New fluorinated materials – ionic liquids, conducting salts, cationic dyes and strong acids.

Nikolai Ignat`ev, PLS R&D, Merck KGaA, Darmstadt, Germany

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Plan of the Presentation

- Application of the Simons process for synthesis of organofluorine compounds:

- Synthesis and application of fluoroalkyl-phosphoranes

  - conducting salts for battery applications

  - new strong acids

  - ionic liquids

  - new cationic dyes

- Alkylation of organic compounds with alcohols

The Periodic Table

Period	1	2	3	4	5	6	7	8	9	10	11	12	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	La-Lu	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 210.0	85 At 210.0	86 Rn 222.0
7	87 Fr 223.0	88 Ra 226.0	Ac-Lr	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	......								
	s block		*d* block										*p* block					

Lanthanides	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 144.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
Actinides	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 239.1	95 Am 243.1	96 Cm 247.1	97 Bk 247.1	98 Cf 252.1	99 Es 252.1	100 Fm 257.1	101 Md 256.1	102 No 259.1	103 Lr 260.3
	f block														

History of Organo-Fluorine Chemistry

1764 - First synthesis of hydrofluoric acid (A.S. Marggraf)

1886 - First synthesis of elemental fluorine (H. Moissan)

1890 - Beginning of halofluorocarbon chemistry

1920s - Synthesis of fluoroarenes via Balz-Schiemann reaction

1930s - Refrigerants ("Freon")

1940s - Polymers ("Teflon"), Electrochemical Fluorination (H. Simons)

1941-1954 - Manhattan Project

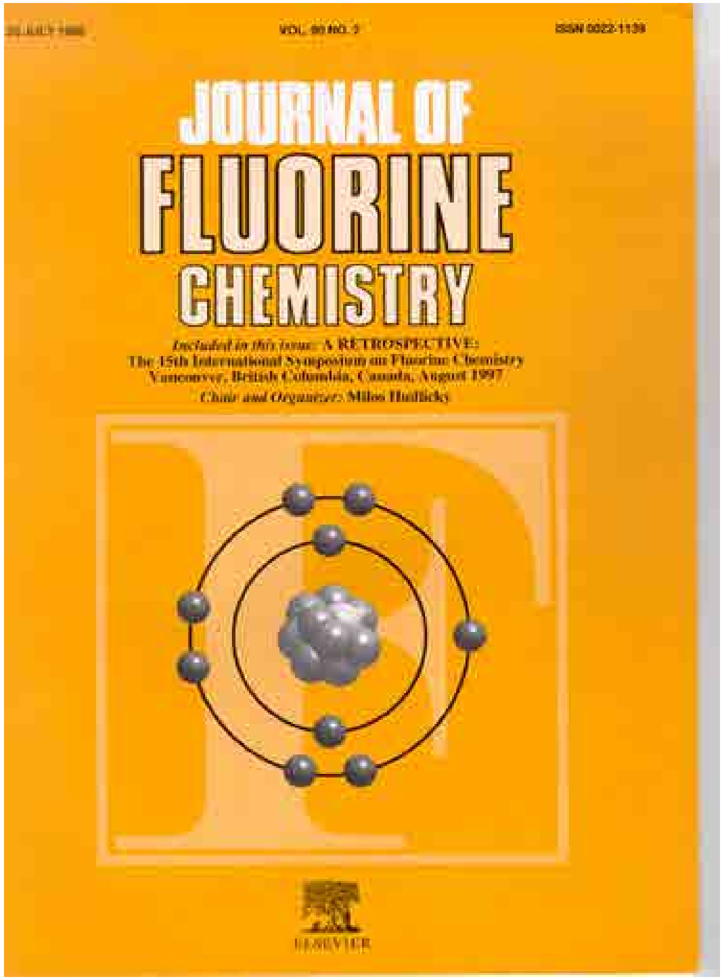
1950s - Fluoropharmaceuticals, Agrochemicals, Artificial blood

1980s - Chemicals for the semiconductor industry

1990s - Fluorinated liquid crystals

2000s - Fluorinated photoresists for 157 nm photolithography

P. Kirsch, Modern Fluoroorganic Chemistry, Wiley-VCH, 2004, p. 3.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CHEMISTRY
Included in this issue: A RETROSPECTIVE:
The 15th International Symposium on Fluorine Chemistry
Vancouver, British Columbia, Canada, August 1997
Chair and Organizer: Milos Hudlicky

Fluorine Chemistry and Industrial Application of Fluorochemicals

Fluorine Chemistry

Fluoro-polymeric Materials:
- Fluoroplastics (PTFE, FEP, PFA, Kel-F).
- Fluoroelastomers.
- Fluoropolymer Coating.
- Fluorinated Membranes.

Fluorochemicals for Industrial Applications:
- Refrigeration.
- Special Solvents and Cleaning Agents.
- Surfactants.
- Lubricants.
- Liquid Crystals.
- Materials for Energy-Storage Devices.

Fluoro-Chemicals in Medicine:
- Fluorine-Containing Drugs.
- Fluorinated Inhalation Anesthetics.
- Blood Substitutes.
- Contrast Media and Diagnostic Imaging.

Fluorine-Containing Agrochemicals:
- Herbicides.
- Insecticides.
- Fungicides.
- Plant Growth Regulators.

Electrochemistry in the Preparation of Fluorine and it's Compounds

1. Electrochemical production of Fluorine:

$$KF \cdot nHF \xrightarrow{-e} F_2$$

2. Electrochemical fluorination (Simons Process):

$$CH_3SO_2Cl \xrightarrow[HF]{-e,\ Ni} CF_3SO_2F$$

3. Anodic fluorination

$$Ar{-}H \xrightarrow[CH_3CN]{-e,\ F^-} Ar{-}F$$

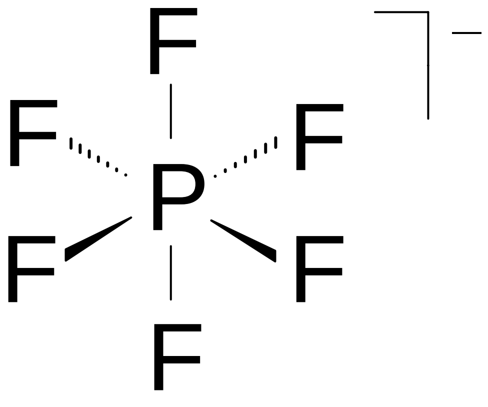
4. Electrochemical synthesis of organofluorine compounds:

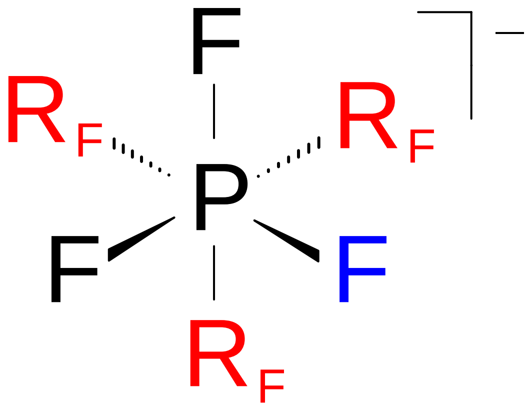
Fluorine Containing Starting Material → (Electrochemical Conversion) → New Organo-Fluorine Compound

Industrial Fluor-Phosphorus Compounds

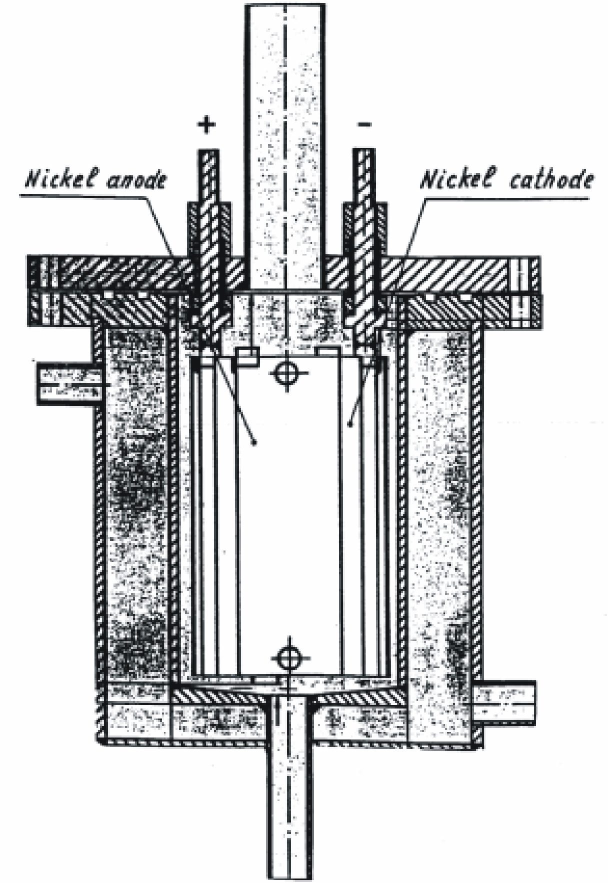
PF_5 HPF_6 $LiPF_6$

Can we improve the properties of Hexafluorophosphates ?





Electrochemical fluorination (Simons Process) - the process of the choice



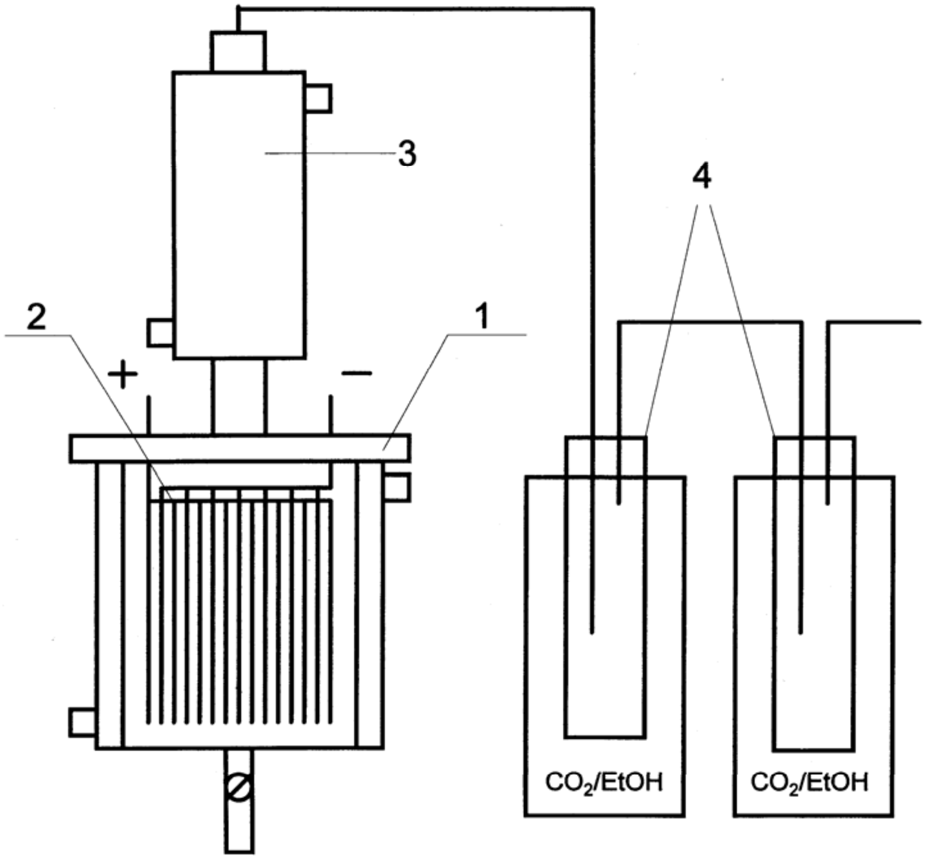
Operating parameters:

Cell voltage: 4.5 - 6.5 V

Current densities: 0.5 - 2.0 A/dm2

Cell temperature: 0 – 15° C

Laboratory equipment



1. Cell
2. Nickel electrodes
3. Condenser
4. Traps

Electrochemical Fluorination (ECF) of Trialkylphosphines

$$R_3P \xrightarrow[HF]{e\ ,\ Ni} (R_F)_3P{<}^{F}_{F}$$

R =	R_F	Yield, %
C_2H_5	C_2F_5	74
$n-C_3H_7$	$n-C_3F_7$	53
$n-C_4H_9$	$n-C_4F_9$	49

N. V. Ignat'ev and P. Sartori, ***J. of Fluorine Chem.***, 103 (2000), 57-61;

U. Heider, V. Hilarius, P. Sartori, N. V. Ignatiev, **WO 00/21969**, Merck Patent GmbH, Darmstadt, Germany

ECF of Triethylphosphine

$$(C_2H_5)_3P \xrightarrow{\text{ECF}} (C_2F_5)_3PF_2 + C_2F_6 + PF_5$$

Phosphorane **I**

yield ⩾ 74 %

Side product ;

