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New preparation of 1,1,2,2-tetrafluoro-2-(trifluoroethenyloxy)-ethanesulfonyl fluoride

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Abstract

A new preparation method of 1,1,2,2-tetrafluoro-2-(trifluoroethenyloxy)-ethanesulfonyl fluoride (**8**) has been developed utilizing the unique performance of the imidazole protective group. Namely, the electrodonating character of the imidazole protective group on the sulfonyl group enables the formation of the novel intermediate monomer, which can be easily converted to **8** by the reaction with HF.

Keywords: Monomer; Fluorine; Polymer electrolyte; Imidazole; Protective group

1. Introduction

Polymer electrolyte fuel cell (PEFC) has been investigated as an environmentally clean energy source with high efficiency. The perfluorosulfonic acid ionomers such as DuPont's Nafion® **1** and Dow's short side chain ionomer **2** have been used for the polymer electrolytes due to their chemical stability and proton conductivity (Fig. 1) [1].

Both **1** and **2** are prepared by the copolymerization of tetrafluoroethylene with the perfluorosulfonyl fluoride monomer (**7**, **8**). The monomer **7** is prepared by the decarboxylation reaction of the acyl fluoride **6** with Na_2CO_3 (Scheme 1) [2]. However, the monomer (1,1,2,2-tetrafluoro-2-(trifluoroethenyloxy)-ethanesulfonyl fluoride) (**8**) cannot be obtained by the reaction of the acyl fluoride **5** with Na_2CO_3 in the same manner, and the cyclic compound **9** is produced.

The proposed reaction mechanism is shown in Scheme 2. The acyl fluoride **5** reacts with Na_2CO_3 to form the sodium salt **10**. The pyrolytic decarboxylation of the sodium salt **10** generates the carbanion, which attacks the sulfonyl fluoride group to form the cyclic compound **9** quantitatively. The exclusive formation of five-membered ring **9** seems to be thermodynamically and/or kinetically favorable.

On the other hand, Ezzell et al. reported that the epoxide **11** containing the chlorine atom is useful for the suppression of the cyclization reaction [3]. Namely, as shown in Scheme 3, the chlorine atom works as a good leaving group, leading to the formation of the vinyl group instead of the ring formation. However, the drawback of the process in Scheme 3 is that the preparation of the epoxide **11** is more complicated than that of hexafluoropropylene oxide **3**, which is a commercially available material.

We report here a new preparation method of the monomer **8** via the imidazole derivatives (**15**, **16**) without using the epoxide **11** (Scheme 4).

2. Results and discussion

As shown in Scheme 5, the protonated compound **13** was prepared in one pot by the modification of Ref. [4]. The acyl fluoride **5** was added to Na_2CO_3 in tetraglyme while keeping the temperature below 40 °C to form the sodium salt **10**, and then, in the presence of the proton source (the mixture of H_3PO_4 and water), decarboxylation of the sodium salt **10** was carried out at 160 °C to produce the protonated compound **13** in 86% yield.

The proposed reaction mechanism is shown in Scheme 6. The carbanion generated by the pyrolytic decarboxylation of the sodium salt **10** reacts with the proton to produce the protonated compound **13**. In the presence of the proton source,

