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Green Innovative Synthesis of Chlorofluoroarenes from Nitrohaloarenes

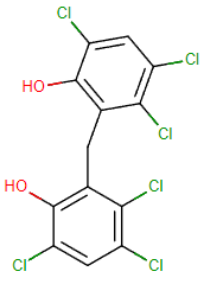
Dipak S. More[1], Dr. Pushpendra Sharma[2], Dr. Neelu Jain[3]
[1]*Research student SSSUTMS, Sehore, Bhopal*
[2]*Professor of Chemistry, SSSUTMS, Sehore, Bhopal*
[3]*Associate Professor of Chemistry, SSSUTMS, Sehore, Bhopal*

ABSTRACT: A new series of Haloarenes is synthesized by the de-nitrochlorination of difluoronitrobenze with dichlorobenzene as solvent without presence of catalyst. The synthesized compounds have been characterized by boiling point, elemental analysis, MS, one-dimensional NMR (1H & 13C) spectroscopic data.

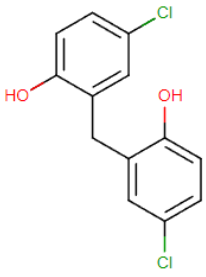
Keywords: Nitrofluoroarenes, De-nitrochloroination, NMR, Mass Spectroscopy etc.

Introduction

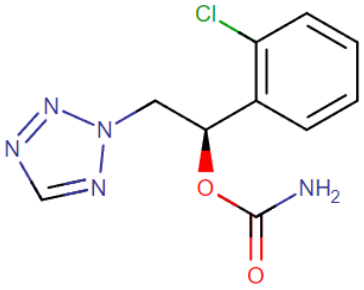
Active learning and open ended problem solving activities in chemistry are becoming ever more popular as their effectiveness in helping to produce more highly skilled and motivated graduates is recognized. This paper describes an active learning approach to introducing some of the principles of green chemistry. Aromatic chlorides are an important class of compounds, widely used in organic chemistry as synthetic intermediates for coupling or substitution reactions, allowing the preparation of natural products and medicinally active compounds. Because of the relative stability of the carbon–chlorine bond, aryl chlorides are also found as components in a vast array of natural products and used as structural motifs in pharmaceuticals, agrochemicals, and other biologically active compounds. The Cenobamate applicable in a small molecule drug indicated to treat partial onset seizures in adults, Dichlorophen is an antimicrobial agent shown to exert activity against cestodes, protozoa, fungi, and bacteria.



Hexachlorophene



Dichlorophen



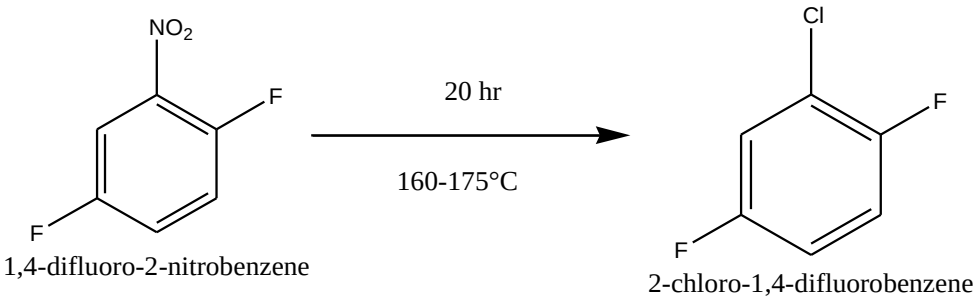
Cenobamate

Chlorination is the core chemical reaction technology and this applies to various pharmacetical,agrochemical intermediates and to chlorinated reagentsand there derivatives which are used as fine chemicals. Enviorenmental, health and safety reason the process activity carried out in safe manner and all byproduct gases generated during the chlorination process are converted to a stable compounds either gaseous or liquid.

