Journal of Fluorine Chemistry 131 (2010) 743–745

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

# Graphical Abstracts/J. Fluorine Chem. 131 (2010) 743–745

*J. Fluorine Chem., 131 (2010) 746*

## Sodium dithionite initiated fluoroalkylation of trimethoxybenzenes, mesitylene and pyrroles with $BrCF_2CF_2Br$

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$$ArH \xrightarrow[\text{Na}_2\text{S}_2\text{O}_4,\ \text{NaHCO}_3\ /\ \text{MeCN / H}_2\text{O}]{BrCF_2CF_2Br} ArCF_2CF_2Br$$

ArH = trimethoxybenzenes, mesitylene, pyrroles

Sodium dithionite initiated reaction of 1,2-dibromotetrafluoroethane with 1,3,5-trimethoxybenzene (**1a**) in an acetonitrile–water mixture proceeded efficiently at ambient temperature to give 1-(2-bromotetrafluoroethyl)-2,4,6-trimethoxybenzene (**2**) almost quantitatively. Similar reaction with 1,2,3-trimethoxybenzene (**1b**) gave only reasonable yield of regioisomers of (2-bromotetrafluoroethyl)-trimethoxybenzenes **3** and **4** and small amount of a substitution product of the central trimethoxy group, 1-(2-bromotetrafluoroethyl)-2,6-dimethoxybenzene (**5**). The results of the reactions with mesithylene (**6**) gave complex mixtures from which, depending on the temperature and a mesithylene/$BrCF_2CF_2Br$ ratio, the expected (2-bromotetrafluoroethyl)mesithylene (**8**) or a dimeric product, 4,4′-bis(2-bromo-1,1,2,2-tetrafluoroethyl)-1,3,5,1′,3′,5′-hexamethylbicyclohexyl-2,5,2′,5′-tetraene (**7**), were isolated in a 18 and 13%, respectively. The reactions of $BrCF_2CF_2Br$ with pyrrole (**9**) and 1-methylpyrrole (**11**) gave the respective alkylated compounds, 2-(2-bromotetrafluoroethyl)pyrrole (**10**) and 2-(2-bromotetrafluoroethyl)-1-methylpyrrole (**12**) in over 70% yields; the former was found to be fairly unstable. The reactivity of the terminal bromine atom in 1-(2-bromotetrafluoroethyl)-2,4,6-trimethoxybenzene (**2**) was also investigated.

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## Experimental and chemical kinetic study of the pyrolysis of trifluoroethane and the reaction of trifluoromethane with methane

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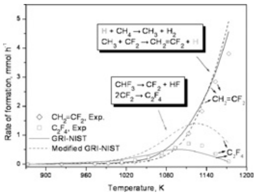

A detailed reaction mechanism is developed and used to model experimental data on the pyrolysis of $CHF_3$ and the non-oxidative gas-phase reaction of $CHF_3$ with $CH_4$ in an alumina tube reactor at temperatures between 873 and 1173 K and at atmospheric pressure. t was found that $CHF_3$ can be converted into $C_2F_4$ during pyrolysis and $CH_2{=}CF_2$ via reaction with $CH_4$. Other products generated include $C_3F_6$, $CH_2F_2$, $C_2H_3F$, $C_2HF_3$, $C_2H_6$, $C_2H_2$ and $CHF_2CHF_2$. The rate of $CHF_3$ decomposition can be expressed as $5.2\times1013[s^{-1}]e^{-295[kJmol^{-1}]/RT}$. During the pyrolysis of $CHF_3$ and in the reaction of $CHF_3$ with $CH_4$, the initial steps in the reaction involve the decomposition of $CHF_3$ and subsequent formation of $CF_2$ difluorocarbene radical and HF. It is proposed that $CH_4$ is activated by a series of chain reactions, initiated by H radicals. The NIST HFC and GRI-Mech mechanisms, with minor modifications, are able to obtain satisfactory agreement between modelling results and experimental data. With these modelling analyses, the reactions leading to the formation of major and minor products are fully elucidated.

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## Determination of p$K_a$ values of fluoroalkanesulfonamides and investigation of their nucleophilicity

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The p$K_a$ values of a series of fluoroalkanesulfonylamides were measured by potentiometric titration. Different kinds of alkyl halides and tosylates were employed to investigate the nucleophilicity of fluoroalkanesulfonylamides. Fluoroalkanesulfonylamides with longer fluoroalkyl chain have weaker nucleophilicity.

$$RfSO_2F + NH_3\ (\text{liquid}) \xrightarrow{< -60^{o}C} \xrightarrow{\text{acid}} \underset{\textbf{1a-i}}{RfSO_2NH_2} \quad (\mathbf{p}\boldsymbol{K_a}\mathbf{1\ and\ p}\boldsymbol{K_a}\mathbf{2})$$

$$RfSO_2NH_2 + RX \xrightarrow[\text{THF, Temp.}]{K_2CO_3} RfSO_2NR_2$$

doi:10.1016/S0022-1139(10)00138-7

*J. Fluorine Chem., 131 (2010) 767*

## Synthesis and characterization of fluorinated polyimides derived from novel unsymmetrical diamines

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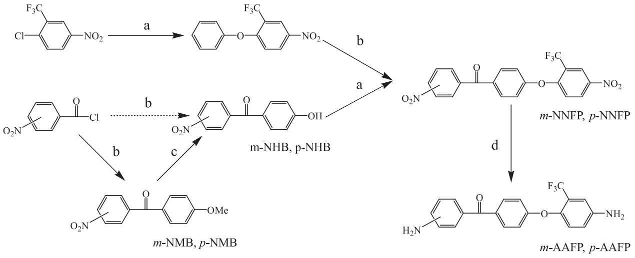
Two kinds of novel diamines were designed and synthesized. The unsymmetrical structure, $CF_3$ and ether–ketone group were introduced to polymer chains to improve its solubility. The $CF_3$ group could result in the polyimides with lower moisture absorption. The ketone group could crosslink with amine group, that can make the polyimides exhibit better thermal properties and mechanical properties.