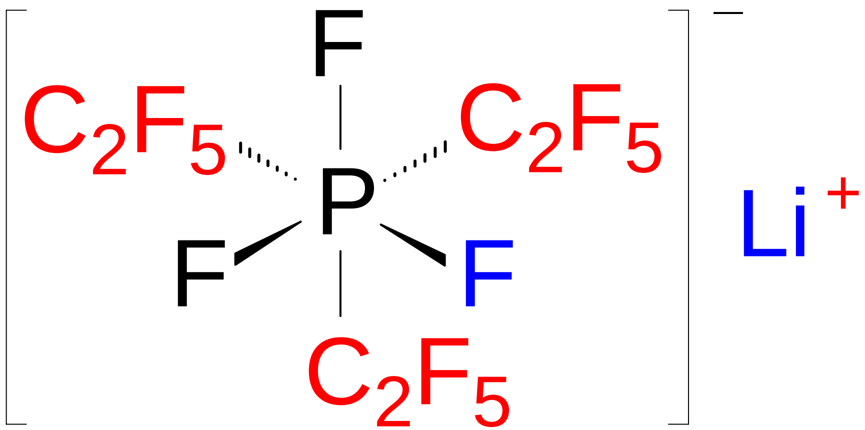
can be sold

N. V. Ignat'ev and P. Sartori, ***J. of Fluorine Chem.***, 103 (2000), 57-61;

U. Heider, V. Hilarius, P. Sartori, N. V. Ignatiev, **WO 00/21969**, Merck Patent GmbH, Darmstadt, Germany

Conversion into Li-Salts

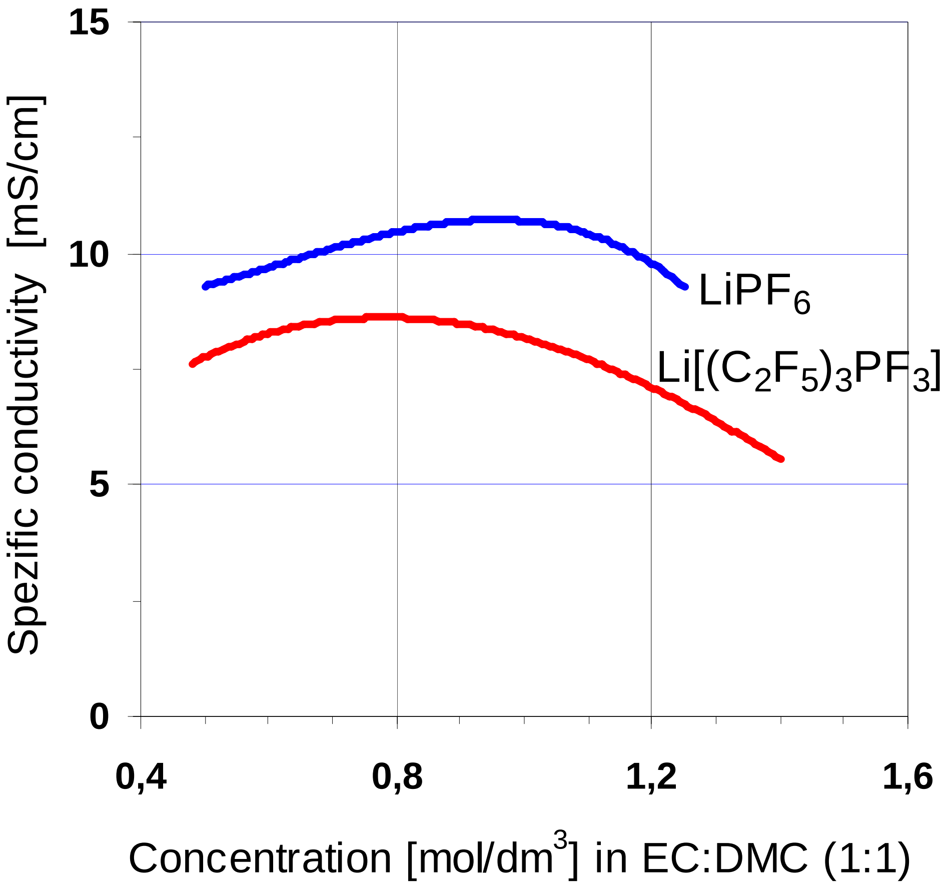
$$(C_2F_5)_3PF_2 \;+\; LiF \xrightarrow{\text{Solv.}} [(C_2F_5)_3PF_3]^- \, Li^+ \cdot \text{Solv.}$$



LiFAP

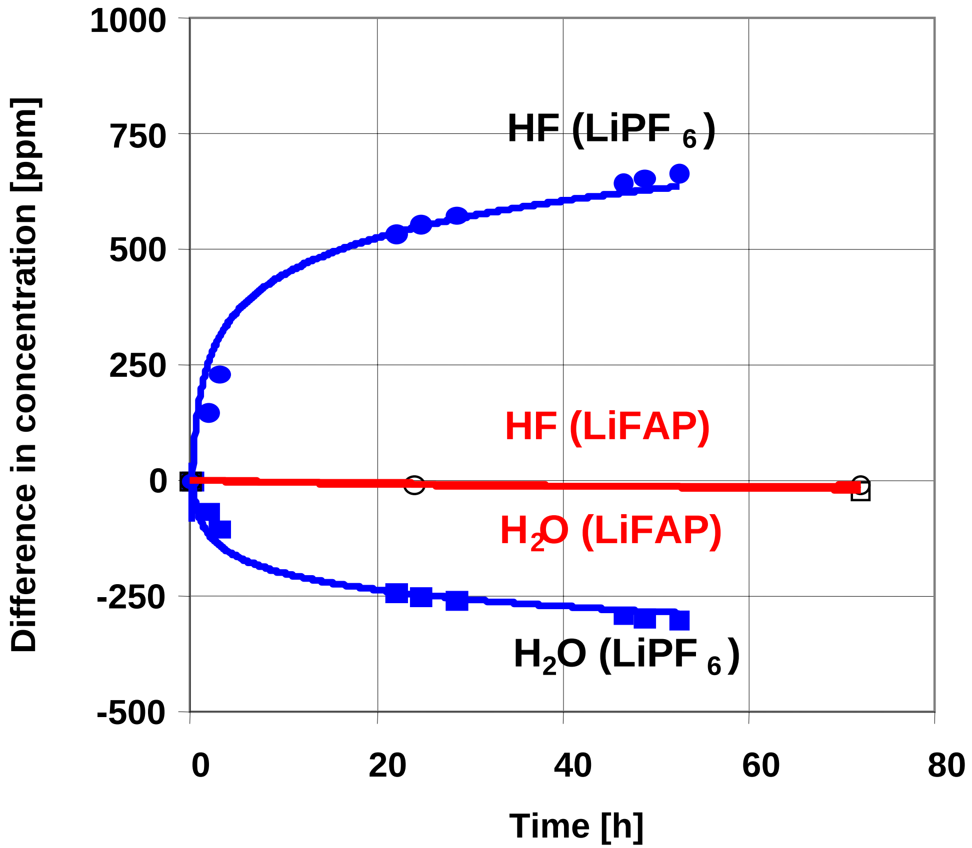
P. Sartori, N. Ignatiev, **WO 98/15562,**
Merck Patent GmbH, Darmstadt, Germany

Concentration Dependence *vs.* Conductivity



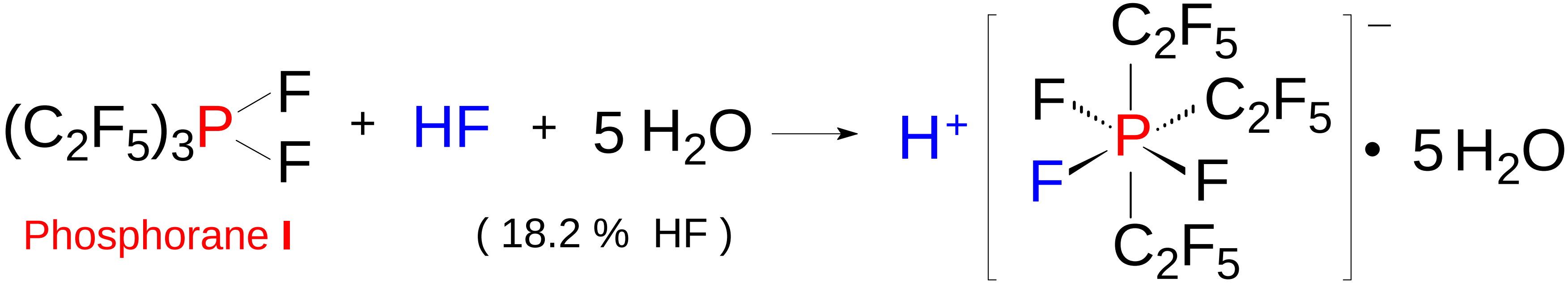
M. Schmidt, U. Heider, A. Kuehner, R. Oesten, M. Jungnitz, N. Ignat'ev, P. Sartori, ***J. of Power Sources***, 97-98 (2001), p. 557-560.

Hydrolytic Stability of LiFAP



M. Schmidt, U. Heider, A. Kuehner, R. Oesten, M. Jungnitz, N. Ignat'ev, P. Sartori, ***J. of Power Sources***, 97-98 (2001), p. 557-560.

Synthesis of HFAP



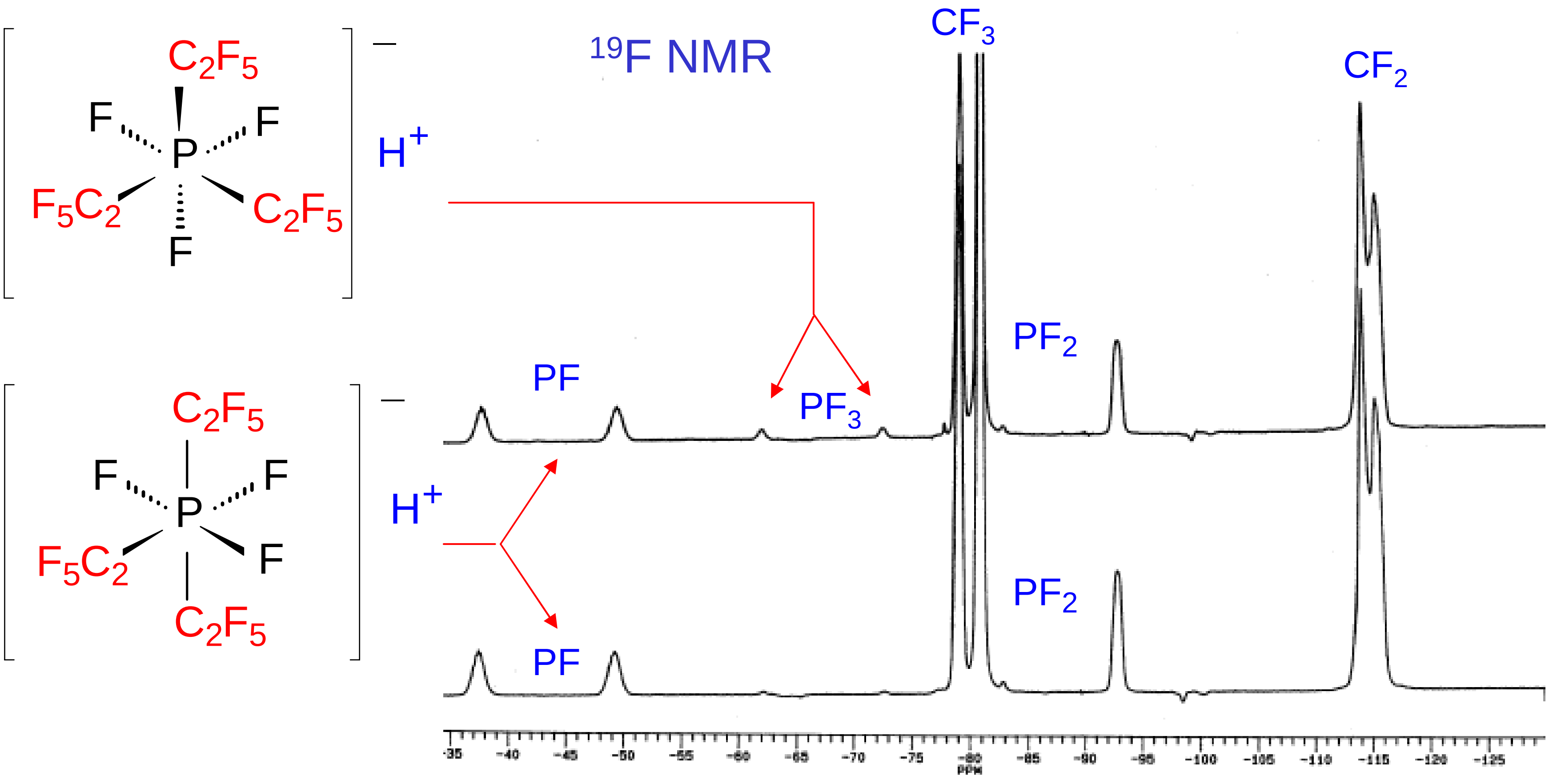
HFAP

Mixture of isomers with
meridional and facial structures

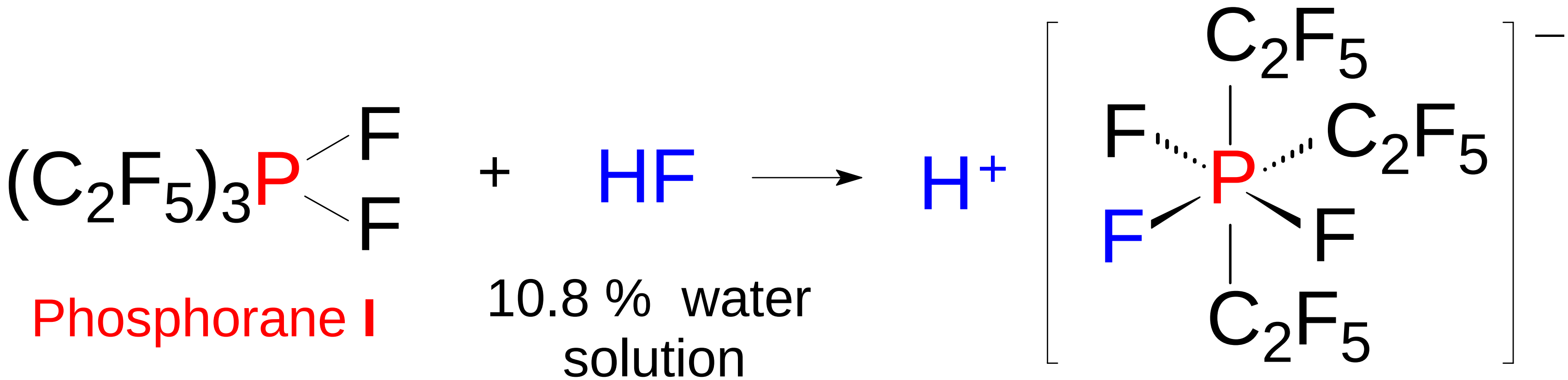
HFAP is a new strong acid

N. V. Ignatiev, M. Schmidt, A. Kuener, V. Hilarius, U. Heider, A. Kucheryna, P. Sartori, H. Willner, **WO 03/002579**, Merck Patent GmbH, Darmstadt, Germany

