

Table Synthesis of FITS-Nafion 1

<u>1</u>	E.C. ^{a)}	Y. (%) ^{b)}
FITS-8-Nafion <u>1a</u>	0.39	65
FITS-6-Nafion <u>1b</u>	0.44	70
FITS-4-Nafion <u>1c</u>	0.39	54
FITS-3-Nafion <u>1d</u>	0.46	68
FITS-2-Nafion <u>1e</u>	0.36	51
FITS(F)-8-Nafion <u>1f</u>	0.43	72

a) Effective concentration (mmol/g)

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

high reactivity. FITS-8-Nafion was heated in benzene and thiophene at 80°C for 2 h in the presence of pyridine ⁸⁾ 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.



References

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- 2) a) T.Umemoto and Y.Kuriu, *Tetrahedron Lett.*, **22**, 5197 (1981). b) T.Umemoto, Y.Kuriu, and S.Nakayama, *ibid.*, **23**, 1169 (1982). c) T.Umemoto, Y.Kuriu, and O.Miyano, *ibid.*, **23**, 3579 (1982). d) T.Umemoto, Y.Kuriu, S.Nakayama, and O.Miyano, *ibid.*, **23**, 1471 (1982). e) T.Umemoto, Y.Kuriu, and H.Shuyama, *Chem. Lett.*, 1981, 1663. f) T.Umemoto and Y.Kuriu, *ibid.*, 1982, 65.
- 3) T.Umemoto, Y.Kuriu, and S.Nakayama, *Tetrahedron Lett.*, **23**, 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-fluoriodobenzene, 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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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 quantitatively when FITS reacted with nucleophiles, the effective concentration of FITS-Nafion resins was determined by GLC analysis of iodobenzene or p-fluoriodobenzene ⁷⁾ liberated by the reaction with an excess of propanethiol (Table).

FITS-Nafion resins were found to have sufficient stability and