

Recent advances in practice and theory of polyfluoroarene hydrodehalogenation

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Dedicated to the memory of Academician I.L. Knunyants on the occasion of his 100th birthday.

Abstract

The development of concise and highly selective ways to prepare partially fluorinated arenes from readily available polyfluoro ones, the former being valuable building blocks in fine synthesis and material production but much less accessible, remains a challenging synthetic problem. Results achieved in this area over the last one and a half decade, particularly those relating to reductive hydrodehalogenation/defluorination of perfluoro- and perfluorochloroarenes by zinc, are reviewed in the present article. Mechanistic aspects of this chemistry as associated with structure and reactivity of intermediate polyfluoroarene radical anions are also considered.

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1. Introduction

Since about half a century ago there has been a rush into the polyfluoroarene area, which has become possible owing to the methods of partial and/or complete arene fluorination using one-pot procedures. In doing so, perfluoro- and perfluorochloroarenes, and also some of the functional derivatives became more accessible, than partially fluorinated arenes, which themselves could only be prepared through step by step repeated inconvenient and laborious procedures, each inserting but a single fluorine. Thus, considering the great value of partially fluorinated arenes as versatile synthetic intermediates, one can understand why the development of concise and highly selective ways to proceed from perfluoro- and perfluorochloroarenes to less fluorinated arenes by substitution of hydrogen for halogen remains a live and challenging problem.

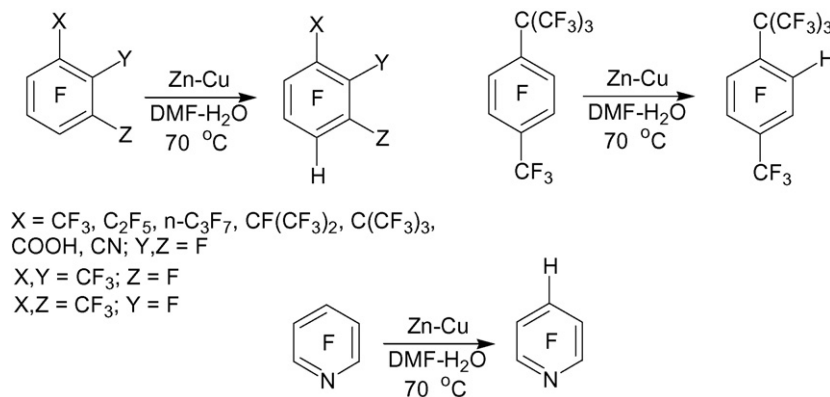
The work in this direction was done for a long time, and approaches found can be divided into two categories. The first one embraces methods involving insertion into a perfluoro- or a perfluorochloroarene of a functional group (carboxylic, hydrazo, metallic group) which can be subsequently substituted

by hydrogen. These “indirect” methods, being earlier reviewed [1], are not considered in the present article. However, despite a diversity of such approaches, multistep routes do not completely solve the problem of restricted accessibility of partially fluorinated arenes.

Evidently, the direct hydrogen substitution for halogen (hydrodehalogenation) in readily available highly fluorinated arenes is a most expeditious achievement of the goal. Rather attractive is reductive hydrodehalogenation but its scope of application, particularly that of hydrodefluorination, was quite limited until recently [2–4]. To replace halogens heavier than fluorine, catalytic hydrogenation and reduction by metals (Zn, Cu(I)) in the presence of proton sources were used [1]. However, polyfluoroarenes with heavy halogens, especially functionalized ones, are, as a whole, less accessible than perfluoroarenes. Already at the initial stage of polyfluoroarene chemistry, hydrodefluorination by metal hydrides was practiced as one of the fluorine nucleophilic substitution reactions which are most typical for these compounds [5,6]. However, this mode of hydrodefluorination is often insufficiently selective and only restrictedly applicable to functionalized polyfluoroarenes.

Thus, the problem of easy transition from highly to less fluorinated arenes, first of all by means of selective hydrodehalogenation, remains relevant. The present article reflects

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Scheme 1.

the progress achieved in this area in the last one and a half decade.