Structure of HFAP



Synthesis of HFAP



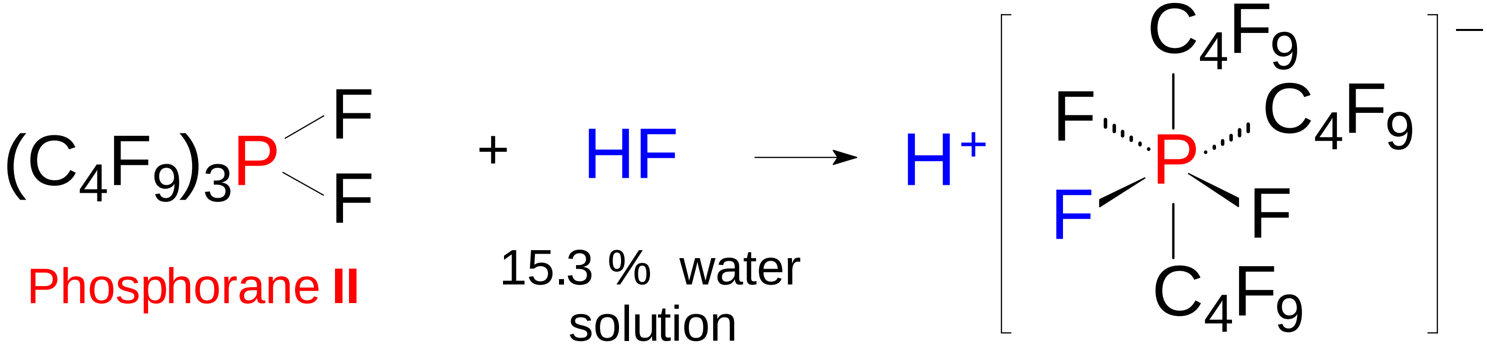
Phosphorane **I**

10.8 % water solution

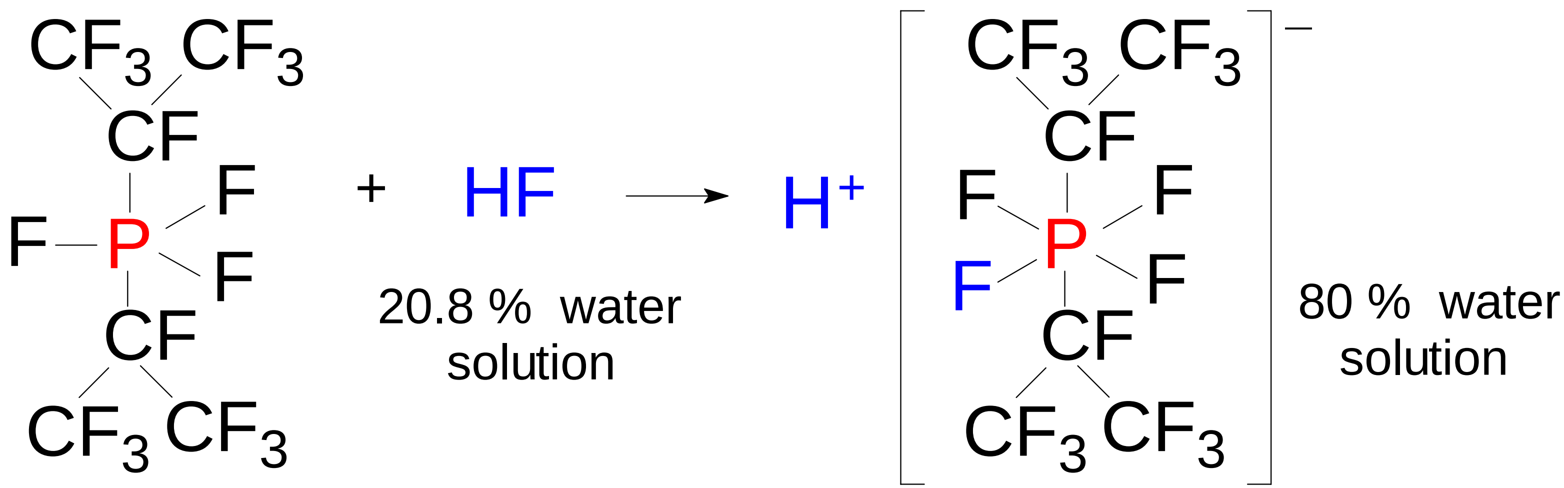
HFAP (73 % water solution)

Mainly the isomer with meridional structure is formed

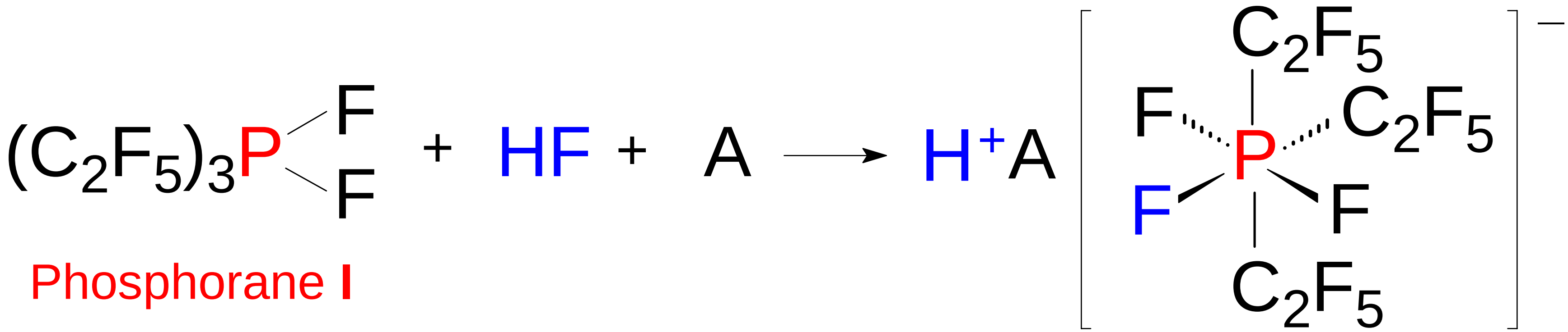
Synthesis of HFAP



HFAP II (83 % water solution)



Synthesis of HFAP



Phosphorane **I**

HFAP

A = alcohols,
ethers, esters,
dilakyl sulphides,
carboxylic acids,
amides, amines,
phosphines *etc*.

Synthesis of the salts with FAP-anion

$$2\,H^+\left[(C_2F_5)_3PF_3\right]^- \bullet 5\,H_2O + Li_2CO_3 \longrightarrow 2\,Li\left[(C_2F_5)_3PF_3\right] \bullet 5\,H_2O + H_2O + CO_2$$

(Concentration: 83 % in water)

$$4\,H^+\left[(C_2F_5)_3PF_3\right]^- + CuCO_3 \bullet Cu(OH)_2 \longrightarrow 2\,Cu\left[(C_2F_5)_3PF_3\right]_2 + CO_2$$

(43.2 % water solution)

(Concentration: 44 % in water)

$$2\,H^+\left[(C_2F_5)_3PF_3\right]^- + Ag_2CO_3 \longrightarrow 2\,Ag\left[(C_2F_5)_3PF_3\right] + CO_2$$

(27.9 % water solution)

(Concentration: 32 % in water)

Possible applications: Conducting salts ; Catalysts

N. V. Ignatiev, M. Schmidt, A. Kuener, V. Hilarius, U. Heider, A. Kucheryna, P. Sartori, H. Willner, **WO 03/002579**, Merck Patent GmbH, Darmstadt, Germany

Synthesis of the salts with FAP-anion

$$H^+ [(C_2F_5)_3PF_3]^- + (CH_3)_4N^+ \, {}^-OH \longrightarrow (CH_3)_4N^+ [(C_2F_5)_3PF_3]^- + H_2O$$

M. p. = 112° C

$$H^+ [(C_2F_5)_3PF_3]^- + (C_4H_9)_4N^+ \, {}^-OH \longrightarrow (C_4H_9)_4N^+ [(C_2F_5)_3PF_3]^- + H_2O$$

M. p. = 62° C

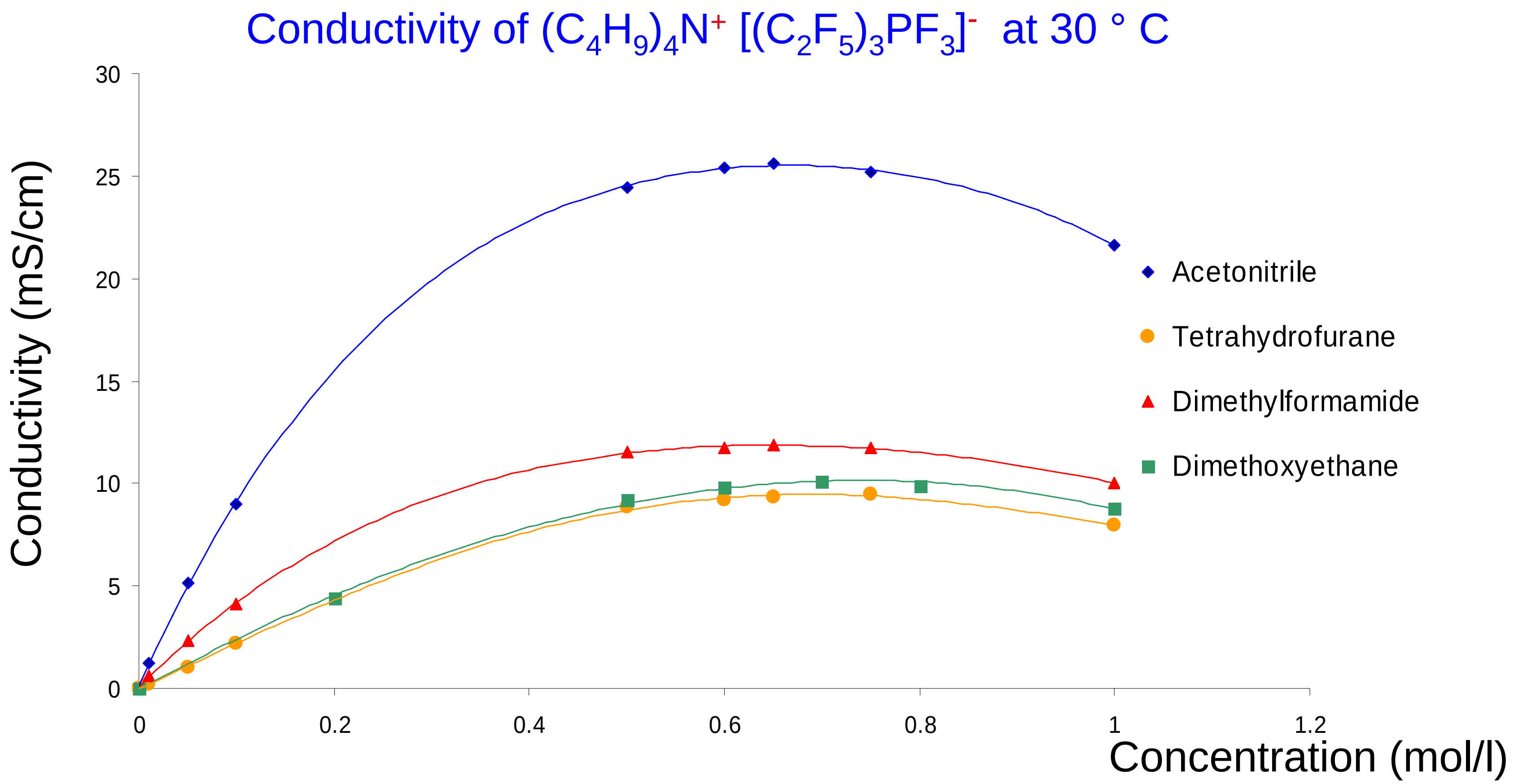
$$H^+ [(C_2F_5)_3PF_3]^- + (C_4H_9)_4P^+ \, Cl^- \longrightarrow (C_4H_9)_4P^+ [(C_2F_5)_3PF_3]^- + HCl$$