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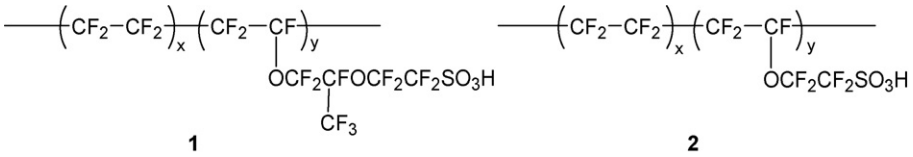
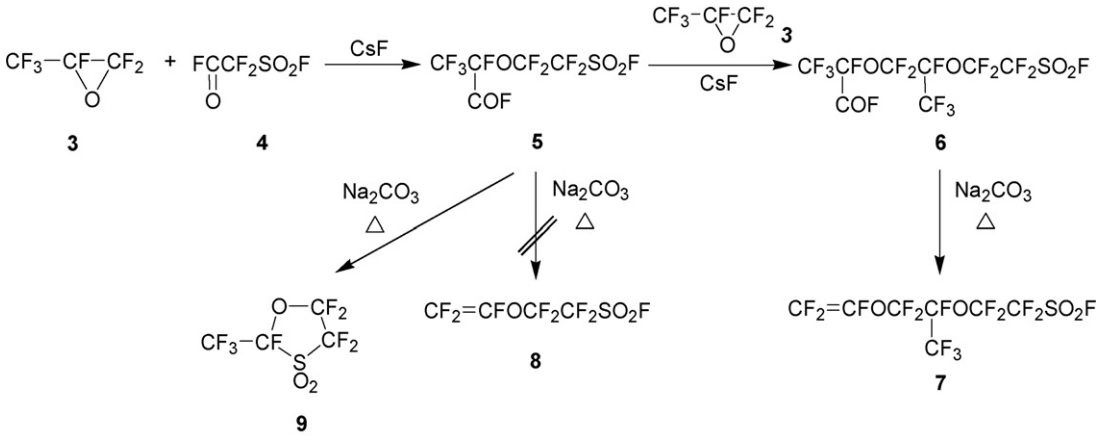
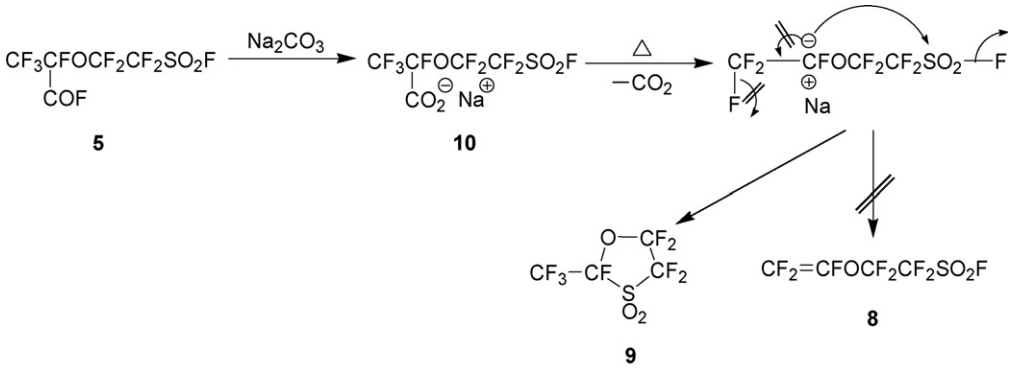


Fig. 1. Perfluorosulfonic acid ionomers.



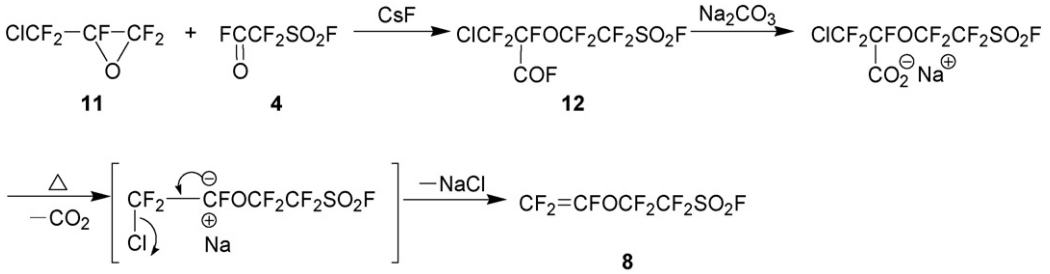
Scheme 1.