Objective: The specific objectives of the work was to synthesize chlorofluoroarenes byusing halogenated solvent without using any catalyst.

Synthesis of 2, 5-Difluorochloroarene from 2,5-difluoronitrobenzene

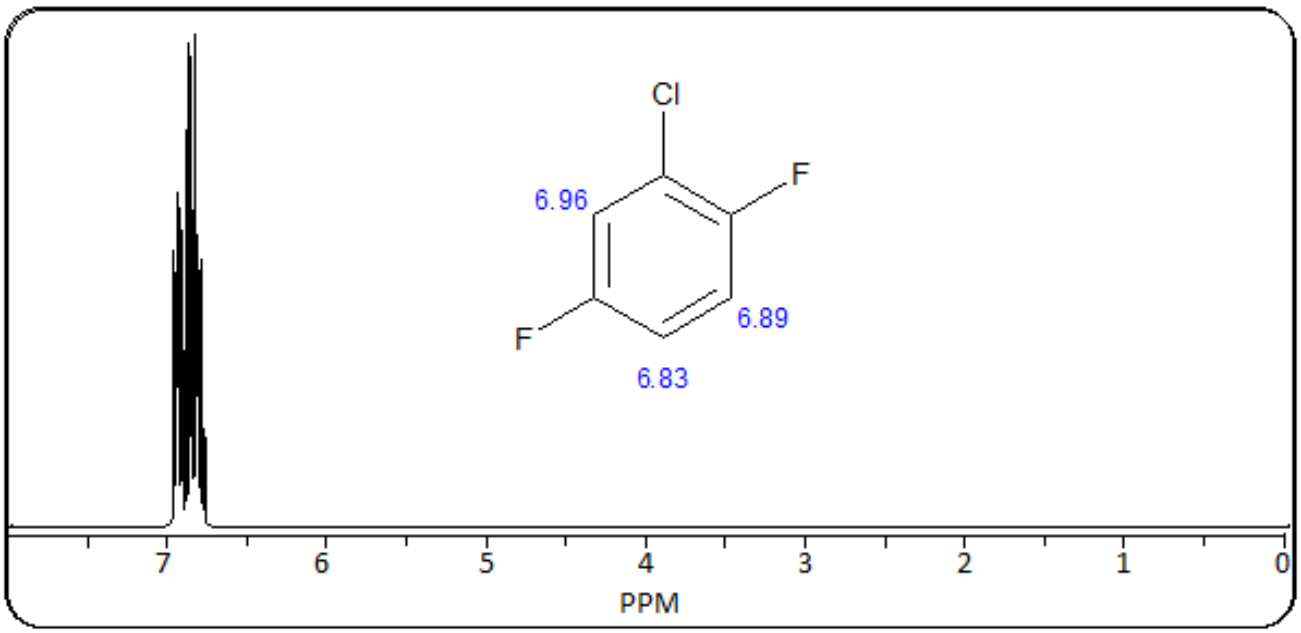
Reaction taken in 50ml 4N RBF, gas purging tube, reflux condenser all set up over oil bath, Charge 20 g (0.13mol) of 2,5-Difluoroonitroarene, 40 gm 1,2-Dichlorobenzene and 22.31 g (0.31 mol) chlorine gas was introduced at a rate of 1.2 g/hr at 165°C for 19-20 hours. The reaction monitoring by Gas chromatography, whereby the conversion of the starting material to 2, 5-difluorochlorobenzene was 85.35%. Purification done by distillation under reduced pressure 12.3 gm **(Yield: 65.9%)**



