



Alkaline aqueous solution promoted debromination of 1,2-dibromo-fluorocarbons – A convenient method for electron deficient perfluorovinyl ethers



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ABSTRACT

A facile and efficient base-mediated protocol for debromination of vic-dibromides in perfluoroalkyl(aryl) compounds in aqueous medium has been demonstrated. With mild reaction conditions, the developed strategy has a good substrate scope and electron-deficient olefin products were obtained in good yields. A mechanistic explanation of the debromination is offered with three key experimental observations: (1) the reactions are accelerated by the more electron-rich nucleophiles, (2) the reactions are promoted by the more electron poor vic-dibromides in perfluoroalkyl compounds, and (3) the nucleophilic side reaction is preventable. It is evident that the electronic factors strongly dictate vic-dibromides elimination to the perfluorovinyl ethers, which are the precursors for various perfluorinated polymers. The different reaction conditions were tested in implicit solvent (water) conditions, which helped to confirm the E2-like mechanism.

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Introduction

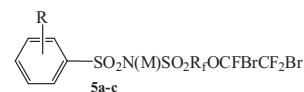
It is well known that protection/deprotection of double bonds via bromination-debromination is widely utilized to prevent the undesirable side reaction to the olefins.¹ Except for the traditional methods with metal zinc/acetic acid or sodium iodide/acetone, recent reports on debrominations include reactions with strong nucleophiles, such as sodium dithionite and selenium tellurides, and low-valent metals, such as lithium, sodium, copper, iron, samarium, indium, and the organic solvent DMF.² The different debrominating agents and methods were explored depending on the substituent patterns and other functionality in the substrates being inert to the conditions of debromination.³ However, none of them efficiently provided electron-deficient poor olefins, such as perfluorovinyl ethers, from vic-dibromides under mild conditions.

Perfluorovinyl ethers ($R_f\text{OCF}=\text{CF}_2$) are main components of monomers to be copolymerized in fluoroelastomers and to be used to modify the crystallinity in fluoroplastics.⁴ At elevated temperature, those copolymers exhibit excellent chemical and mechanical properties for wide industrial applications.⁵ During the past several years, our research groups have been actively involved in preparing

various of diazonium perfluoroalkyl(aryl) sulfonimides (PFSIs) compounds for proton exchange membrane (PEM) fuel cells and photo acid generators.⁶ Among them, a series of diazonium PFSI zwitterionic monomers, containing the polymerizable perfluorovinyl ether moiety, are employed to yield desired polymer electrolytes in PEM fuel cells.⁷

Interestingly, the debromination of vic-dihalides occurred while refluxing one intermediate of diazonium PFSI monomer, $\text{ArSO}_2\text{N}^+(\text{M})\text{SO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCFBrCF}_2\text{Br}$ (compound **5b** in Fig. 1) with Cs_2CO_3 water/acetone solution.⁸ This observation intrigues the exploration of more convenient and efficient routes toward protection/deprotection versatile perfluorovinyl ethers in PFSI compounds (Fig. 1).

Here, we wish to report the reflux-assisted or sonication assisted debromination of vic-dibromides in the case of PFSIs with

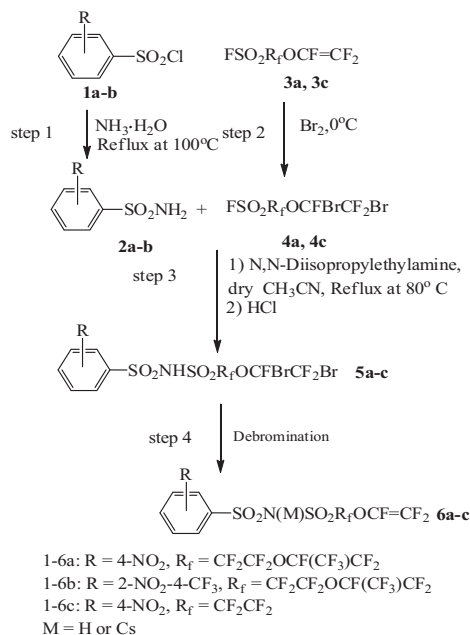


- a: R = 4-nitro, $R_f = \text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2$
 b: R = 2-nitro-4- CF_3 , $R_f = \text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2$
 c: R = 4-nitro, $R_f = \text{CF}_2\text{CF}_2$
 M = H or Cs

Fig. 1. Nitro substituted aromatic PFSIs.

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Scheme 1. Part of synthetic route for diazonium PFSI monomers.

moderate base/nucleophiles, which provides the perfluorovinyl ether moiety with excellent yield.

