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PERFLUOROPOLYMER-SUPPORTED FITS REAGENTS

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Perfluoropolymer-supported FITS reagents (FITS-Nafion) were synthesized by treatment of bis(trifluoroacetoxy)iodoperfluoroalkanes with perfluorosulfonic acid resin (Nafion-H) and benzene or fluorobenzene.

We have previously originated FITS reagents¹⁾ acting as remarkable sources of electrophilic perfluoroalkyl and developed such new, fundamental reactions as electrophilic perfluoroalkylations^{1b,2)} and oxy-perfluoroalkyla-

Rf-I-OTf Ph FITS

tions.^{1b,3)} FITS reagents have left two problems on experimental procedure, (1) isolation of FITS from the reaction mixture needs repeated crystallizations, (2) separation of the products and recovery of expensive triflic acid are troublesome after the use of FITS reagents. We planned to immo-

bilize FITS on a resin to solve the problems.⁴⁾ We report here the synthesis of perfluoropolymer-supported FITS reagents (FITS-Nafion).

Preparation and high reactivity of FITS are characterized by using triflic acid as a superacid. We used perfluorosulfonic acid resin (Nafion-H)⁵⁾ as a solid superacid in the place of triflic acid. Nafion-H (0.86 mmol/g)⁶⁾ was treated with bis(trifluoroacetoxy)iodoperfluoroalkanes $\underline{2}$ (1 eq) and benzene or fluorobenzene (1.2 eq) in trifluoroacetic acid - trifluoroacetic anhydride (4/1) at 0°C (6 h) and then at room temperature (4 d). FITS-Nafion resins $\underline{la-f}$ were readily isolated from the reaction mixture by filtration, followed by washing with 1,1,2-trichlorotrifluoroethane and/or methylene chloride, and drying under vacuum at room temperature.

The formation of FITS-Nafion was confirmed by ir analysis and the following reactions. Their ir spectra showed absorption bands characteristic of

$$\begin{array}{c} \text{Rf-I}(\text{OCOCF}_3)_2 & \underbrace{\text{Nafion-H}}_{\text{ArH}} & \text{Rf-I-OSO}_2\text{CF}_2\text{CF}_2\text{O}(\text{CFCF}_2\text{O})_2\text{CF}_2 \\ \underline{2} & (\text{Rf=n-CmF}_2\text{m}+1) & \\ & \underline{1a-e} & \text{FITS-m-Nafion} & (\text{Ar=Ph}) \\ & & \\$$

Table Synthesis of FITS-Nafion 1

<u>1</u>	E.C. ^{a)}	Y.(%) ^{b)}
FITS-8-Nafion <u>la</u>	0.39	65
FITS-6-Nafion <u>lb</u>	0.44	70
FITS-4-Nafion <u>lc</u>	0.39	54
FITS-3-Nafion <u>ld</u>	0.46	68
FITS-2-Nafion <u>le</u>	0.36	51
FITS(F)-8-Nafion <u>lf</u>	0.43	72

a) Effective concentration (mmol/g)

b) Yields were calculated on the basis of effective concentrations.

phenyl (1495, 1480, 1450, 1430 cm^{-1}) or p-fluorophenyl nucleus (1585, 1490), and the iodonium structure (910-880). Based on the fact that iodobenzene was liberated guantitatively when FITS reacted with nucleophiles, the effective concentration of FITS-Nafion resins was determined by GLC analysis of iodobenzene or p-fluoroiodobenzene⁷⁾ liberated by the reaction with an excess of propanethiol (Table). FITS-Nafion resins were found

to have sufficient stability and

high reactivity. FITS-8-Nafion was heated in benzene and thiophene at 80°C for 2 h in the presence of pyridine⁸⁾ to produce Rf-benzene and α -Rf-thiophene in 89% and 95% isolated yields, respectively. These reactions are heterogeneous because of insolubility of the resins in such reaction solvents. Therefore, the products could easily be separated from the resins by filtration only. Nafion-H was recovered quantitatively as the pyridinium salt and readily regenerated by treating the salt with an acid. Such an acid-neutralizing agent as pyridine was used to prevent acid-catalyzed side-reactions which contaminated the reproduced Nafion-H and the products.

Nafion-H (Salt) FITS-8-Nafion Rf-Nu Pyridine

References

- 1) a) T.Umemoto, Y.Kuriu, H.Shuyama, O.Miyano, and S.Nakayama, J. Fluorine
- a) T.Umemoto, Y.Kuriu, H.Shuyama, O.Miyano, and S.Nakayama, J. Fluorine Chem., <u>20</u>, 695 (1982). b) T.Umemoto, J. Syn. Org. Chem. Japan, 251 (1983).
 a) T.Umemoto and Y.Kuriu, Tetrahedron Lett., <u>22</u>, 5197 (1981). b) T.Umemoto, Y.Kuriu, and S.Nakayama, ibid., <u>23</u>, 1169 (1982). c) T.Umemoto, Y.Kuriu, and O.Miyano, ibid., <u>23</u>, 3579 (1982). d) T.Umemoto, Y.Kuriu, S.Nakayama, and O. Miyano, ibid., <u>23</u>, 1471 (1982). e) T.Umemoto, Y.Kuriu, and H.Shuyama, Chem. Lett., <u>1981</u>, 1663. f) T.Umemoto and Y.Kuriu, ibid., <u>1982</u>, 65.
 T.Umemoto, Y.Kuriu, and S.Nakayama, Tetrahedron Lett., <u>23</u>, 4101 (1982).
- 4) Other fluoropolymer-supported reagents; a) S.Murata and R.Noyori, Tetrahedron Lett., 21, 767 (1980).
 b) D.D.DesMarteau, J. Fluorine Chem., 21, 249 (1982).
- 5) Nafion is a registered trademark of Du Pont Co.; J.D.McClure and S.G. Brandenberger, U.S.Patent, 4,038,213 (1977). Nafion-511 available as a granular potassium salt was converted to the acid form (Nafion-H) by treatment with hydrochloric acid, followed by drying under vacuum at 100°C.
- 6) The concentration was determined by titration with alkali.
- 7) Other isomers, o- and m-fluoroiodobenzene, were not detected by GLC.
- 8) The amount of pyridine is the sum of moles of FITS-Nafion and the remaining sulfonic acid.

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NuH

Nu=Ph(89%), Thiophene(95%)