M. p. = 73-74° C

Possible applications: Salts for Super-Capacitors ; Ionic Liquids ; Surfactants

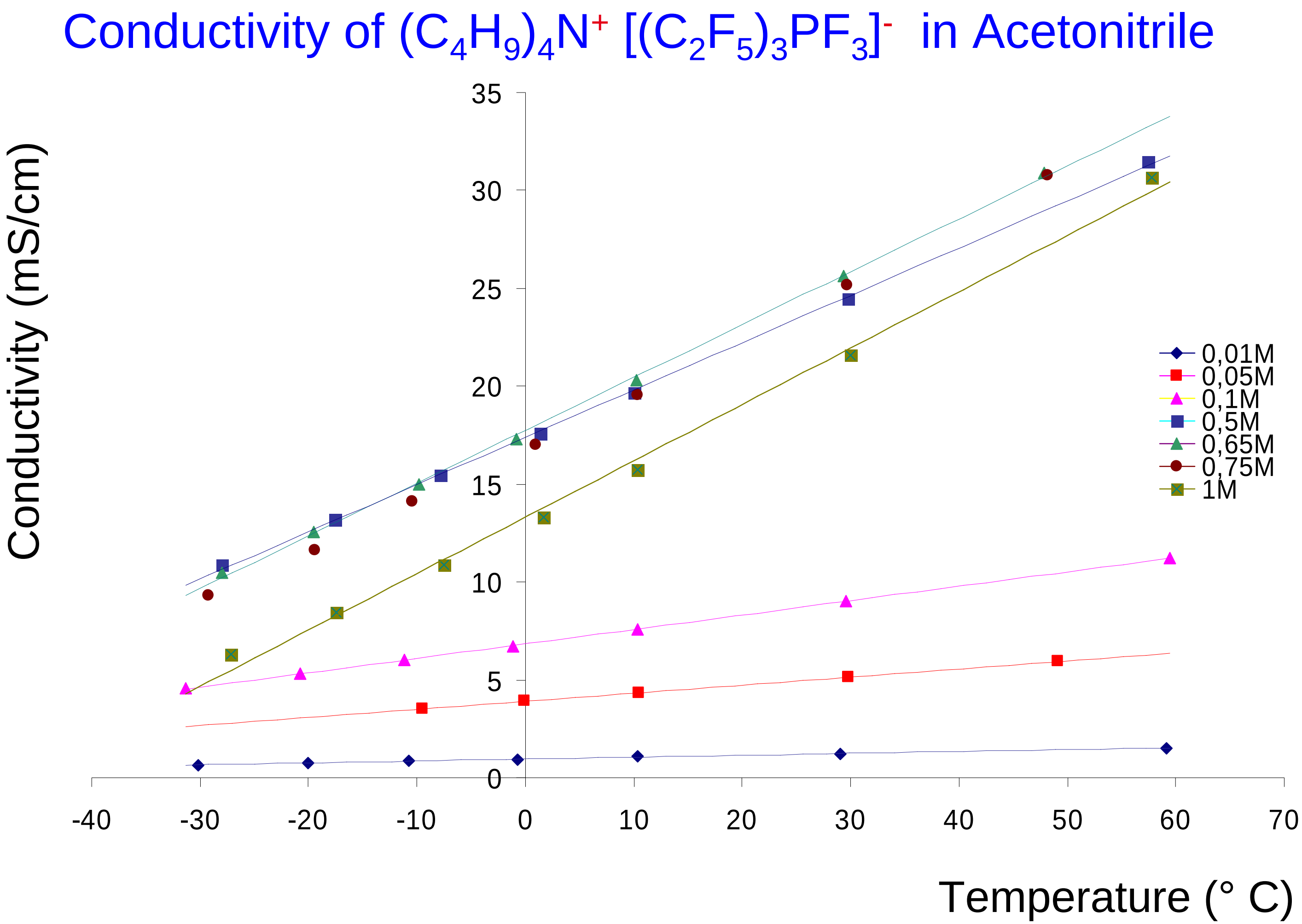
N. V. Ignatiev, M. Schmidt, A. Kuener, V. Hilarius, U. Heider, A. Kucheryna,
P. Sartori, H. Willner, **WO 03/002579**, Merck Patent GmbH, Darmstadt, Germany

Conductivity of $(C_4H_9)_4N^+$ $[(C_2F_5)_3PF_3]^-$

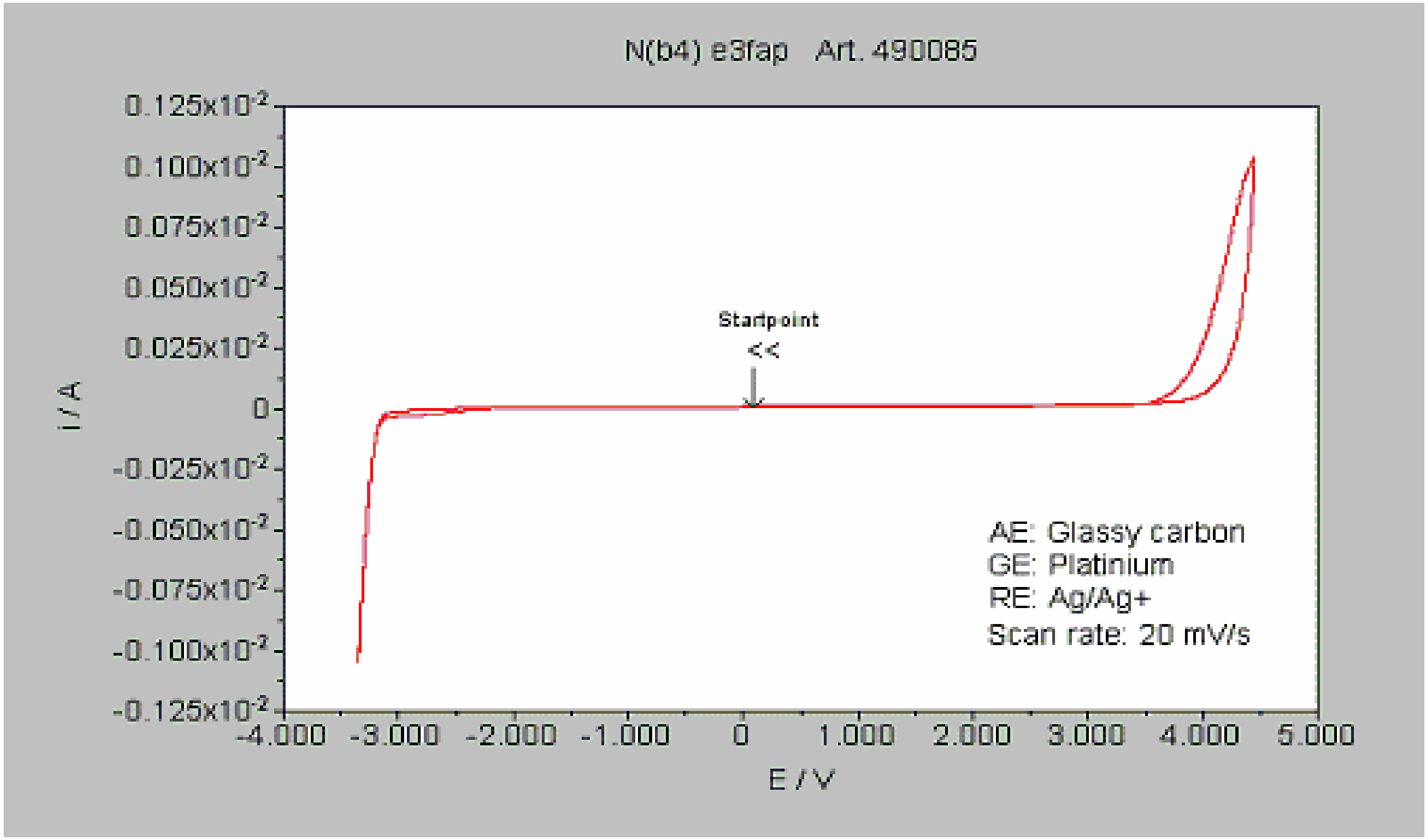


N. V. Ignat'ev, U. Welz-Biermann, A. Kucheryna, G. Bissky, H. Willner, ***J. of Fluorine Chem.***, 126 (2005), p.1150-1159.

Conductivity of $(C_4H_9)_4N^+$ $[(C_2F_5)_3PF_3]^-$



Electrochemical Stability of $(C_4H_9)_4N^+ [(C_2F_5)_3PF_3]^-$



N. V. Ignat'ev, U. Welz-Biermann, A. Kucheryna, G. Bissky, H. Willner, ***J. of Fluorine Chem.***, 126 (2005), p.1150-1159.

Ionic Liquids – Molten Salts

Room temperature ionic liquids, or molten salts, are defined as materials containing only ionic species without any neutral molecules and having a melting point of lower than 298° K.

R. Hagiwara and Y. Ito, *Journal of Fluorine Chem*., 105 (2000), p. 221-227

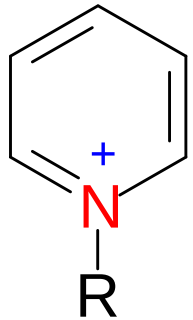
Ionic Liquids Properties

Ionic Liquids are:

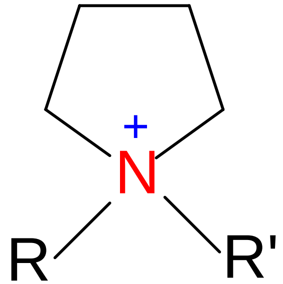
- non-volatile
- non-flammable
- possess high thermal and electrochemical stability
- liquid over a wide temperature range
- dissolve many organic and inorganic compounds
- have variable miscibility with water and organic solvents,

but ……., they are much more viscous then conventional organic solvents

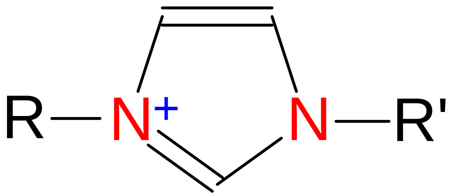
Typical Cations



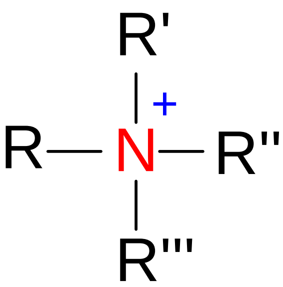
Pyridinium



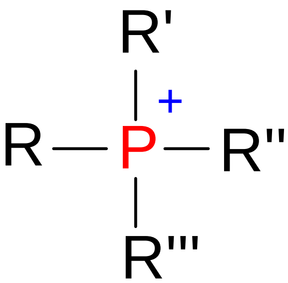
Pyrrolidinium



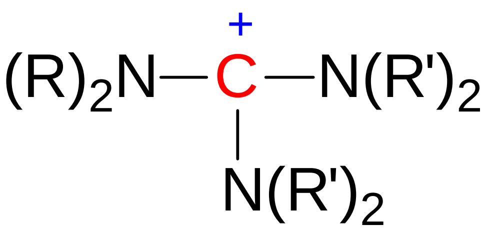
Imidazolium



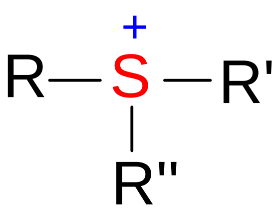
Ammonium



Phosphonium



Guanidinium



Sulfonium

Viscosity of Ionic Liquids

MERCK

Ionic Liquid	Viscosity (20° C), $mm^2 \cdot s^{-1}$	Density $g \cdot cm^{-3}$
1-Hexyl-3-methylimidazolium Cloride	7453	1.050
1-Hexyl-3-methylimidazolium $[PF_6]^-$	548	1.297
1-Hexyl-3-methylimidazolium $[BF_4]^-$	195	1.150
Water	1.0	1.0
Methanol	0.73	0.79

Ionic Liquids - Anions

Typical Anions

- Halogenides (Cl^-, Br^-, I^-)
- Cloroaluminates ($AlCl_4^-$, $Al_2Cl_7^-$)
- Alkylsulfates and sulfonates (for example $CH_3OSO_3^-$, $CH_3C_6H_4SO_3^-$)
- BF_4^-, PF_6^-, AsF_6^-, SbF_6^-
- Perfluorinated organic anions [$CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $CF_3CO_2^-$]

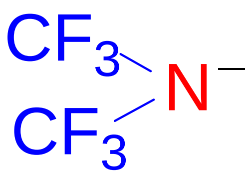
TFSI

New Anions for low viscosity Ionic Liquids

$[(C_2F_5)_3PF_3]^-$ FAP - Anion

$[(R_F)_{4-n}BF_n]^-$ n = 0 - 3

$[(C_2F_5)_2P(O)O]^-$ Phosphinat - Anion



Synthesis of new Ionic Liquids

$$H^{+}\left[(C_2F_5)_3PF_3\right]^{-} \quad + \quad (C_6H_{13})_3(C_{14}H_{29})P^{+}\,Cl^{-}$$

(water solution) (solution in methanol)

$$\longrightarrow \left[(C_6H_{13})_3(C_{14}H_{29})P\right]^{+}\left[(C_2F_5)_3PF_3\right]^{-}\downarrow \quad + \quad HCl$$

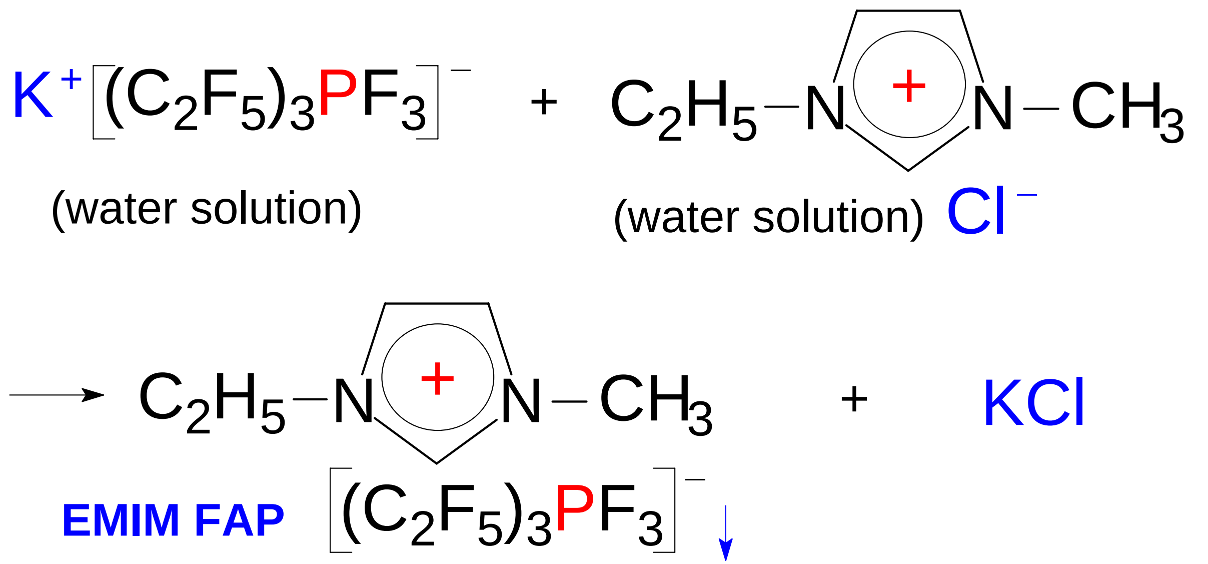
Liquid at room temperature; Viscosity: $393\ mm^2 \cdot s^{-1}$;

Density: $1.18\ g \cdot cm^{-3}$

Possible applications: Ionic Liquid ; Surfactant

N. V. Ignatiev, M. Schmidt, A. Kuener, V. Hilarius, U. Heider, A. Kucheryna, P. Sartori, H. Willner, **WO 03/002579**, Merck Patent GmbH, Darmstadt, Germany