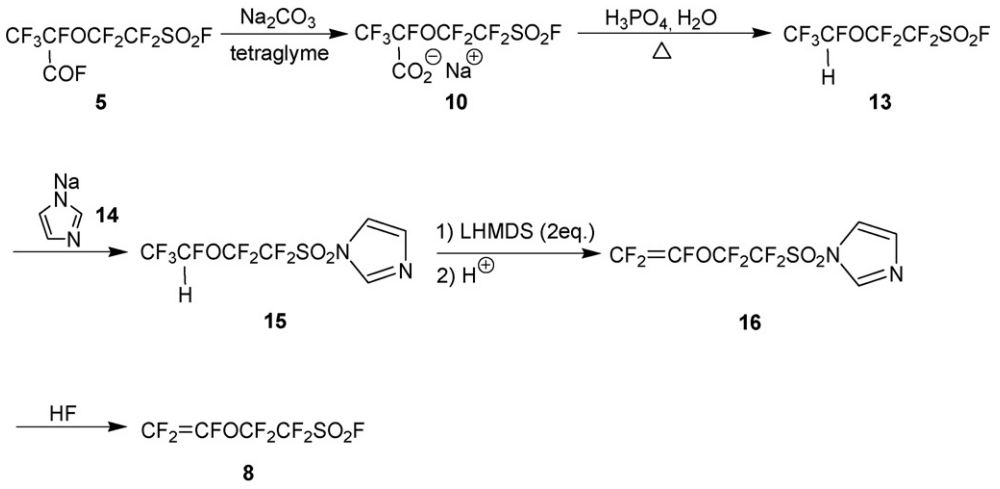
Scheme 2.

the rate of protonation of the carbanion is very rapid compared to that of formation of five-membered ring **9**.

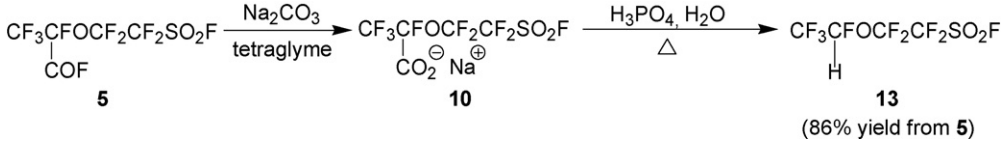
In the absence of H_3PO_4, the decarboxylation reaction of the sodium salt **10** showed the poor yield of the protonated compound **13** (43% yield). The reason of the poor yield is that the base (NaOH) is formed with the progress of the reaction of the carbanion with the proton, which reacts with the sulfonyl fluoride group to form the sulfonic acid salt ($CF_3CFHOCF_2$



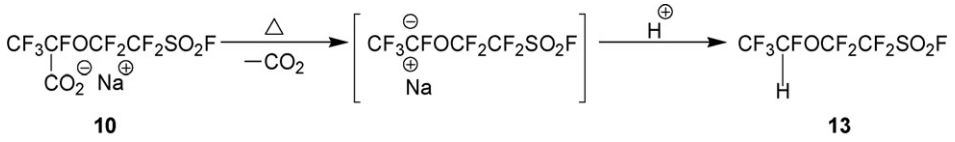
Scheme 3.



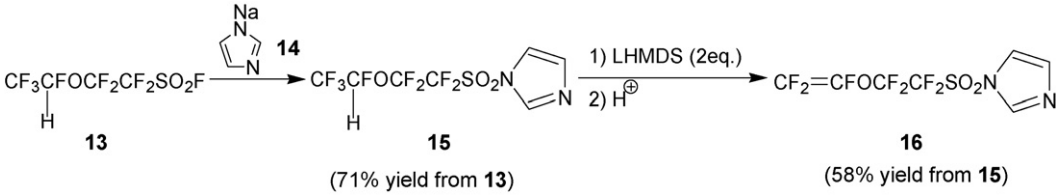
Scheme 4.



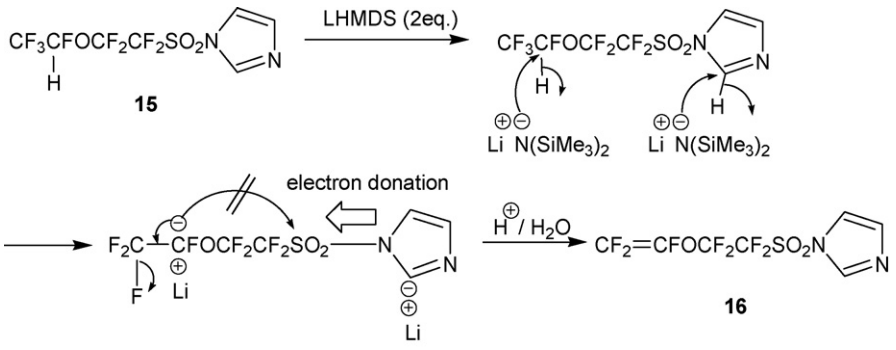
Scheme 5.