1,4-difluoro-2-nitrobenzene

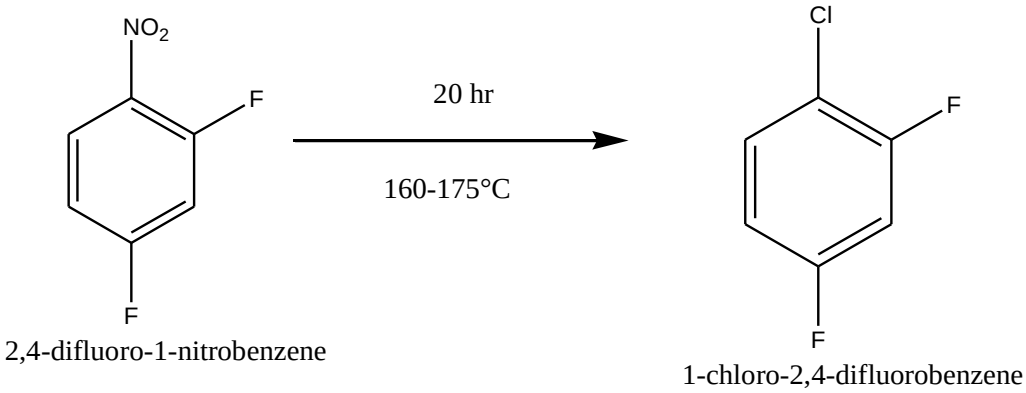
2-chloro-1,4-difluorobenzene

^{1}H NMR: δ 6.96-6.89 (2H, 6.96 (dd, *J* = 8.2, 1.7 Hz), 6.83 (dd, *J* = 1.7, 0.6 Hz)), 6.89 (1H, dd, *J* = 8.2, 0.6 Hz).



Synthesis of 2, 4-Difluorochloroarene from 2,4-Difluoronitrobenzene

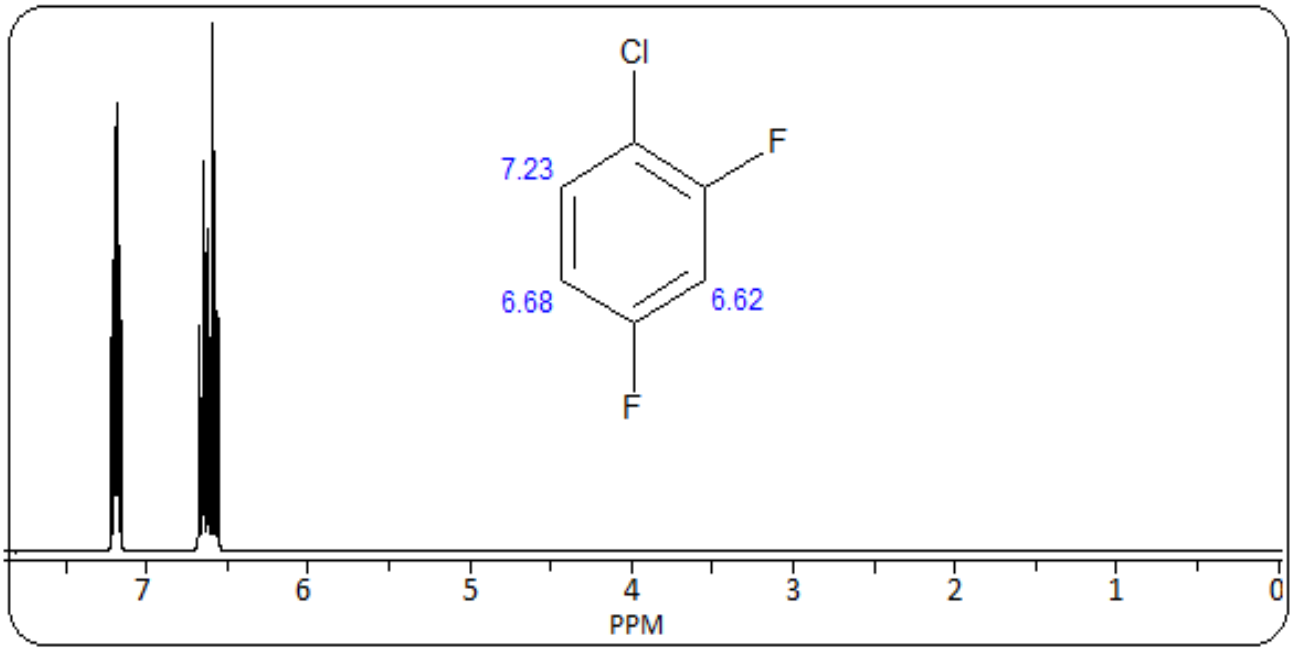
Reaction taken in 50ml 4N RBF, gas purging tube, reflux condenser all set up over oil bath, Charge 20 g (0.13mol) of 2,4-DFNA, 40 gm 1,2-Dichlorobenzene and 22.31 g (0.31 mol) chlorine gas was introduced at a rate of 1.2 g/hr at 165°C for 19-20 hours. The reaction monitoring by Gas chromatography, whereby the conversion of the starting material was to 2, 4-DFCB was 89 %. Further, purification done by distillation under vacuum 15.2 gm **(Yield: 81.4%)**



