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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.

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 electrondeficient poor olefins, such as perfluorovinyl ethers, from vic-dibromides under mild conditions.

Perfluorovinyl ethers (R_fOCF=CF₂) 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, $ArSO_2N^{-}(M)SO_2CF_2CF_2OCF(CF_3)CF_2OCFBrCF_2Br$ (compound **5b** in **Figure 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 (**Figure 1**).

Here, we wish to report the reflux-assisted or sonication assisted debromination of vicdibromides in the case of PFSIs with moderate base/nucleophiles, which provides the perfluorovinyl ether moiety with excellent yield.



Figure 1. Nitro Substituted Aromatic PFSIs

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**).



Scheme 1. Part of Synthetic Route for Diazonium PFSI Monomers

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 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 to discover and optimize the reaction conditions for debromination of vic-dibromides to perfluorovinyl ether with inexpensive reagents and environmental benign reaction conditions. The cesium salt of vic-dibromide of 4-nitrobenzene PFSI compound (**5a** in **Scheme 1**), because of the accessibility, was first chosen as a probe for the optimization process. The initial trials were carried out as the similar process of the last two steps to work-up the coupling product of

5a, which involved neutralization by Cs_2CO_3 and next refluxing in the co-solvent of acetone/water. Entries 1 to 4 in **Table 1** represent the examples of debromination of **5a** via refluxing.

These examples illustrate the issues that must be considered in optimizing reaction protocol. The major factors are the refluxing time, the amount of base, and solvents ratio. Entry 1 shows that the debromination will not happen if just stirring the base with the dibromides **5a**. Particularly, heating or sonication is essential for the completion of debromination. Comparing Entries 2 and 3, the required minimum refluxing time is around 30 minutes. It is also suggested that less amount of water for recrystallization can lead to higher final yield according to Entries 3 and 4, which represents the optimization condition for this method.

Meanwhile, the resulting purified **6a** can be simply reduced to aromatic amino compounds with the ultrasound assistance. It was contemplated to pursue the sonicated debromination for a more efficient and general method. Unlike the refluxing, sonication procedure can take place at room temperature. Moreover, extraction for purification of product replaced the recrystallization, which was expected to increase the overall yield. Some examples of sonicated debromination of **5a** (Entry 5-15) are shown in **Table 1**.

Table 1. Debromination of Vic-Dibromides of Perfluorovinyl Ether in 4-Nitrobenzene PFSI Compound (5a).

 O_2N . O_2N M SO2NSO2CF2CF2OCFCF2OCFBrCF2Br SO2NSO2CF2CF2OCFCF2OCF=CF2 ĊF₃ 6a 5a

Entry	Base	n (base): n (dibromides) ^A	Solvent ^B	Time ^C (mins)	Debr% ^D	Yield % ^E
1	Cs ₂ CO ₃	9.2 : 1	2:1	0	$0^{\rm H}$	0
2	Cs_2CO_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	9.2:1	0.8:1	30	100 ^G	45.5

	&					
	DIEA					
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 mins without reflux.

Owing to the solubility issues, slightly more water was used in the sonication (acetone: water = 0.8:1) than the refluxing procedure. The higher overall percentage yields resulted from extraction in Entries 5-11 after sonication. Because of the cost and availability, the regular inorganic bases, such as Cs₂CO₃, Na₂CO₃, NaOH, organic base N, N-diisopropylethylamine (DIEA), were tried for sonication process (Entries 5-13 in Table 1). For example, under the same condition in Entries 5 and 6, sonicated debromination resulted in higher percentage yield and full debromination with Cs₂CO₃ compared to Na₂CO₃. The possible reasons can be summarized in the following. Due to high polarizability and size, $C_{s_2}CO_3$ is the most basic of the alkali carbonates of the group I metals, referred as the "cesium effect". The preference of cesium carbonate also rests on practical considerations, particularly low hygroscopicity relative to the hydroxide and better organic solvent solubility.¹² Furthermore, the alkali metal hydroxide not only can initiate the debromination but also immediately attack the recovery double bond in Entries 12 and 13. Such phenomenon can attribute to the perfluorovinyloxyl ether moieties, which are unexpectedly susceptible to the aqueous bases at high temperature or sonication but resistant to acids compared to other regular alkenes.¹³ Interestingly, the reaction was high yielding when assisted by an inorganic base and DIEA (Entry 8), which represented the optimal purification procedure: omitting the acidification step during work-up of crude product 5a. Among the alkali carbonates, Na₂CO₃ was further investigated due to the low cost (Entries 6, 7-11). Even with longer time consumed in Entry 8, the debromination was not completed with less than around 9 equivalent of the base catalyst. Replacing the aprotic polar solvent acetone with protic polar solvent methanol, Entries 11 and 12 reduced the solubility of base and dibromides and led to no debromination at all. To our satisfaction, the best-optimized procedures were established as indicated in Table 1, Entries 4, 5, 8 for compound 5a with Cs₂CO₃ or Na₂CO₃ catalysts.

Our investigations for the envisaged debromination protocol continued by examining electronic factors on other vic-dibromides, including compound 5c (Scheme 1) and meso-1, 2dibromo-1, 2-diphenyl ethane (e). Several exemplary results are chosen to list in Table 2.