Results and discussion

Although the debromination of vic-dibromides generally proceeds smoothly to provide the olefins with high yields, the regular methods encounter quite a few challenges towards brominated perfluorovinyl ether pendant in perfluoroalkyl(aryl) compounds.⁹ In general, highly fluorinated alkenes are very electron deficient

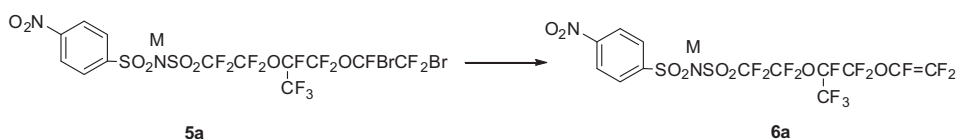
species and therefore susceptible to attack by a wide range of nucleophiles.¹⁰ Therefore, the nucleophiles promoted debromination, which often used for regular olefins, is not tried for perfluorovinyl ethers. On the other hand, due to the specific electronic and steric properties of F-alkyl groups, perfluorinated olefins, particularly those containing one or two perfluoroalkyl groups, are extremely resistant towards electrophilic attack.

As part of our research project to prepare polymer electrolytes for PEM fuel cells from diazonium PFSI monomers, perfluorovinyl ether was protected with bromination first (Step 2 in Scheme 1) against the strong nucleophiles (2a–d in Scheme 1) at high temperature. The debromination (Step 5 in Scheme 1) was anticipated to recover the perfluorovinyl ether group after the nucleophilic substitution reaction (Step 3 in Scheme 1).

Initially, NaI/acetone, the metallic zinc, and iron in acid were attempted to debrominate brominated perfluorovinyl ethers in PFSIs because of low cost and availability. Except for the first one, the rest of transition metals/acid systems worked but often offered moderate yields around 50–75% with unavoidable hydrogenated by-products.¹¹ For example, during the zinc redox reaction, the maximum conversion was achieved via refluxing with more than the tenfold excess of activated zinc powder in dry acetonitrile overnight.⁹ Due to strong electron-withdrawing perfluoroalkyl pendant, the zinc insertion product (ArOSO₂N(M)SO₂R_fOCF₂CF₂-ZnBr) exhibits unusual stability in these sluggish redox reactions. Care must be taken that the PFSI vic-dibromides do not debromination completely with a small amount of moisture. Thus, those traditional methods suffer from harsh reaction conditions, tedious purification procedures, and moderate yields in addition to characterization and waste handling problems.¹¹

As reported earlier, the work up the process to purify the crude nitro-substituted aromatic PFSI compound 5b involved first acidification, followed by neutralization with Cs₂CO₃ aqueous solution and recrystallization with acetone/water. The unusual partial debromination took place during the recrystallization process.⁵ Encouraged by this result, our investigation started with an effort

Table 1
 Debromination of vic-dibromides of perfluorovinyl ether in 4-nitrobenzene PFSI compound (5a).



Entry	Base	n (base): n (dibromides) ^a	Solvent ^b	Time ^c (min)	Debr ^d %	Yield ^e %
1	Cs ₂ CO ₃	9.2: 1	2:1	0	0 ^h	0
2	Cs ₂ CO ₃	9.2:1	1:5	15	58.5	35.1
3	Cs ₂ CO ₃	9.2:1	1:5	30	73.4	18.4
4	Cs ₂ CO ₃	1.9:1	5:1	30	100	74.0
5	Cs ₂ CO ₃	9.2:1	0.8:1	30	100	83.3
6	Na ₂ CO ₃	9.2:1	0.8:1	30	100	66.7
7	Na ₂ CO ₃	7.7:1	0.8:1	40	94.2	60.2
8	Na ₂ CO ₃ & DIEA	9.2:1	0.8:1	30	100	77.6
9	Na ₂ CO ₃	2.3:1	20:3	30	1.4	1.4
10	Na ₂ CO ₃	9.2:1	0.8:1 ^f	30	0	0
11	Na ₂ CO ₃	9.2:1	1:4 ^f	30	0	0
12	NaOH & DIEA	9.2:1	0.8:1	30	100 ^g	45.5
13	NaOH	9.2:1	0.8:1	30	100 ^g	22.2

^a 0.33 mmol of 5a.

^b The solvent ratio (acetone:water).

^c Entries 1–4: refluxing time; Entries 5–14: Sonication time.

^d The calculated debromination percentage base on the fluorine NMR spectra.

^e The isolated recovery weight of debromination product.

^f The solvent ratio (Methanol:water).

^g The hydrolysis occurs.

^h The solution was only stirred for 30 min without reflux.

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