2,4-difluoro-1-nitrobenzene

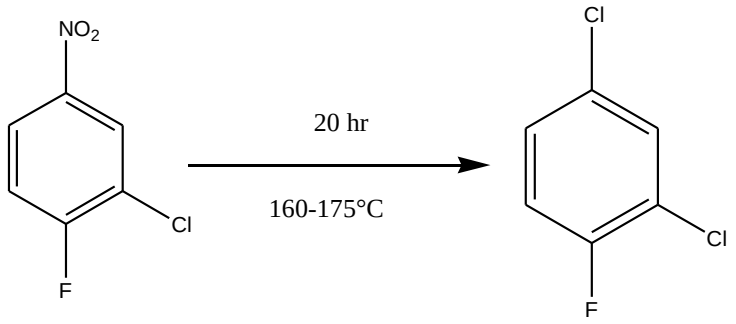
1-chloro-2,4-difluorobenzene

^{1}H NMR: δ 6.62-7.23 (1H, 6.62 (dd, *J* = 8.2, 1.62 Hz), 6.62-7.23 (2H, dd, ***J* = 8.2, 0.55 Hz**), 6.89 (dd, *J* = 1.6, 0.55 Hz)



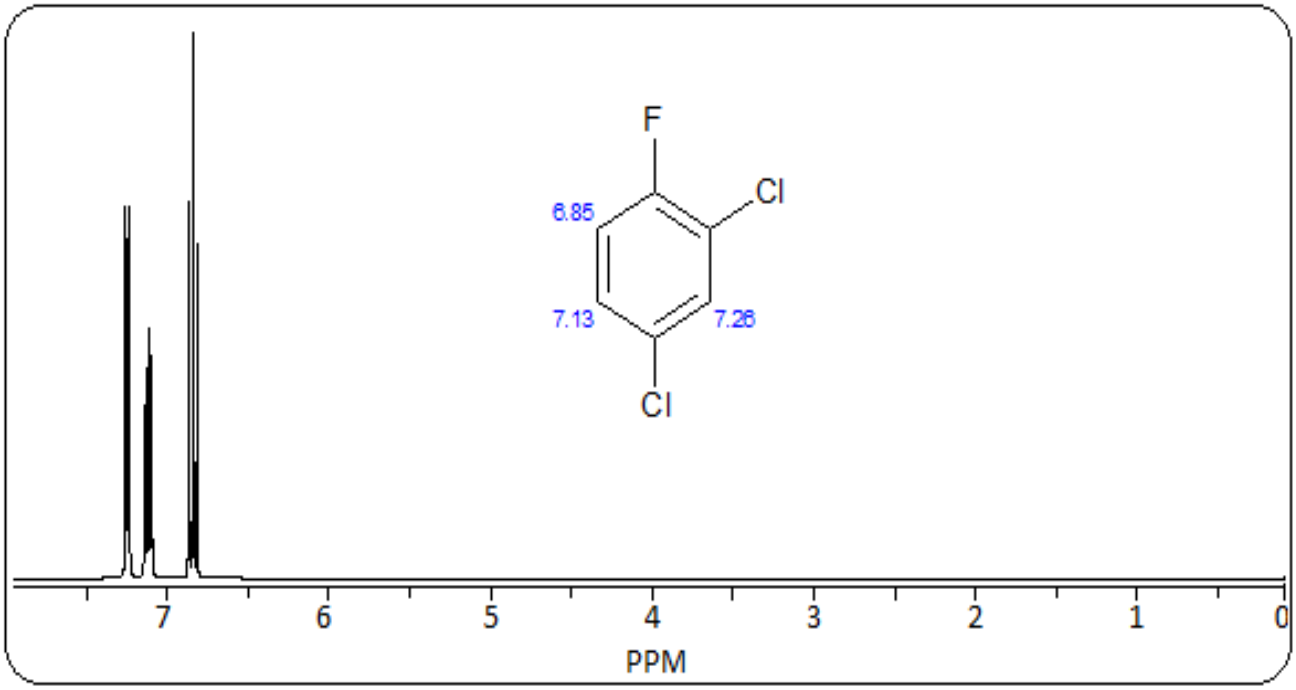
Synthesis of 2,4-Dichloro fluoro arene from 3-chloro-4-fluoro nitroarene