Table 2. Debromination of Other Vic-Dibromides (5c and e) via Sonication Procedure



Br

		Br		_	×>		\square	
		e						
Entry	Sub ^A	Amount (mmol)	Base	Ratio ^B	Solvent	Time ^C	Debr % ^D	Yield % E
14	5c	0.16	Na ₂ CO ₃	12:1	Acetone: water 1:7.3	90 min	85.7	61.2
15	5c	0.16	Na ₂ CO ₃	14:1	Acetone: water 1:1.1	5 h	56.6	42.8
16	5c	0.32	Na ₂ CO ₃	28:1	Acetone: water 1:1.8	48 h	100	85.7
17	5c	0.46	NaOH	2:1	Acetone-water 1.3:1	12 h	67.8 ^{<i>F</i>}	66.7
18	5c	2.35	NaOH	1.3:1	Acetone-water 1:2.4	7 h	100	90.8
19	5c	0.46	NaOH	2.6:1	Methanol: water 2.3:1	12 h	0	0
20	e	0.33	Na ₂ CO ₃	9.2:1	Acetone-water 0.8:1	60 min	0	0
21	e	0.33	Na ₂ CO ₃	9.2:1	Methanol: water 0.8:1	60 min	0	0
22	e	0.33	Na ₂ CO ₃	9.2:1	DMSO: Water 0.8:1	60 min	0	0
23	e	0.33	NaOH	9.2:1	Acetone-water 0.8:1	60 min	0	0

^{*A*}: Substrate: the dibromides ^{*B*}: n (base): n (dibromides)

C: Sonication time;
 D: The calculated debromination percentage base on the fluorine NMR spectra;
 E: The isolated recovery weight of debromination product

^{*F*}: The hydrolysis occurs.

After some experimentation, it was found that the PFSI group, as a strong electronwithdrawing group, strongly affected the reaction rate. A unique feature of 5c is that the shorter PFSI group, compared to 5a, potentially carries less electron withdrawing effect onto the vicdibromides. As a consequence, longer time and more bases are desirable for the planned debromination procedure for 5c (Entries 14-16). Similar to 5a, the stronger base NaOH promotes the debromination of **5c** in Entry 17, and the following nucleophilic addition or addition-elimination also is often accompanied for producing perfluorovinly olefin **6c**. The mechanism was earlier reported by Dr. Feriring et al..¹⁰ The fluorocarbon anions readily

generated in situ (I in **Scheme 2**) can be trapped by electrophiles, such as protons or bromine cation (I to II or III in **Scheme 2**).¹⁴ Or the substituted fluoroolefin was isolated (I to IV in **Scheme 2**) after loss of fluoride ion. Unexpectedly, such side reaction is preventable for **6c** if the debromination was controlled with short reaction time and a small amount of NaOH, as outlined in Entry 18. It is suggested to avoid the prolonged contact between the dehalogenated product and the strong base, as the secondary reactions take place in the reaction raw product with consequent detriment of the yields. Compared to **6c**, **6a** is more reactive toward the nucleophiles since the stronger EW groups stabilize the corresponding fluorocarbon anion. Similar to Entries 10 and 11, either the solubility problem or the side reaction (I to II in **Scheme 2**) prohibits the debromination to perfluorovinyl ether of **5c** in the protic organic solvent, such as methanol in Entry 19.



Scheme 2. The Possible Side Reactions of Vic-Dibromides Debromination in PFSIs

Besides, the debromination method is ineffective for the debromination of meso-1, 2dibromo-1, 2-diphenyl ethane (e) as Entries 20-23 show. Even after dissolving in the polar solvent, DMSO/water, Entries 20-23 still give the negative result.

From the above results, it is evident that the electronic factors strongly dictate vic-dibromides elimination to the perfluorovinyl ethers, resulting in the observed relatively better reactivity towards more electron poor dibromides. It is believed that the nearby strong electron withdrawing group, such as PFSI group, is crucial for such debromination of vic-dibromides. Among the two mechanisms proposed by Detty et al.¹⁵ (Scheme 3), nucleophilic attack bromides (E2-like) model is believed to be accountable for the observations: (1) the reaction was accelerated by the more electron-rich nucleophiles, and (2) the reaction was promoted by the

more electron poor vic-dibromides in perfluoroalkyl compounds. On the other hand, since the intermediate bromonium carbocation is extremely unstable with neighboring fluorine and perfluoroalkyl groups, the bromonium ion model is not a likely pathway. Hydroxide anion acts as nucleophile is the basic aqueous condition in our case.



Scheme 3. Possible Mechanisms for Debromination of Vic-Dibromides in PFSIs

Conclusion

Our experiments outlined in the experimental section indicate a versatile, direct method for dehalogenation of vic-dibromide in perfluoroalkyl compounds. Notably, ultrasound technology can be used in the process, which avoids heating and results in a much shorter reaction time and simpler operation. The method provides a straightforward synthesis of electron-deficient olefins, such as perfluorovinyl ethers in PFSI compounds. Those compounds are not only troublesome to prepare from debromination by classical means but also likely to have further nucleophilic/nucleophilic-elimination reactions. To our delight, the electron withdrawing PFSI group sufficiently promotes the debromination under the moderate basic conditions, which also proves the reaction progress through nucleophilic attack bromides (E2 like) model.

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A Supplementary Material

Supplementary data associated with this article can be found, in the online version, at xxxxx.

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Graphical Abstract