2. Experimental data and synthetic applications

Recently hydrodefluorination of polyfluoroarenes by the reducing systems based on zinc was intensively studied. Being treated with Zn/Cu couple in aqueous DMF at 70 °C, perfluoroarenes with electron-accepting substituents and pentafluoropyridine undergo single hydrodefluorination at *para*- or *ortho*-position (γ - and α -position in a pyridine framework) to give corresponding products in 30–50% yields [7–9]. The yields can be increased up to 70–80% by using an electrolyte (NH₄Cl, NaCl) additive [10] (Scheme 1).

Unlike perfluoroalkylbenzenes depicted, perfluoro-*para*-xylene and -*para*-cymene undergo hydrogenolysis on the α -C–F bond of a perfluoroalkyl substituent. Hexafluorobenzene stays intact under these conditions [8].

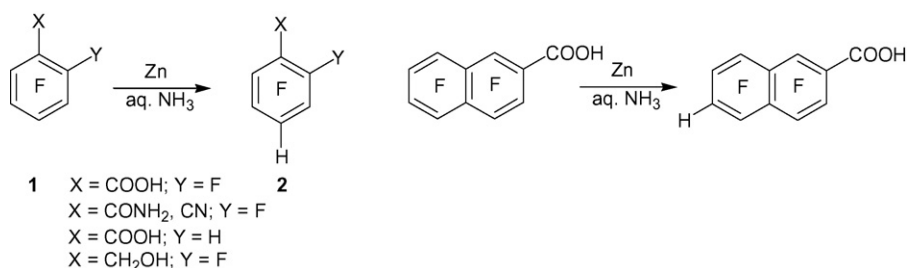
para-Hydrodefluorination of pentafluorobenzonitrile to yield 2,3,5,6-tetrafluorobenzonitrile was accomplished by metals, e.g. zinc, in aqueous solution in the presence of salts, e.g. KH₂PO₄, to prevent formation of HF [11].

Electrochemical hydrodefluorination of pentafluorobenzoic acid (**1**) is known to occur at the *para*-position to provide 2,3,5,6-tetrafluorobenzoic acid (**2**) [12]. Unlike this, *ortho*-fluorine is predominantly removed upon reduction of acid **1** by Yb(II) compounds followed by hydrolysis to give 2,3,4,5-tetrafluorobenzoic acid (**3**) [13].

Reduction of acid **1** (actually pentafluorobenzoate under the experiment conditions) with sodium in liquid ammonia [14] is non-selective and occurs as multiple hydrodefluorination even

at small conversion. Regardless of the order of reactants mixing the reaction gives a complex product mixture consisting of small and comparable (1–9%) quantities of acid **2**, 3,5-difluoro-, 3-fluorobenzoic and benzoic acid (alongside with significant amounts of unidentified products, obviously, cyclohexadiene derivatives). The reason of such non-selectivity is believed to be much faster electronic diffusion as compared with molecular diffusion [15]. Owing to this electrons occupy much more quickly the limited zone tightly contiguous with a reagent species carried into the reaction medium (a particle of acid **1** added to a liquid ammonia solution of sodium or a sodium bit added to a solution of **1**). As a consequence, a primary hydrodefluorination product undergoes further reduction in this unequilibrium zone before molecules of starting compound come there. So far as one can judge from the product distribution, the positional hydrodefluorination rate increases in the order *meta* < *ortho* < *para*.

The situation changes dramatically with replacement of sodium by zinc. In the last case electrons do not get off from the metal into the solution, and the reduction occurs much more slowly and, apparently, at the immediate contact of a substrate molecule with the metal surface. In so doing the effective zinc reduction potential appears to suffice for reducing acid **1**, but not products of its hydrodefluorination. As a result, acid **2** is formed in a more than 90% yield. Some later *para*-hydrodefluorinations of acid **1**, as well as its amide, pentafluorobenzyl alcohol and *ortho*-hydrodefluorination of acid **2** were shown to smoothly occur in aqueous ammonia at room temperature (70–95% yields). The primary *para*-hydrodefluorination of pentafluorobenzonitrile also proceeds, but the reaction is complicated by formation of significant amounts of by-products. In these



Scheme 2.

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