Reaction taken in 50ml 4N RBF, gas purging tube, reflux condenser all set up over oil bath, Charge 20 g (0.13mol) of -3-chloro-4-fluoronitroarene, 40 gm 1,2-Dichlorobenzene and 22.31 g (0.31 mol) chlorine gas was introduced at a rate of 1.2 g/hr at 165°C for 19-20 hours. The reaction monitoring by Gas chromatography, whereby the conversion of the starting material to 2, 4-dichlorofluorobenzene was 75.83%. Purification done by distillation under reduced pressure 15.23 gm **(Yield: 80.7%)**



2-chloro-1-fluoro-4-nitrobenzene 2,4-dichloro-1-fluorobenzene

^{1}H NMR: δ 6.81-6.96 (3H, 6.85 (dd, *J* = 1.79, 0.55 Hz), 7.13 (dd, *J* = 8.1, 0.0.55 Hz), 7.26 (dd, *J* = 8.1, 1.79 Hz)



Properties of Haloarens:

Final Products	Molecular Formula	Molecular weight	Melting point	Boiling point	Density (g/ml)
2,4-DCFA	$C_6H_4Cl_2F$	164.99	-28.2ºC	173.2ºC	1.43
2,5-DFCA	C6H3ClF2	148.54	-8.8ºC	127.21ºC	1.35
2,4-DFCA	C6H3ClF2	148.54	-18ºC	126.89ºC	1.34

Comparative study using same parameters of Haloarens:

Compounds	Molecular Formula	Reaction Temperature	Chlorine Rate	Theoretical Yield Gm/%	Practical Yield Gm/%
2,4-DCFA	$C_6H_4Cl_2F$	160-175ºC	1.2 g/hr	18.85/100	15.23/80.7
2,5-DFCA	$C_6H_3ClF_2$	160-175ºC	1.2 g/hr	18.66/100	12.3/65.9
2,4-DFCA	$C_6H_3ClF_2$	160-175ºC	1.2 g/hr	18.50/100	15.2/81.4

Conclusion:

In this study the eco-friendly, inexpensive, facile and fast green synthesis of haloarenes using a chlorinated solvent as preventer for formation of residual impurities in the reaction and the molecule confirm by spectroscopic analysis H-NMR. The procedure that no utilizes any catalyst for the de-nitrochlorination to activated arene substrates, while the use of chlorobenzene as a solvent was effective for more activated aromatic compounds.

Acknowledgments:

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