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*J. Fluorine Chem., 131 (2010) 776*

## Proton conductivity properties of acid doped fluoroalkylated 1,2,3-triazole

Sedat Coşgun[a], Sevim Ünügür Çelik[a], Şehmus Özden[a], Suat Tüysüz[a], Ayhan Bozkurt[a], Christine Gérardin-Charbonnier[b]

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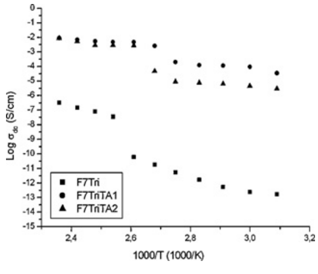
Novel proton conducting organic electrolyte containing fluoroalkylated 1,2,3-triazole was synthesized via intramolecular cyclisation of vinyl azides. FT-IR, elemental analysis and NMR were used for the characterization of the resulting organic molecule. Proton conductivity was investigated with impedance spectrometer. The maximum proton conductivity was measured as $10^{-2}$ S/cm at 150 °C.



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*J. Fluorine Chem., 131 (2010) 780*

## A simplified and efficient bromine-facilitated $SF_4$-preparation method

Rolf Winter[a,b], Paul W. Cook[b]

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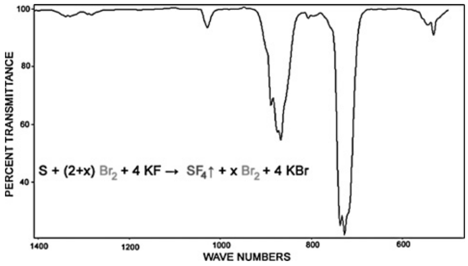

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*J. Fluorine Chem., 131 (2010) 784*

## Fluorophilicity of alkyl and polyfluoroalkyl nicotinic acid ester prodrugs

Vivian Ojogun[a], Barbara L. Knutson[a], Sandhya Vyas[b], Hans-Joachim Lehmler[b]

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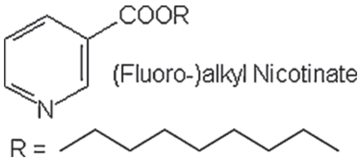

The fluorophilicity of hydrocarbon and fluorocarbon-functionalized nicotinates is measured and predicted from their partitioning in biphasic perfluoro(methylcyclohexane)/toluene solvents. Varying the hydrocarbon or fluorocarbon alkyl chain length of the ester (one–twelve carbon atoms) provides a systematic comparison of the effect of molecule structure on fluorophilicity.

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## Selenium(IV) fluoride and oxofluoride anions

Karl O. Christe[a], David A. Dixon[b], Ralf Haiges[a], Mathias Hopfinger[a],
Virgil E. Jackson[b], Thomas M. Klapötke[c], Burkhard Krumm[c], Matthias Scherr[c]

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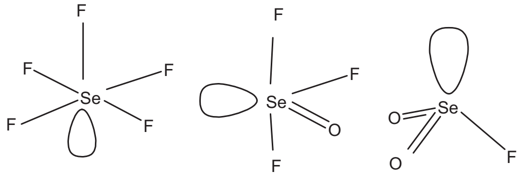

The three Se(+IV) fluoride and oxofluoride anions, $SeF_5^-$, $SeOF_3^-$ and $SeO_2F^-$, have been studied using experimental and theoretical methods. The first crystal structures of a well-isolated undistorted $SeF_5^-$ and of an oxotrifluoro-chalcogenite anion are reported. The pair-wise substitution of two fluorine atoms by a doubly bonded oxygen atom reduces the CN of Se from 6 to 4, and the presence of a sterically active free valence electron pair on Se has a strong influence on the bonding of the fluorine ligands.

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## An alternative route for synthesis of *o*-trifluoroacetylanilines as useful fluorine-containing intermediates

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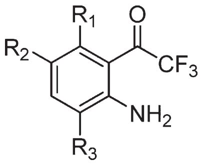
A series of *o*-trifluoroacetyl aniline derivatives were synthesized in three steps. In this method, we first utilized trifluoroacetic anhydride to introduce trifluoroacetyl group to the *ortho* position of aniline with higher yield than that of some previously reported methods.



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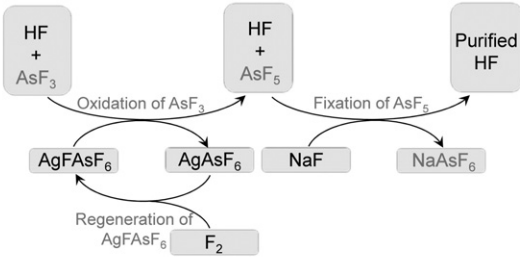
## Elimination of $AsF_3$ from anhydrous HF using $AgFAsF_6$ as a mediator

Kazuhiko Matsumoto, Rika Hagiwara

Graduate School of Energy Science, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan



Elimination of $AsF_3$ from anhydrous HF has been demonstrated using $AgFAsF_6$ as a mediator.