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Short communication

Studies on sulfinatodehalogenation: The addition of polyfluoroalkyl iodides to olefins promoted by sodium bisulfite and sodium sulfite

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Abstract

The reaction of polyfluoroalkyl iodides with alkenes or 4-pentenoic acid promoted by sodium bisulfite or sodium sulfite in DMF aqueous solution was realized. The reaction of alkenes gave corresponding adducts, while γ-lactones were obtained in the case of 4-pentenoic acid in good yields.

Keywords: Polyfluoroalkylation; Sodium bisulfite; Sodium sulfite; Addition reaction; Lactonization

1. Introduction

Recently, the application of fluorinated compounds in agricultural chemistry, medicinal chemistry, material science and organic synthesis is growing. Therefore, the development of new methodologies for selective introduction of fluorinated functions into organic molecules is of great importance [1]. The addition reaction of polyfluoroalkyl halides to olefins or alkynes is traditionally accomplished with photochemical [2], thermal [3], electrolytic [4], redox systems [5], especially, sulfur oxy-acid salts, such as sodium dithionite [6], rongalite [7], thiourea dioxide [8], sodium disulfite [9], and so on, which is one of the most efficient and versatile methods for the direct introduction of the fluoroalkyl groups into organic molecules [10].

Sodium bisulfite as well as sodium sulfite was recently reported to be a sulfinatodehalogenation reagent for polyfluoroalkyl iodides and bromides, and the reaction mechanism was considered to be a radical one [10b,11]. The polyfluoroalkyl radical intermediates formed in the reaction could be trapped by olefins. Here we described the results of the addition of polyfluoroalkyl iodides to double bonds promoted by sodium bisulfite and sodium sulfite.

2. Results and discussion

2.1. The reaction of polyfluoroalkyl iodides with olefins

Polyfluoroalkyl iodides reacted with olefins in DMF aqueous solution in the presence of sodium bisulfite or sodium sulfite, giving the corresponding adducts under mild conditions. The reaction proceeded readily at 40–60 °C for about 6–7 h. 1.5 eq. of olefin was used as the optimal amount. It gave the expected addition products in good yields, providing a new application of sodium bisulfite or sodium sulfite in polyfluoroalkylation reaction (Scheme 1). The detailed results were summarized in Table 1.

The addition of polyfluoroalkyl iodides to allyl ether (**2h**) gave the radical cyclization products with tetrahydrofuran structure (Scheme 2), which indicated the involvement of free radical intermediate.

The 1:1 adducts (E/Z) were separated in good yields after the addition of polyfluoroalkyl iodides to cyclohexene (**2i**) (Scheme 3).

However, the addition products of polyfluoroalkyl iodides with alkynes, for example, 1-hexyne (**2j**), under similar conditions were obtained in low yields, because alkynes, as expected, were less reactive than alkenes (Scheme 4). In case of acrylonitrile or phenylacetylene, no adducts were formed except the sulfinates.

In the addition reaction of polyfluoroalkyl iodides with olefins, both sodium bisulfite and sodium sulfite lead to high

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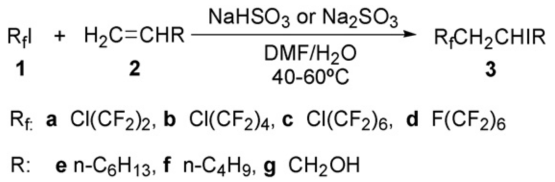
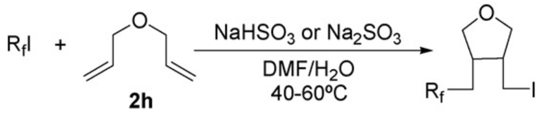


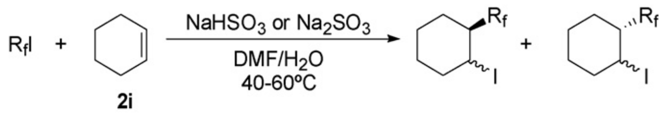
Scheme 1.

Table 1
The addition reaction of polyfluoroalkyl iodides with alkenes initiated by sodium bisulfite or sodium sulfite

Entry	RfIs	Olefins	Initiators	Adducts	Yields (%)
1	**1b**	**2e**	$NaHSO_3$	**3a**	89
2	**1b**	**2h**		**3b**	78
3	**1c**	**2g**		**3c**	85
4	**1b**	**2f**		**3d**	87
5	**1c**	**2i**		**3e**	81
6	**1b**	**2j**		**3f**	38
7	**1b**	**2h**	Na_2SO_3	**3b**	72
8	**1c**	**2f**		**3g**	75
9	**1a**	**2e**		**3h**	70
10	**1b**	**2e**		**3a**	85
11	**1d**	**2f**		**3i**	80
12	**1c**	**2i**		**3e**	70
13	**1c**	**2j**		**3j**	40



Scheme 2.

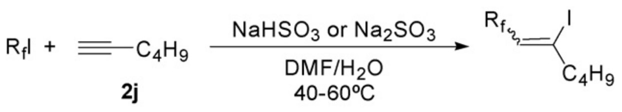


Scheme 3.