Synthesis of new Ionic Liquids

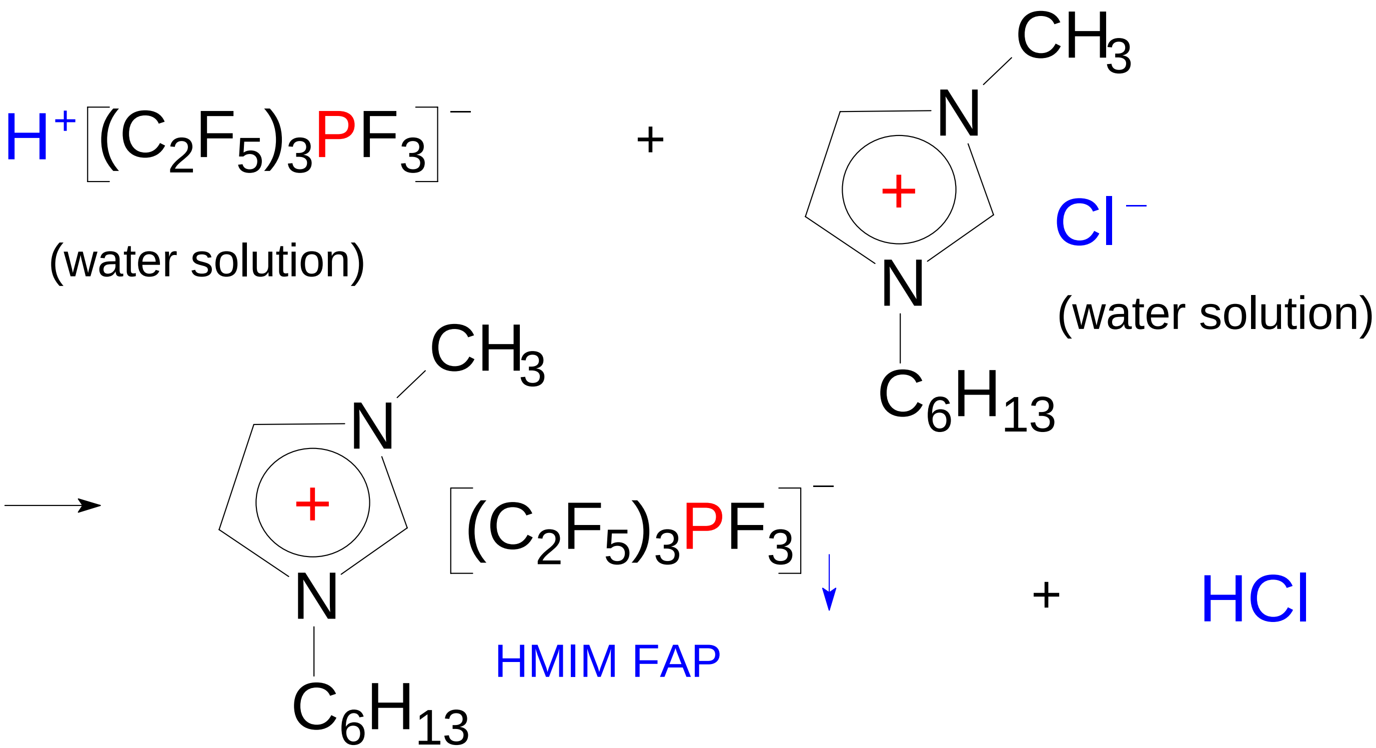


Liquid at room temperature; Viscosity: $44\ mm^2 \cdot s^{-1}$;

Density: $1.71\ g \cdot cm^{-3}$

M. Schmidt, W. Geissler, N. V. Ignatiev, V. Hilarius,
EP 1 162 204 A1 (2001), Merck Patent GmbH, Darmstadt, Germany

Synthesis of new Ionic Liquids



Liquid at room temperature; Viscosity: $74\ mm^2 \cdot s^{-1}$;

Density: $1.56\ g \cdot cm^{-3}$

Tris(perfluoroalkyl)trifluorophosphates

Ionic Liquid	Viscosity (20° C), $mm^2 \cdot s^{-1}$	Density $g \cdot cm^{-3}$
1-Hexyl-3-methylimidazolium Cloride	7453	1.050
1-Hexyl-3-methylimidazolium $[PF_6]^-$	548	1.297
1-Hexyl-3-methylimidazolium $[(C_2F_5)_3PF_3]^-$	74	1.560
1-Hexyl-3-methylimidazolium $[(C_3F_7)_3PF_3]^-$	227	1.620
1-Pentyl-3-methylimidazolium $[(C_4F_9)_3PF_3]^-$	594	1.693

N. V. Ignat'ev, U. Welz-Biermann, A. Kucheryna, G. Bissky, H. Willner, ***J. of Fluorine Chem.***, 126 (2005), p.1150-1159.

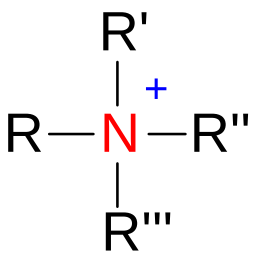
Water uptake by hydrophobic IL

	Max. Water Uptake, [ppm]
1-Hexyl-3-methylimidazolium FAP	2030
1-Hexyl-3-methylimidazolium TFSI	10670
1-Butyl-1-methylpyrrolidinium FAP	3500
1-Butyl-1-methylpyrrolidinium TFSI	14800
1-Butyl-3-methylimidazolium PF_6^-	22600

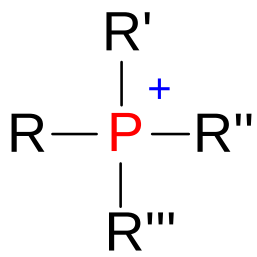
N. V. Ignat'ev, U. Welz-Biermann, A. Kucheryna, G. Bissky, H. Willner, ***J. of Fluorine Chem.***, 126 (2005), p.1150-1159.

Ionic Liquids - Cations

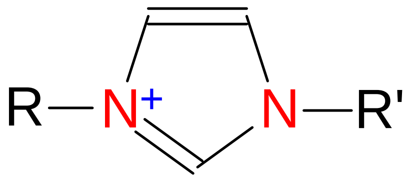
Typical Cations



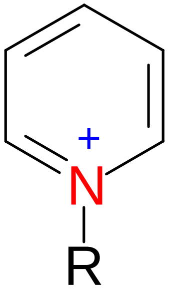
Ammonium



Phosphonium

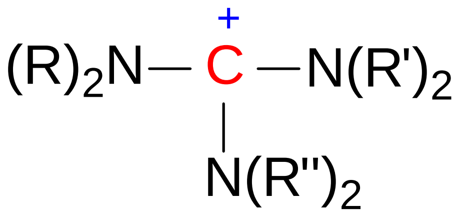


Imidazolium

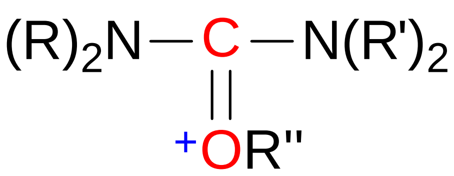


Pyridinium

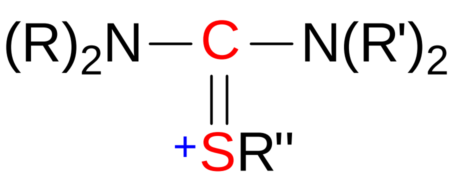
New Cations for the preparation of Ionic Liquids



Guanidinium



Uronium



Thiouronium

Alkylating reagents:

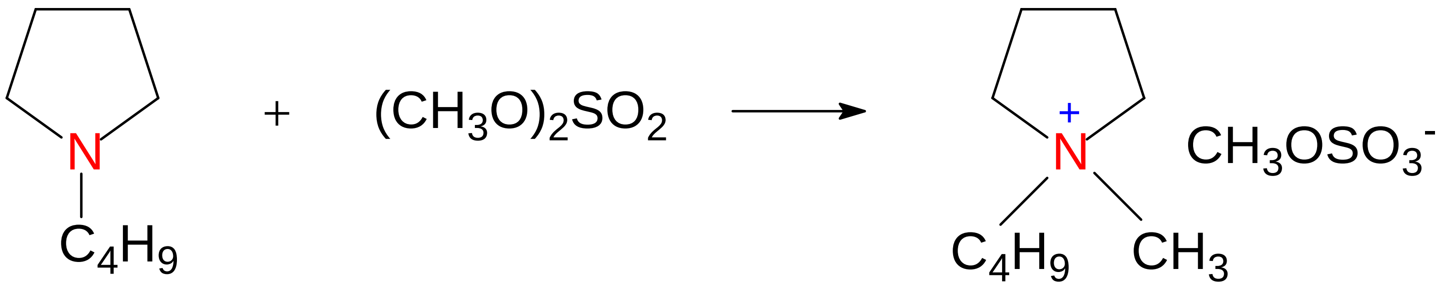
- Alkylhalogenides (AlkCl, AlkBr, AlkI)

- Alkylsulfates (for example: $CH_3OSO_2OCH_3$, $CH_3C_6H_4SO_2OCH_3$)

- Alkyltriflates (for example: $CF_3SO_2OCH_3$, $CF_3SO_2OC_2H_5$)

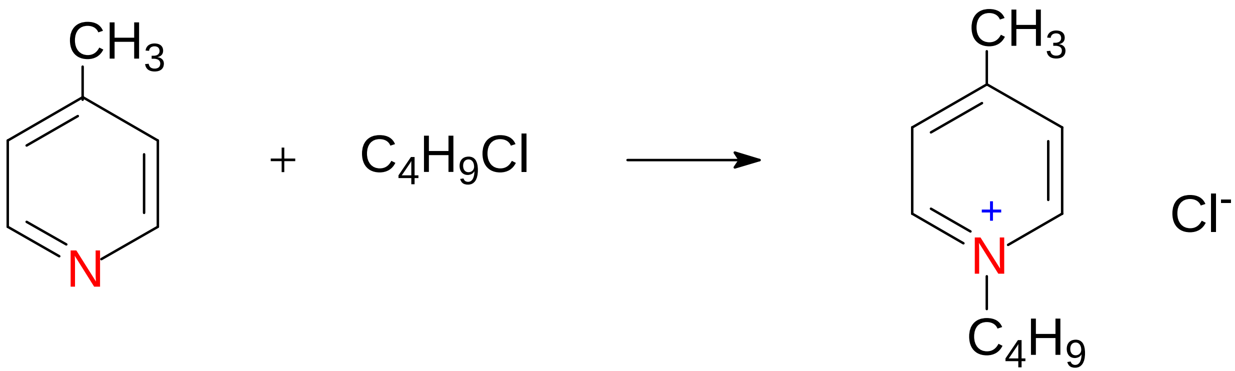
- Alkyltrifluoroacetates (for example: $CF_3C(O)OCH_3$, $CF_3C(O)OC_2H_5$)

Ionic Liquids synthesis. Alkylation:



N-Butylpyrrolidine

N-Butyl-N-methylpyrrolidinium methylsulfat



4-Methylpyridine

N-Butyl-4-Methylpyridinium Cloride

Alkylation with Alkohols ?

Alkyl—OH Alkyl — Cl

Alcohols are cheap and less toxic then Alkylhalides

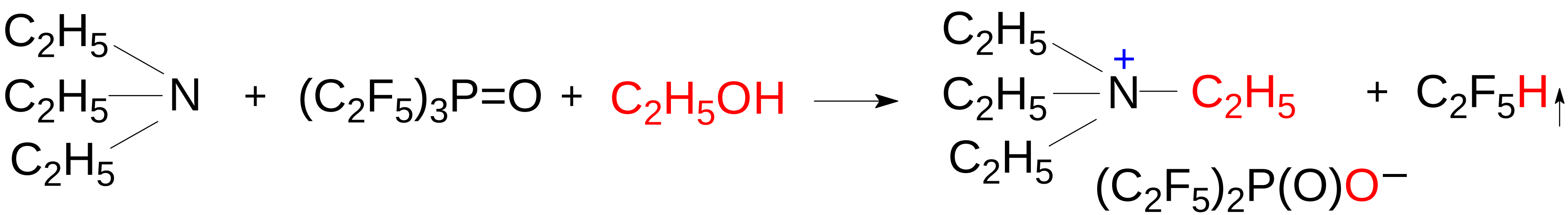
Can we alkylate of organic compounds with Alcohols ?

OH is a bad leaving group in comparison to Halides

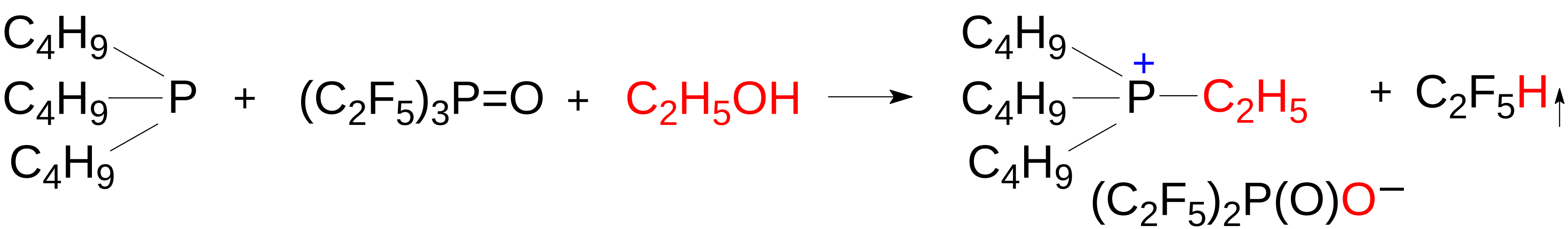
How we can activate the Alcohol ? Acid ?