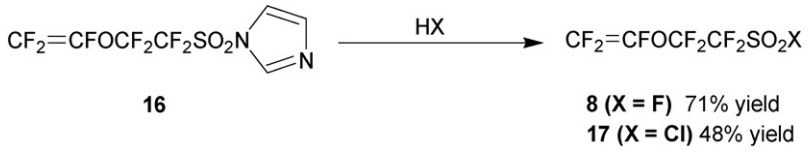
Scheme 6.



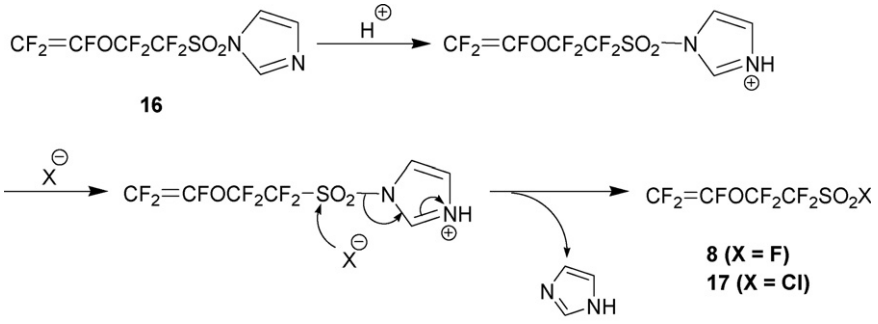
Scheme 7.



Scheme 8.



Scheme 9.



Scheme 10.

CF_2SO_3Na) as a by-product. However, by adding H_3PO_4 to the reaction mixture, the pH of the reaction system is kept acidic, and the yield of the protonated compound **13** was improved (86% yield).

The protonated compound **13** reacted with sodium imidazolide **14** (pre-generated from imidazole and NaH) to produce the imidazole derivative **15**. Dehydrofluorination of the imidazole derivative **15** was completely carried out using 2 equiv. of lithium hexamethyldisilazide (LHMDS) or sodium hexamethyldisilazide (SHMDS) to form the vinyl compound **16** (Scheme 7).

The proposed reaction mechanism is shown in Scheme 8. One equivalent of LHMDS is used for the proton abstraction for the conversion to the vinyl compound **16** and the other 1 equiv. of LHMDS is used for the proton abstraction at the 2-position of the imidazole ring. The carbanion generated by the proton abstraction does not attack the sulfonyl group, because the electron donation from imidazole ring to the sulfonyl group suppresses the nucleophilic attack of the carbanion on the sulfonyl site.

The vinyl compound **16** was added to 46 wt.% HF aqueous solution at room temperature, and then the mixture was stirred at 60 °C for 0.5 h to separate into two layers. The lower layer was separated and washed with water to obtain 1,1,2,2-tetrafluoro-2-(trifluoroethenyloxy)-ethanesulfonyl fluoride **8** as a colorless liquid in 71% yield. In the same manner, treatment of the vinyl compound **16** with concentrated HCl gave 1,1,2,2-tetrafluoro-2-(trifluoroethenyloxy)-ethanesulfonyl chloride **17** (Scheme 9).

The proposed reaction mechanism is shown in Scheme 10. By protonation of the nitrogen at the 3-position of the imidazole ring, the electron donation from the imidazole ring to the sulfonyl group is weakened, and a halide ion attacks the sulfonyl site to form the sulfonyl halide.

3. Conclusion

A new preparation method of 1,1,2,2-tetrafluoro-2-(trifluoroethenyloxy)-ethanesulfonyl fluoride **8** has been developed utilizing the unique performance of the imidazole protective group:

(1) The electrodonating character of the imidazole protective group on the sulfonyl group enables the formation of the novel intermediate **16**.
(2) The proton accepting character and the conjugated electron system of the imidazole protective group afford the substitution by HF to form the valuable monomer **8**.