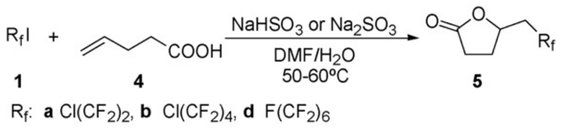
yields, while the results showed that the yields of the former were a little higher than that of the latter (Table 1, entries 1/10, 2/7, 5/12). The reason was thought to be related to the mechanism and would be mentioned infra.

2.2. The reaction of polyfluoroalkyl iodides with 4-pentenoic acid (**4**)

In recent publication of our laboratory [12], it had been reported that polyfluoroalkyl iodides reacted with 4-pentenoic acid (**4**) in the presence of sodium dithionite, giving the corresponding γ-lactones. Hence, the reaction of 4-pentenoic acid (**4**) with polyfluoroalkyl iodides promoted by sodium bisulfite or sodium sulfite in DMF aqueous solution was investigated. As a result, the corresponding lactones (**5**) were obtained in moderate yields (Scheme 5). The detailed results were summarized in Table 2.



Scheme 4.



Scheme 5.

Table 2
The lactonization reaction of polyfluoroalkyl iodides with 4-pentenoic acids initiated by sodium bisulfite or sodium sulfite

Entry	RfIs	Acids	Initiators	Lactones	Yields (%)
1	**1a**	**4**	$NaHSO_3$	**5a**	40
2	**1b**	**4**		**5b**	30
3	**1d**	**4**		**5d**	43
4	**1b**	**4**	Na_2SO_3	**5b**	40

2.3. Mechanism consideration

The formation of the anion radical was relative to the equilibrium in the bisulfite or sulfite solution shown in Scheme 6 [10]. In aqueous DMF solution, the equilibrium favors the formation of $S_2O_5^{2-}$ (*). It was supposed that the anion radicals $SO_3^{\bullet-}$ and/or $SO_2^{\bullet-}$ could be formed through the homolysis of S–S bond similarly to sodium dithionite [6]. Thus, the reaction was thought to be a single electron transfer (SET) process initiated by the anion radicals of $SO_3^{\bullet-}$ and/or $SO_2^{\bullet-}$, as proposed in Schemes 6 and 7. In the reaction, the polyfluoroalkyl radical was trapped by olefins, and corresponding adducts or lactones were prepared.

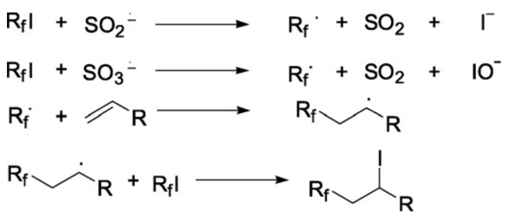
So, it was not difficult to explain why the yields of sodium bisulfite reaction system were a little higher than that of sodium

$$SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + OH^- \tag{1}$$

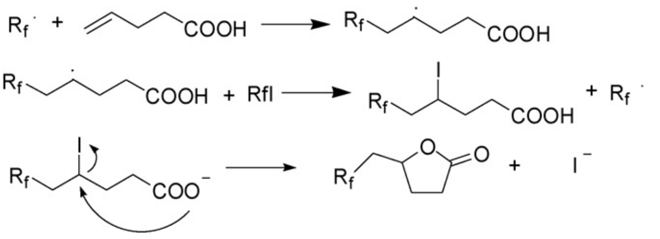
$$2HSO_3^- \rightleftharpoons S_2O_5^{2-}(*) + H_2O \tag{2}$$

$$S_2O_5^{2-} \rightleftharpoons SO_2^{\dot{-}} + SO_3^{\dot{-}} \tag{3}$$

Scheme 6.



Scheme 7.



Scheme 8.

sulfite reaction system (Table 1, entries 1/10, 2/7, 5/12). The reason was thought to be that the basicity and reductivity of former system were a little stronger than that of the latter.

The lactones were formed after an intramolecular S_N2 reaction of the adducts [12] (Scheme 8).

2.4. Conclusions

In conclusion, a mild and convenient method for polyfluoroalkylation promoted by sodium bisulfite and sodium sulfite was presented. Sodium bisulfite and sodium sulfite can also be used to initiate the reaction of polyfluoroalkyl iodides with 4-pentenoic acids. Efforts are in progress to elucidate the mechanistic details of this reaction and to disclose its scope and limitations.

3. Experimental

The general procedure: to the mixture of **2** (5 mmol), water (5 mL), DMF (10 mL) and **1** (5 mmol), sodium bisulfite or sodium sulfite (8 mmol) was added. The mixture was stirred at 40–60 °C for 6–7 h, then extracted with ether for several times. The combined organic layer was washed with saturated brine solution and dried over anhydrous sodium sulfate. After evaporation of ether, the crude product was purified over silica gel to give **3**. For the reaction of **1** with **4**, 7.5 mol of NaOH was added to the mixture before the addition of sodium bisulfite or sodium sulfite.

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