But the acid will immediately protonate organic base
we want to alkylate

Yes ! Alkylation with Alkohols



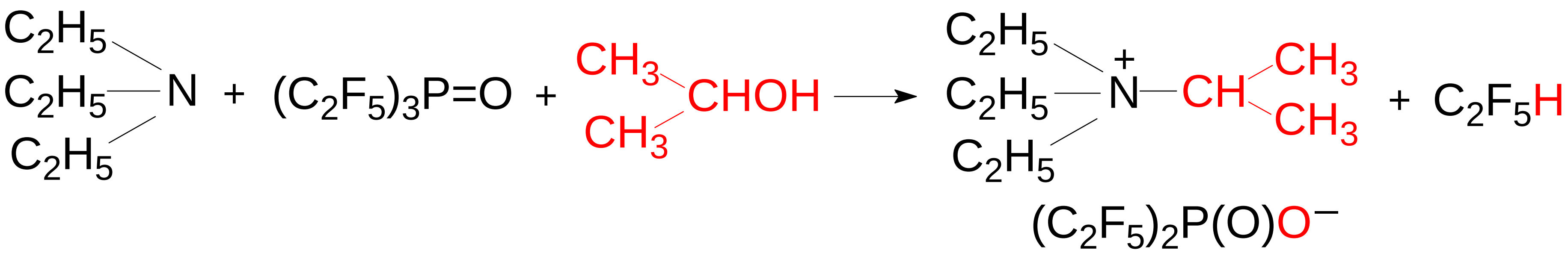
Yield: 97 % ; M.p. 103 -105° C



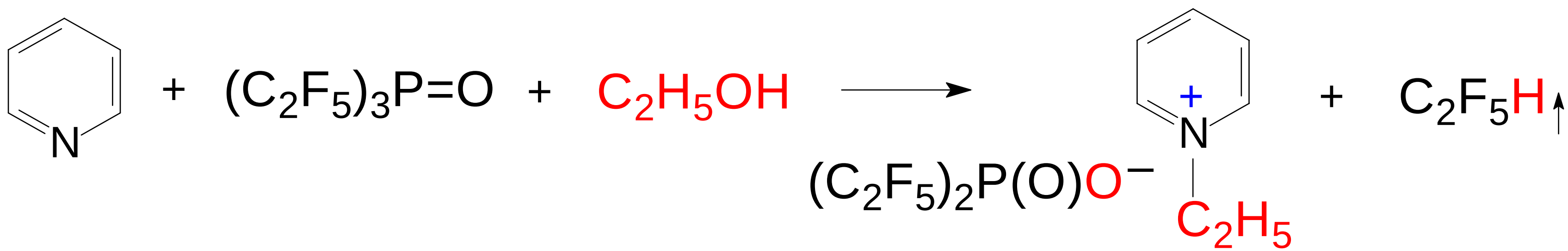
Yield: 99 % ; M.p. 42 - 43° C

N. V. Ignatyev, U. Welz-Biermann, M. Weiden, A. Kucheryna,
H. Willner, **WO 2005/049555**, Merck Patent GmbH, Darmstadt, Germany

Alkylation with Alkohols



Yield: 58 %



Yield: 92 %

N. V. Ignatyev, U. Welz-Biermann, M. Weiden, A. Kucheryna,
H. Willner, **WO 2005/049555**, Merck Patent GmbH, Darmstadt, Germany

Synthesis of Tris(perfluoroalkyl) phosphineoxides

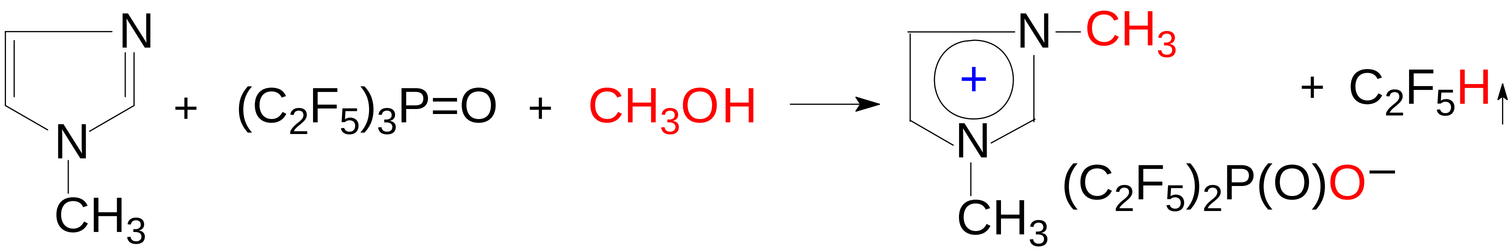
$$R_3P \xrightarrow[\text{HF}]{\text{e , Ni}} (R_F)_3PF_2$$

N. V. Ignat'ev and P. Sartori, *J. of Fluorine Chem.* 103 (2000), 57-61
DE 198 46 636, Merck KGaA, Darmstadt, Germany
WO 00/21969, Merck KGaA, Darmstadt, Germany

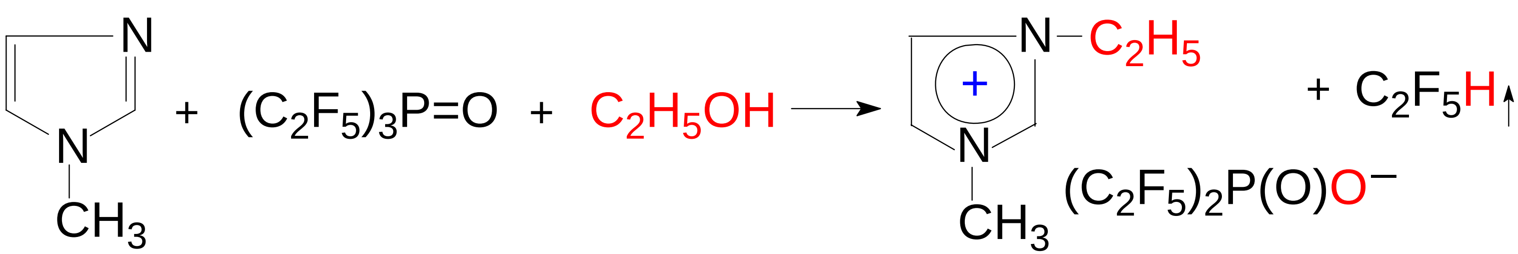
$$(C_2F_5)_3PF_2 + (CH_3)_3SiOSi(CH_3)_3 \longrightarrow (C_2F_5)_3P{=}O + 2\,(CH_3)_3SiF\uparrow$$

V.Ya. Semenii, V.A. Stepanov, N.V. Ignatiev, G.G. Furin and L.M. Yagupolskii, Zh. Obschei Khim. (Russ), 55 (1985), p. 2716-2720

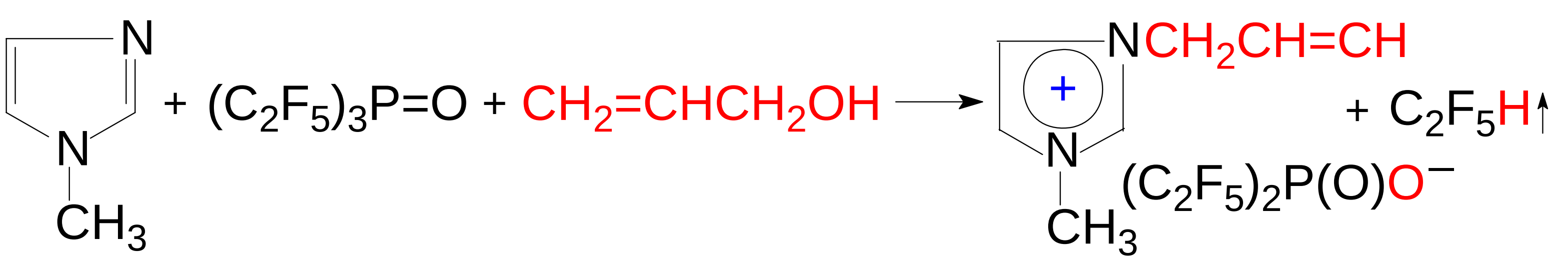
Alkylation with Alkohols



Yield: 95 % ; M.p. 35 -37° C

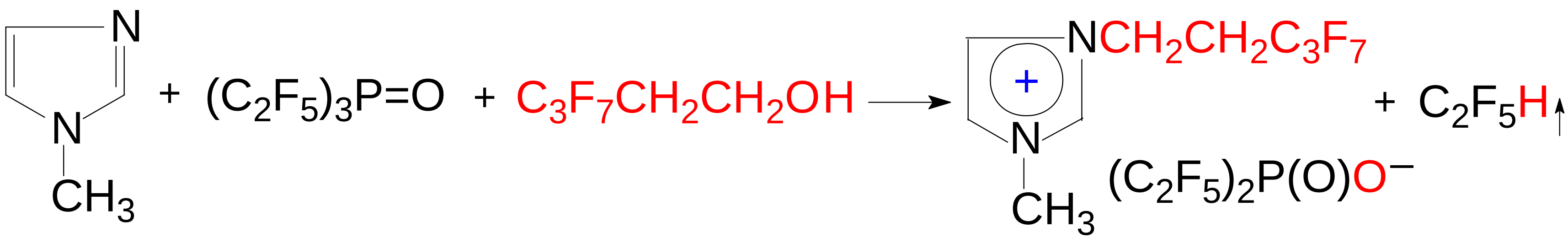


Yield: 93 % ; Liquid at R.T.

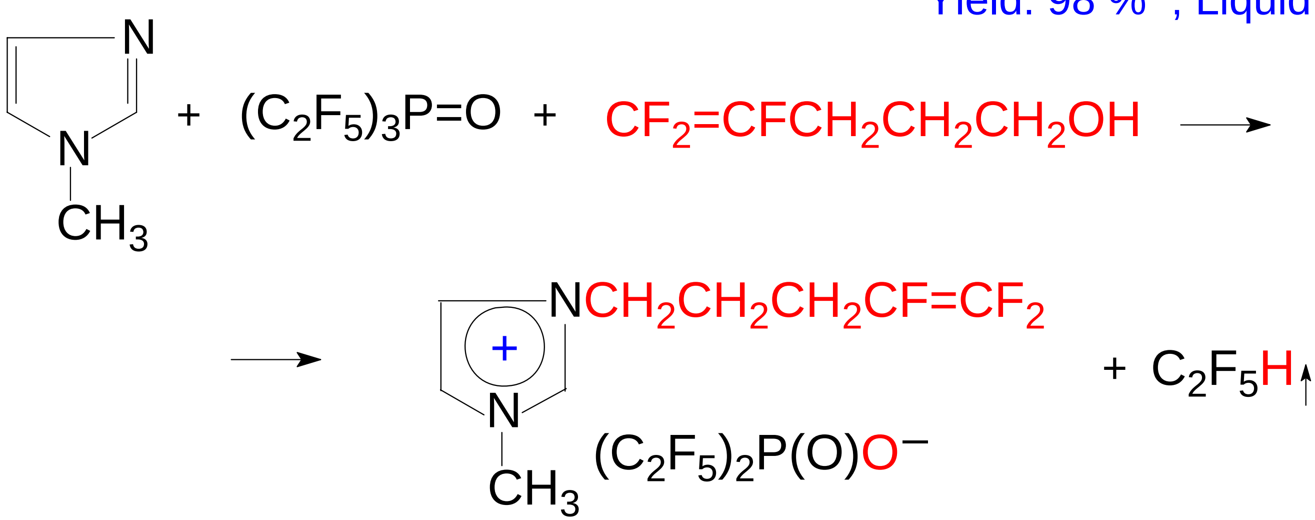


Yield: 93 % ; Liquid at R.T.

Alkylation with Alkohols



Yield: 98 % ; Liquid at R.T.



Yield: 98 % ; Liquid at R.T.

N. V. Ignatyev, U. Welz-Biermann, M. Weiden, A. Kucheryna, H. Willner, **WO 2005/049555**, Merck Patent GmbH, Darmstadt, Germany

Alkylation with Alkohols

$$(CH_3)_2N-\overset{\displaystyle O}{\overset{\|}{C}}-N(CH_3)_2 + (C_2F_5)_3P=O + CH_3OH \longrightarrow (CH_3)_2N-\overset{+}{C}(OCH_3)-N(CH_3)_2 \;\; (C_2F_5)_2P(O)O^- + C_2F_5H\uparrow$$

Yield: 92 % ; Liquid at R.T.

$$CH_3-S-CH_3 + (C_2F_5)_3P=O + C_2H_5OH \longrightarrow CH_3-\overset{+}{S}(C_2H_5)-CH_3 \;\; (C_2F_5)_2P(O)O^- + C_2F_5H\uparrow$$

Yield: 87 %

N. V. Ignatyev, U. Welz-Biermann, M. Weiden, A. Kucheryna, H. Willner, **WO 2005/049555**, Merck Patent GmbH, Darmstadt, Germany

Electrochemical Stability of IL with Bis(pentafluoroethyl)phosphinat-Anion

	$E_{(ox)}$,V	$E_{(red)}$,V	Window, V
1-Ethyl-3-methylimidazolium FAP	3.9	- 2.5	6.4
1-Ethyl-3-methylimidazolium, $(C_2F_5)_2P(O)O^-$	3.6	- 2.6	6.2
1-Ethyl-3-methylimidazolium Triflate	2.8	- 2.5	5.3
1-Ethyl-3-methylimidazolium BF_4^-	2.6	- 2.6	5.2

Bis(perfluoroalkyl)phosphinic acids

$$(C_2F_5)_3PF_2 + HF + 5\,H_2O \longrightarrow H^+[(C_2F_5)_3PF_3]^- \cdot 5\,H_2O$$

Phosphorane **I** → HFAP

$$H^+[(C_2F_5)_3PF_3]^- \cdot 5\,H_2O \xrightarrow{135\text{-}140°\,C\,,\,20\,h} (C_2F_5)_2P(O)OH \cdot 3\,H_2O + C_2F_5H + 3\,HF$$