4. Experimental

The reagents were obtained from commercial sources and used as received unless otherwise stated. $CF_3CF(COF)OCF_2CF_2SO_2F$ (**5**) was prepared as described in literature [5]. ^1H NMR (400 MHz) spectra and ^{19}F NMR (376 MHz) spectra were recorded in $CDCl_3$ on a JEOL GSX-400 and the chemical shifts (δ) were referred to tetramethylsilane (^1H), and $CFCl_3$ (^{19}F), respectively. GC–MS data were obtained on a Hewlett-Packard HP5890 series II gas chromatograph equipped with a HP5973 MSD with chemical ionization (CI) using methane as reagent gas.

*4.1. Preparation of 1,1,2,2-tetrafluoro-2-(1,2,2,2-tetrafluoroethyloxy)-ethanesulfonyl fluoride (**13**)*

To a 2 L round-bottom flask equipped with a mechanical stirring, a dropping funnel and a reflux condenser were added Na_2CO_3 (106.0 g, 1.0 mol), tetraglyme (311 mL). To the flask was added $CF_3CF(COF)OCF_2CF_2SO_2F$ (**5**) (311.0 g, 0.90 mol)

through a dropping funnel, while keeping the temperature below 30 °C over 3 h. After the completion of the addition, the reaction mixture was stirred at 40 °C for 1 h to form the sodium salt **10**. The formation of the sodium salt **10** was confirmed by ^{19}F NMR. To the flask was added the mixture of 85% H_3PO_4 (230.0 g, 2.0 mol) and water (230 mL). Then the flask was heated at 160 °C, and the protonated compound **13** and water were collected in the flask cooled by ice bath. The lower layer was separated, washed three times with water, dried over Na_2SO_4, and filtered to give a colorless liquid **13**. The yield of **13** was determined by ^{19}F NMR (231.1 g, 0.77 mol, 86% yield).

^{19}F NMR δ −147.91 (d, 1F, J = 52 Hz), −114.21 (s, 2F), −86.99 (d, 1F, J = 134 Hz), −86.53 (s, 3F), −84.67 (d, 1F, J = 134 Hz), 42.73 (s, 1F). ^{1}H NMR δ 6.07 (d, 1H, J = 52 Hz).

*4.2. Preparation of 1-[1,1,2,2-tetrafluoro-2-(1,2,2,2-tetrafluoroethyloxy)-ethanesulfonyl]-imidazole (**15**)*

To a 1 L round-bottom flask equipped with a mechanical stirring and a dropping funnel was added a dispersion of 60 wt.% NaH in a mineral oil (25 g, 0.625 mol), and washed with *n*-hexane to obtain a NaH powder. Then dry 1,2-dimethoxyethane (300 mL) was added to the flask, and cooled to 0 °C. To the flask was added a solution of imidazole (38.5 g, 0.566 mol) in dry 1,2-dimethoxyethane (200 mL) through a dropping funnel at 0 °C. After the completion of the addition, the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was cooled to 0 °C followed by addition of **13** (170 g, 0.566 mol) through a dropping funnel. After the completion of the addition, the flask was elevated to room temperature with stirring for 12 h. The formation of the imidazole derivative **15** was confirmed by ^{19}F NMR. The reaction mixture was quenched with water (20 mL), and the solvent was removed under reduced pressure. To the residue was added HFC43-10mee and water. The organic layer was separated and the aqueous layer was extracted twice with HFC43-10mee. The combined HFC43-10mee layers were washed twice with a diluted aqueous NaOH solution and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by reduced distillation to give a colorless liquid **15** (139.8 g, 0.402 mol, 71% yield).

b.p. 65–66 °C/3 mmHg. ^{19}F NMR δ −147.94 (d, 1F, J = 52 Hz), −115.70 (s, 2F), −85.75 (s, 3F), −84.77 (d, 1F, J = 154 Hz), −83.17 (d, 1F, J = 154 Hz). ^{1}H NMR δ 6.57 (d, 1H, J = 52 Hz), 7.15 (s, 1H), 7.38 (s, 1H), 8.03 (s, 1H). GC–MS (CI) m/z 349 $(MH)^+$.

