium Fluoroborates[1]

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SELECTIVE REDUCTION OF ARYL DIAZONIUM FLUOROBORATES[1]

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ABSTRACT : Substituted aryl diazonium fluoroborates have been selectively reduced to the corresponding phenylhydrazines by using borohydride exchange resin (BER).

Substituted phenylhydrazines are important for the synthesis of diphenylcarbazones which are used as an analytical reagents[2] and antibacterial agents against mycobacterium tuberculosis.[3] Recently diphenylcarbazones have been used for *in vitro* study of human cell lines derived from nine types of cancer: leukemia, lung cancer, colon cancer, CNS cancer, melanoma, ovarian cancer, renal cancer, prostate cancer and breast cancer.[4] The Fischer indolization between substituted phenylhydrazines and appropriate carbonyl compounds[5] has been used for the synthesis of 1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-b]indole-1-acetic acid (Etodolac) and similar

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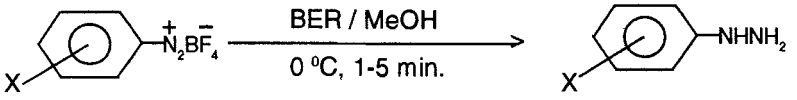
derivatives which are important nonsteroidal analgesic and antiinflammatory drugs.[6] The key phenylhydrazines have commonly been prepared by reduction of the diazonium salts with excess of $SnCl_2$ in the presence of hydrochloric acid. This method is not selective and involves tedious aqueous work-up. We now report here a simple and convenient method involving selective reduction of substituted aryl diazonium fluoroborates to the corresponding phenylhydrazines by using borohydride exchange resin (BER) in methanol (scheme).



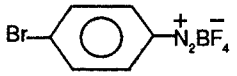
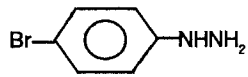
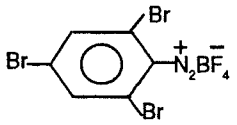
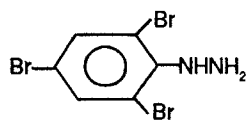
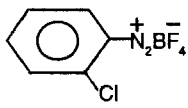
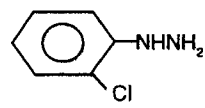
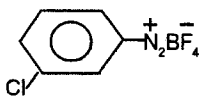
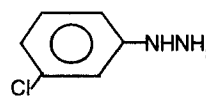
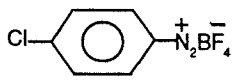
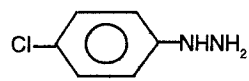
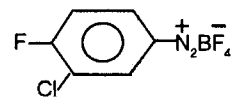
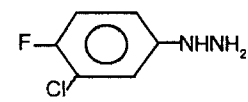
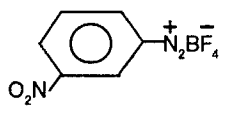
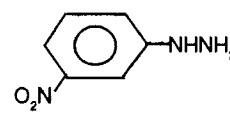
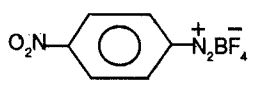
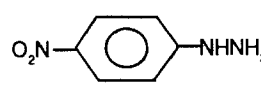
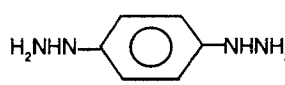
The results of this facile reduction of substituted aryl fluoroborates are summarised in the table. As is evident from the table BER reduces the diazonium fluoroborate group selectively and tolerates other functional groups like bromo, chloro, fluoro and nitro (entries 1-8) in the molecule.

The usefulness of this methodology lies in the fact that the reactions are carried out under mild conditions in a very short time (1-5 min). Easy separation and recyclability of the reagent are noteworthy advantages.

Experimental

All chemicals were of analytical grade. The solvents were distilled before use. Commercially available sodium borohydride was used as received. An ion exchange resin, Tulsion A-27 (chloride form) was obtained from Thermax Chemicals, Pune (India) and was used for supporting borohydride anion. All aryl

Table : Selective reduction of aryl diazonium fluoroborates by using BER

Entry	Diazonium fluoborates	Product[a]	Yield[b](%)
1			66
2			60
3			79
4			91
5			63
6			69
7			81
8			89
9			72

a. Products were characterised by their physical constants, spectral characteristics (IR, ^{1}H NMR) and comparison with authentic samples

b. Yields are of the pure isolated products.

diazonium fluoroborates were prepared by using standard synthetic method.[7]

Preparation of Borohydride Exchange Resin

An aqueous solution of sodium borohydride (0.5 M, 100 mL) was stirred with 10 g of chloride form of resin (Tulsion A-27, anion exchange resin) for 1 h. The resulting resin was washed thoroughly with distilled water until free from excess of sodium borohydride. The borohydride bound ion exchange resin was then dried *in vacuo* at 60 °C for 5 h. The dried resin was analysed for borohydride content by hydrogen evolution on acidification with 0.05 N hydrochloric acid; the average capacity of the ion exchange resin was found to be 3 mmol BH_4^- per gram of dry resin. The dried resin was stored under nitrogen at room temperature. The hydride content was constant over 6 weeks.

General Procedure for Selective Reduction of Substituted Aryl Diazonium Fluoroborates

Solution of aryl diazonium fluoroborate (5 mmol) in methanol (15 mL) was cooled to O °C and BER (2 g, 6 mmol for entries 1-8) or (4 g, 12 mmol for entry 9) was added in it with constant shaking. The reaction was completed in few minutes (1-5 min.). Completion of the reaction was observed by colour change of the resin from black to colourless. The resin was then filtered and washed with ether (3x10 mL). Removal of the solvent under reduced pressure furnished product in good yield.

Acknowledgement

We thank Thermax Chemicals, Pune for the generous gift of Tulsion A-27 and Principal Vijay Kasbekar for his encouragement.

Reference and footnotes

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