HFAP I

Yield: 87 %

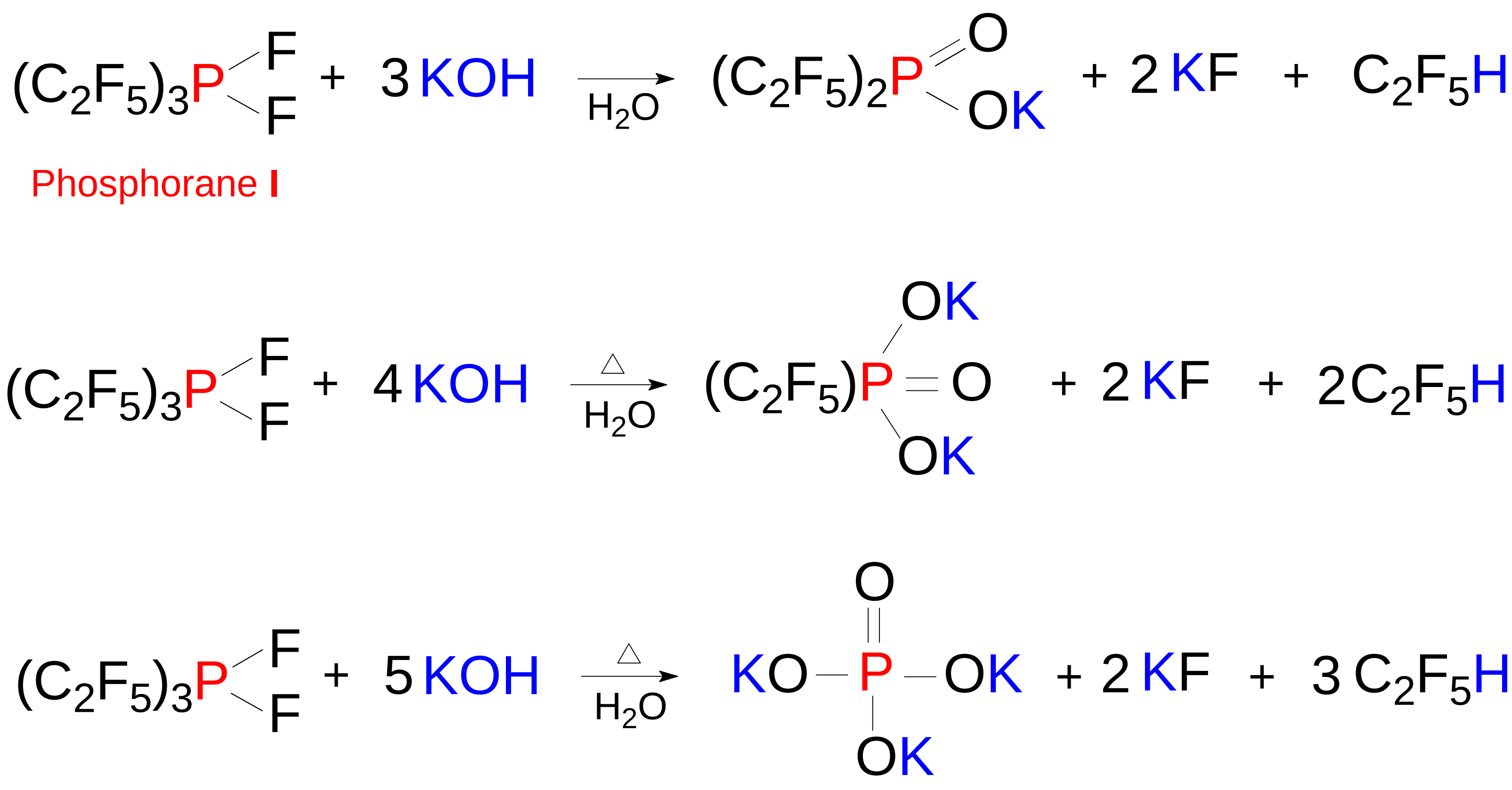
$$H^+[(C_4F_9)_3PF_3]^- \cdot 5\,H_2O \xrightarrow{135\text{-}140°\,C\,,\,20\,h} (C_4F_9)_2P(O)OH \cdot 3\,H_2O + C_4F_9H + 3\,HF$$

HFAP II

Yield: 97 %

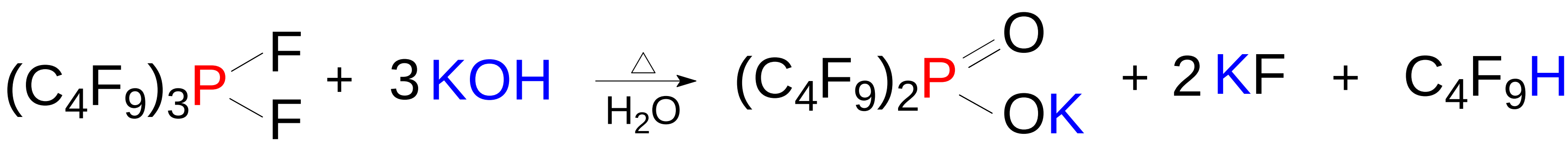
U. Welz-Biermann, N. V. Ignatyev, M. Weiden, U. Heider, A. Kucheryna, H. Willner, P. Sartori, **WO 03/087110**, Merck Patent GmbH, Darmstadt, Germany

Pentafluoroethylphosphinic- and phosphonic- acids Salts

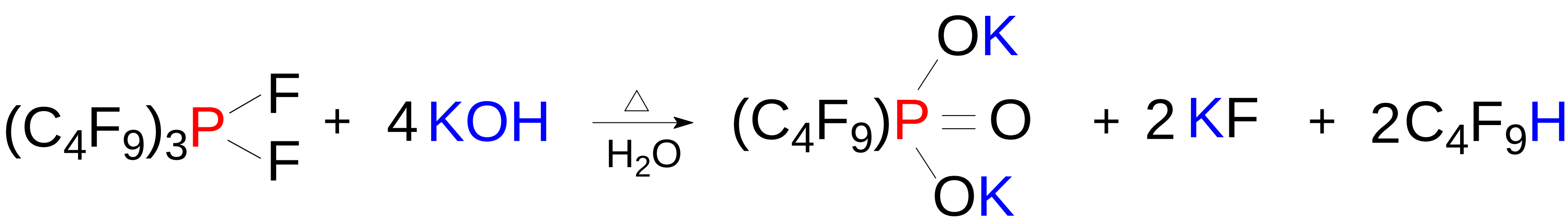


N. Ignatyev, M. Weiden, U. Welz-Biermann, U. Heider, P.Sartori, A. Kucheryna, H. Willner, **WO 03/087111**, Merck Patent GmbH, Darmstadt, Germany

Nonafluorobutylphosphinic- and phosphonic- acids Salts



Phosphorane **II**



N. Ignatyev, M. Weiden, U. Welz-Biermann, U. Heider, P.Sartori, A. Kucheryna, H. Willner, **WO 03/087111**, Merck Patent GmbH, Darmstadt, Germany

Perfluoroalkyl-phosphinic and -phosphonic Acids

$$2\,(C_2F_5)_2P(=O)OK + H_2SO_4 \xrightarrow{\text{Distillation}} 2\,(C_2F_5)_2P(O)OH + K_2SO_4$$

B.p. : 63-64° C / 125 Pa

Bis(pentafluoroethyl)phosphinic Acid

$$[(C_4F_9)P(O)O_2]^{2-}\ Ba^{2+} + H_2SO_4 \xrightarrow[H_2O]{} (C_4F_9)P(O)(OH)_2 + BaSO_4\downarrow$$

Nonafluorobutylphosphonic Acid

N. Ignatyev, M. Weiden, U. Welz-Biermann, U. Heider, P.Sartori, A. Kucheryna, H. Willner, **WO 03/087111**, Merck Patent GmbH, Darmstadt, Germany

Phosphorous Acids

$$H^{+}\left[(C_nF_{2n+1})_3PF_3\right]^{-}$$

HFAP

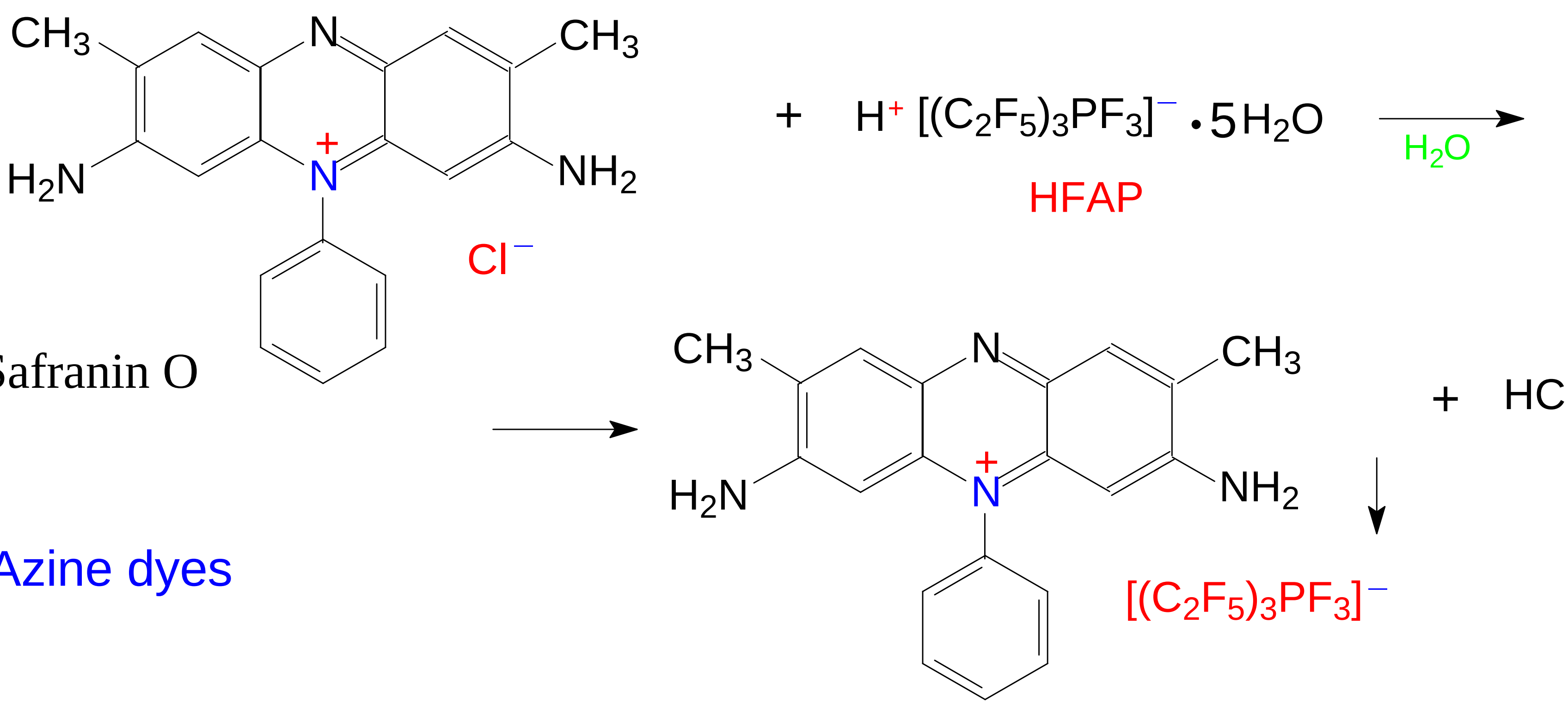
$$(C_nF_{2n+1})_2P(O)OH \qquad (C_nF_{2n+1})P(O)(OH)_2$$

Bis(perfluoroalkyl)phosphinic Acids

Perfluoroalkylphosphonic Acids

Patent Applications, Merck KGaA (Darmstadt, Germany)