*4.3. Preparation of 1-[1,1,2,2-tetrafluoro-2-(trifluoroethenyloxy)-ethanesulfonyl]-imidazole (**16**) using LHMDS*

To a 2 L round-bottom flask equipped with a mechanical stirring and a dropping funnel were added hexamethyldisilazane (111 g, 0.689 mol) and dry THF (500 mL, no stabilization) under a N_2 atmosphere. To the flask was added 1.6 M *n*-BuLi solution in *n*-hexane (431 mL, 0.689 mol) through a dropping funnel at −78 °C. The reaction mixture was stirred at −78 °C for 0.5 h and then elevated to 0 °C. To the flask was added **15** (104.4 g, 0.3 mol) through a dropping funnel at 0 °C. After the completion of the addition, the reaction mixture was stirred at 0 °C for 1 h. The formation of the vinyl compound **16** was confirmed by ^{19}F NMR. Then the reaction mixture was quenched with water, and the solvent was removed under reduced pressure. To the residue was added HFC43-10mee and water. After the insoluble material was filtered off through Celite, the organic layer was separated and the aqueous layer was extracted twice with HFC43-10mee. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by reduced distillation to give a colorless liquid **16** (57.56 g, 0.175 mol, 58% yield).

b.p. 61–62 °C/3 mmHg. ^{19}F NMR δ −137.81 (dd, 1F, J = 112, 66 Hz), −123.11 (dd, 1F, J = 112, 85 Hz), −115.70 (s, 2F), −115.51 (dd, 1F, J = 85, 66 Hz), −84.47 (s, 2F). ^{1}H NMR δ 7.23 (s, 1H), 7.48 (s, 1H), 8.16 (s, 1H). GC–MS (CI) m/z 329 $(MH)^+$.

*4.4. Preparation of 1-[1,1,2,2-tetrafluoro-2-(trifluoroethenyloxy)-ethanesulfonyl]-imidazole (**16**) using SHMDS*

To a 200 mL round-bottom flask equipped with a magnetic stirring and a dropping funnel were added **15** (6.6 g, 0.019 mol) and dry THF (20 mL, no stabilization) under a N_2 atmosphere. To the flask was added 1 M SHMDS solution in THF (40 mL, 0.04 mol) through a dropping funnel at 0 °C. After the completion of the addition, the reaction mixture was stirred at 0 °C for 1 h. The formation of the vinyl compound **16** was confirmed by ^{19}F NMR. Then the reaction mixture was quenched with water, and HFC43-10mee was added. The organic layer was separated and the aqueous layer was extracted twice with HFC43-10mee. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by reduced distillation to give a colorless liquid **16** (1.8 g, 0.0055 mol, 29% yield).

*4.5. Preparation of 1,1,2,2-tetrafluoro-2-(trifluoroethenyloxy)-ethanesulfonyl fluoride (**8**)*

The mixture of **16** (7.87 g, 0.024 mol) and 46 wt.% HF aqueous solution (9 mL) was heated with stirring at 60 °C for 0.5 h to separate into two layers. The lower layer was separated and washed with water to obtain a colorless liquid **8**. The yield of **8** was determined by ^{19}F NMR (4.79 g, 0.017 mol, 71% yield).

^{19}F NMR δ −138.70 (dd, 1F, J = 113, 68 Hz), −123.76 (dd, 1F, J = 113, 85 Hz), −116.38 (dd, 1F, J = 85, 68 Hz), −114.23 (s, 2F), −86.06 (s, 2F), 42.82 (s, 1F). GC–MS (EI) m/z 280 $(M)^+$.

*4.6. Preparation of 1,1,2,2-tetrafluoro-2-(trifluoroethenyloxy)-ethanesulfonyl chloride (**17**)*

The mixture of **16** (23.92 g, 0.073 mol) and concentrated HCl (30 mL) was heated with stirring at 90 °C for 0.5 h to separate into two layers. The lower layer was separated, and washed with water. The crude product was purified by distillation at atmospheric pressure to give a colorless liquid **17** (10.47 g, 0.035 mol, 48% yield).

b.p. 108–110 °C. ^{19}F NMR δ −137.94 (dd, 1F, J = 113, 64 Hz), −123.06 (dd, 1F, J = 113, 84 Hz), −115.58 (dd, 1F, J = 84, 64 Hz), −110.29 (s, 2F), −83.28 (s, 2F). GC–MS (CI) m/z 297 $(MH)^+$.

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