Synthesis of cationic dyes with FAP-anion



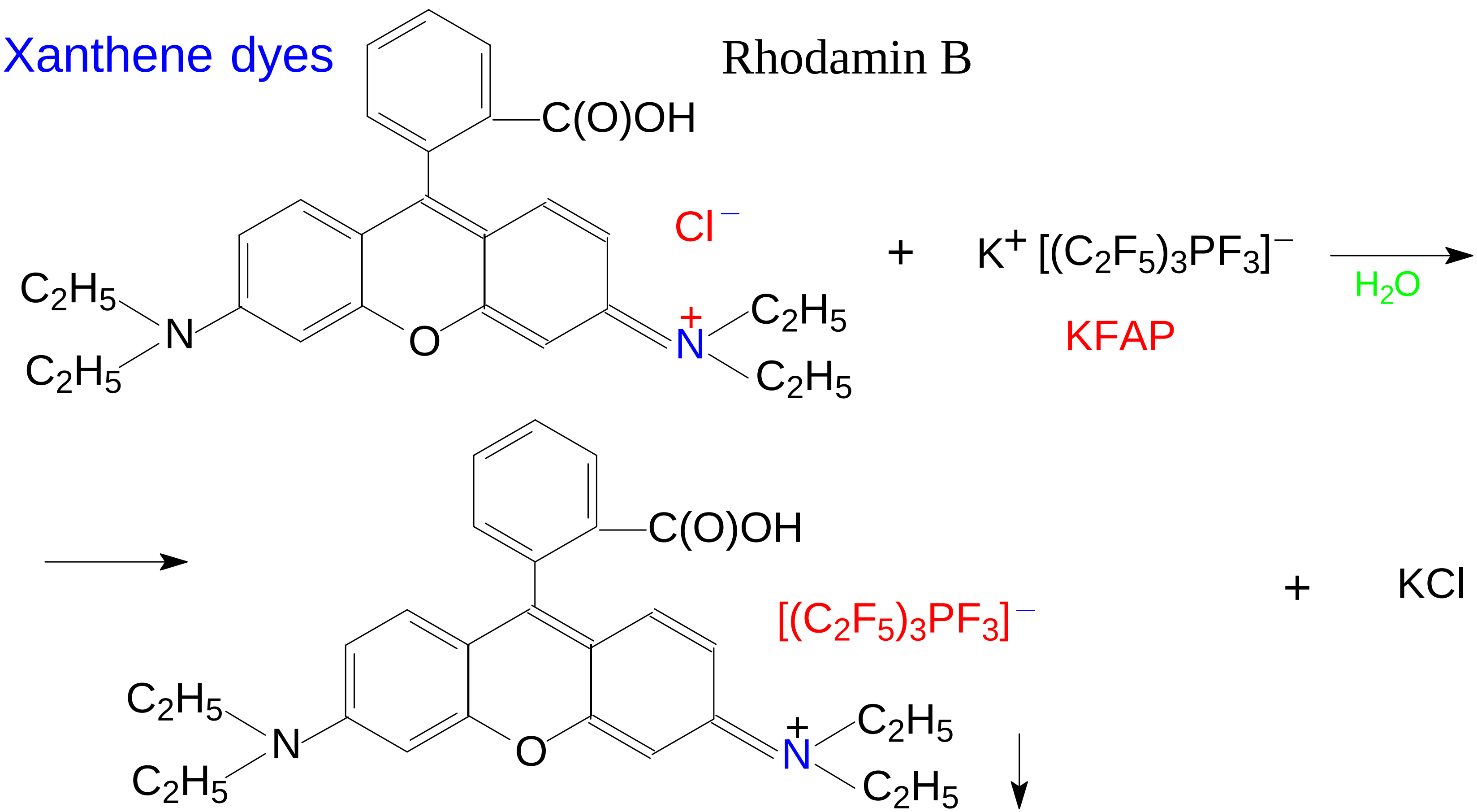
Safranin O

Azine dyes

N. Ignatiev, U. Welz-Biermann, M. Weiden, A. Kucheryna, H. Willner,
DE 10338933.4, Merck Patent GmbH, Darmstadt, Germany

Synthesis of cationic dyes with FAP-anion

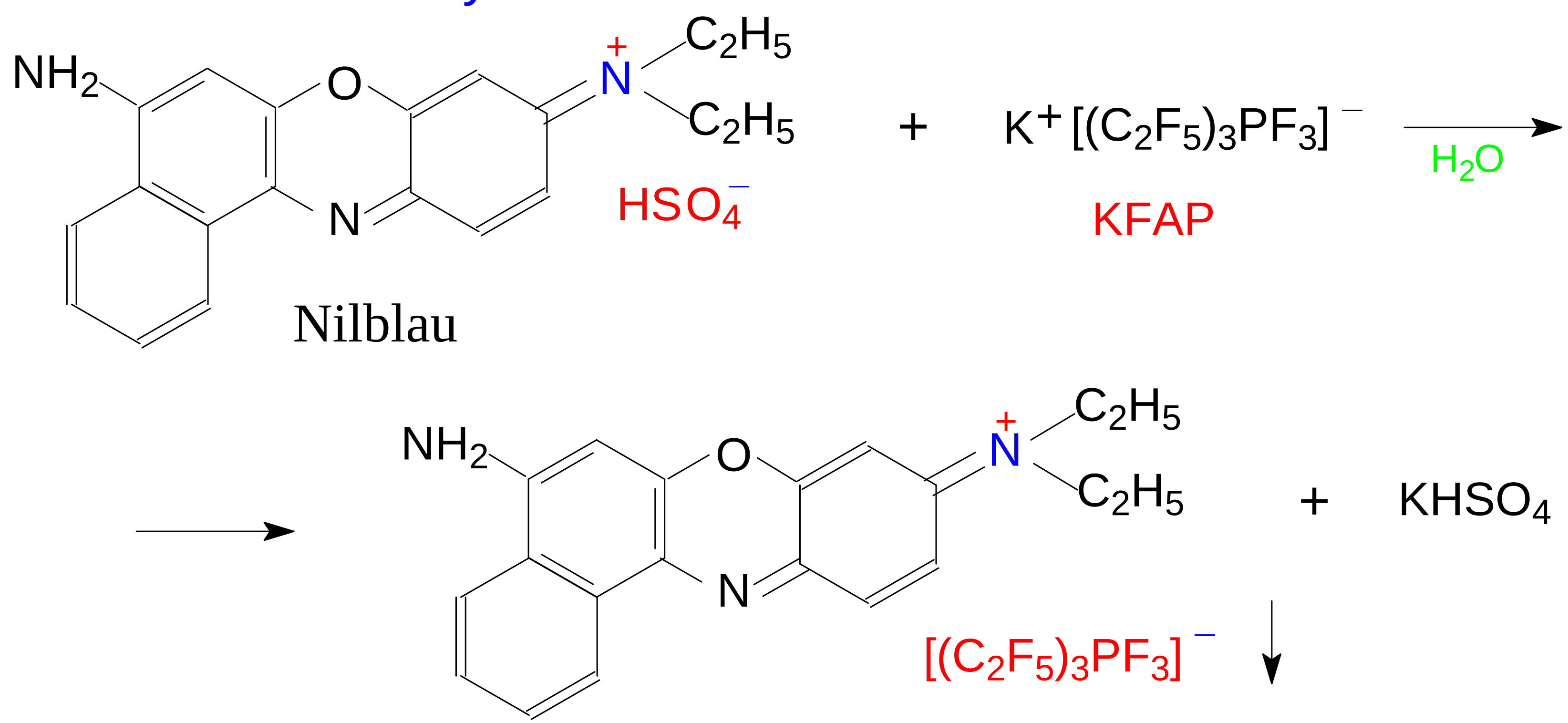
Xanthene dyes



N. Ignatiev, U. Welz-Biermann, M. Weiden, A. Kucheryna, H. Willner,
DE 10338933.4, Merck Patent GmbH, Darmstadt, Germany

Synthesis of cationic dyes with FAP-anion

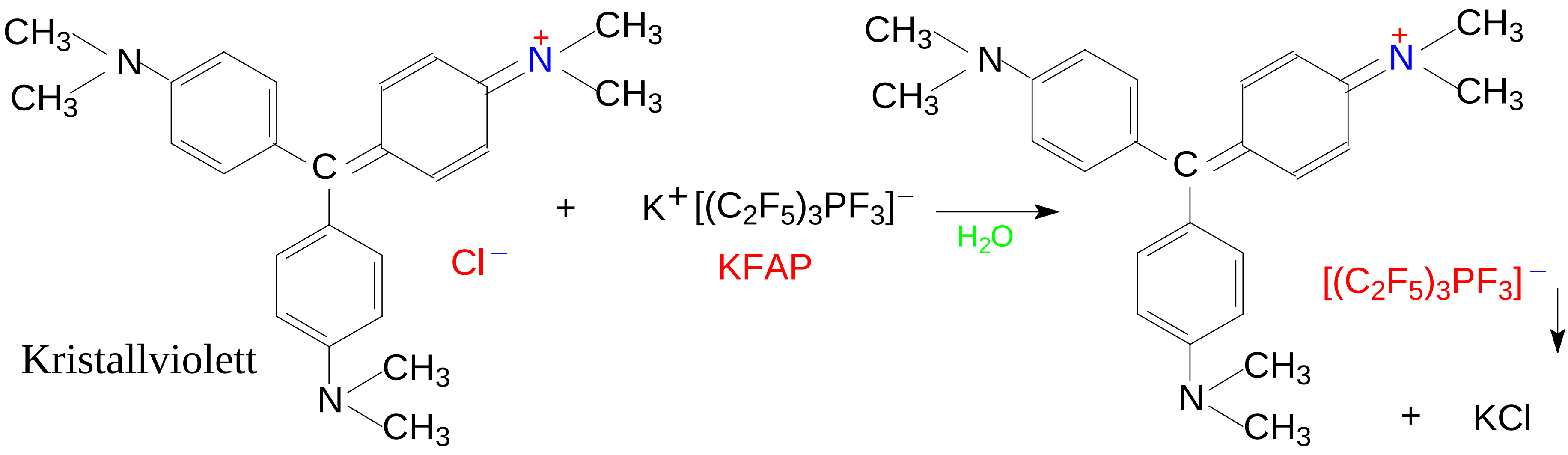
Oxazine Dyes



N. Ignatiev, U. Welz-Biermann, M. Weiden, A. Kucheryna, H. Willner,
DE 10338933.4, Merck Patent GmbH, Darmstadt, Germany

Synthesis of cationic dyes with FAP-anion

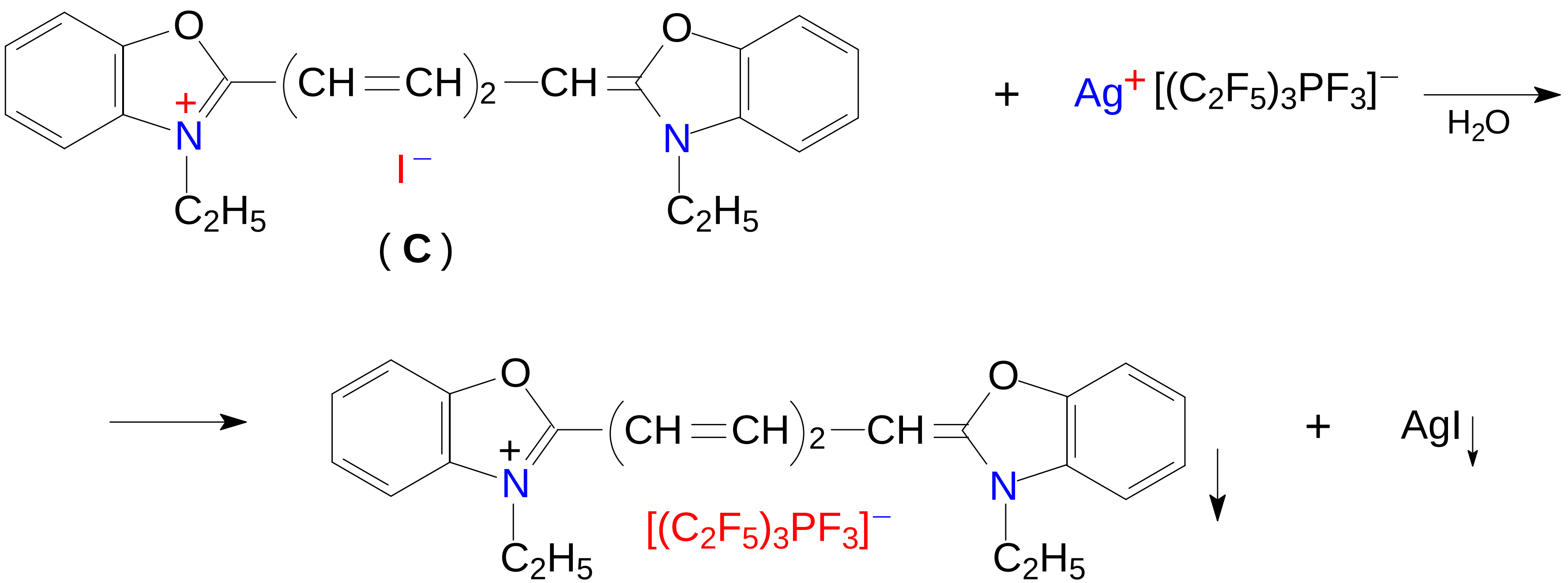
Triphenylmethane Dyes



N. Ignatiev, U. Welz-Biermann, M. Weiden, A. Kucheryna, H. Willner,
DE 10338933.4, Merck Patent GmbH, Darmstadt, Germany

Synthesis of cationic dyes with FAP-anion

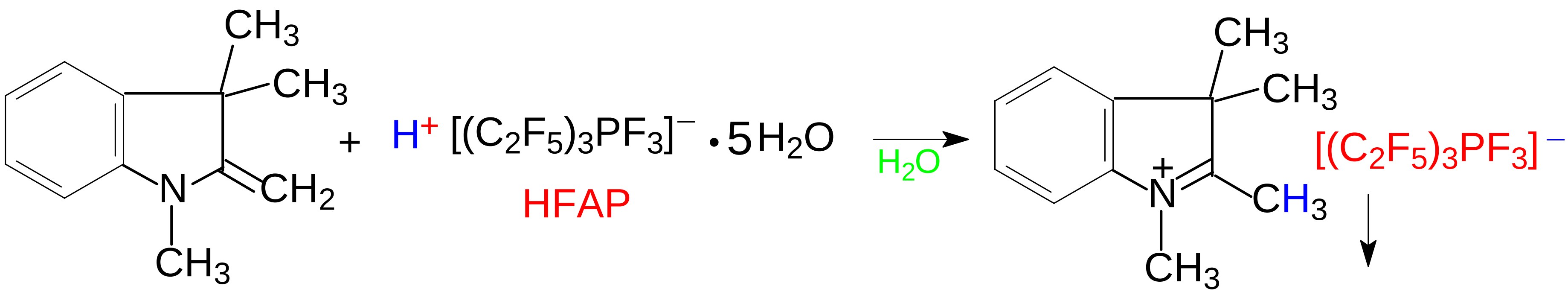
Cyanine dyes



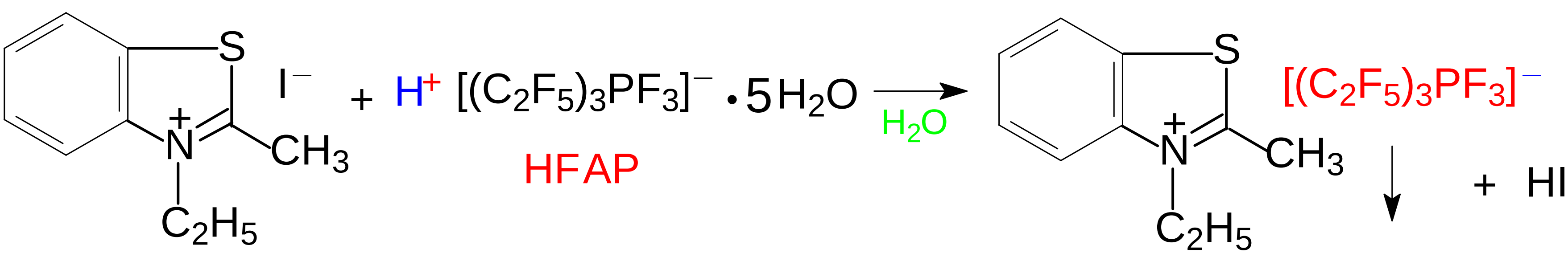
N. Ignatiev, U. Welz-Biermann, M. Weiden, A. Kucheryna, H. Willner,
DE 10338933.4, Merck Patent GmbH, Darmstadt, Germany

Synthesis of cationic dyes with FAP-anion

1,2,3,3-Tetramethyl-3H-indolium FAP



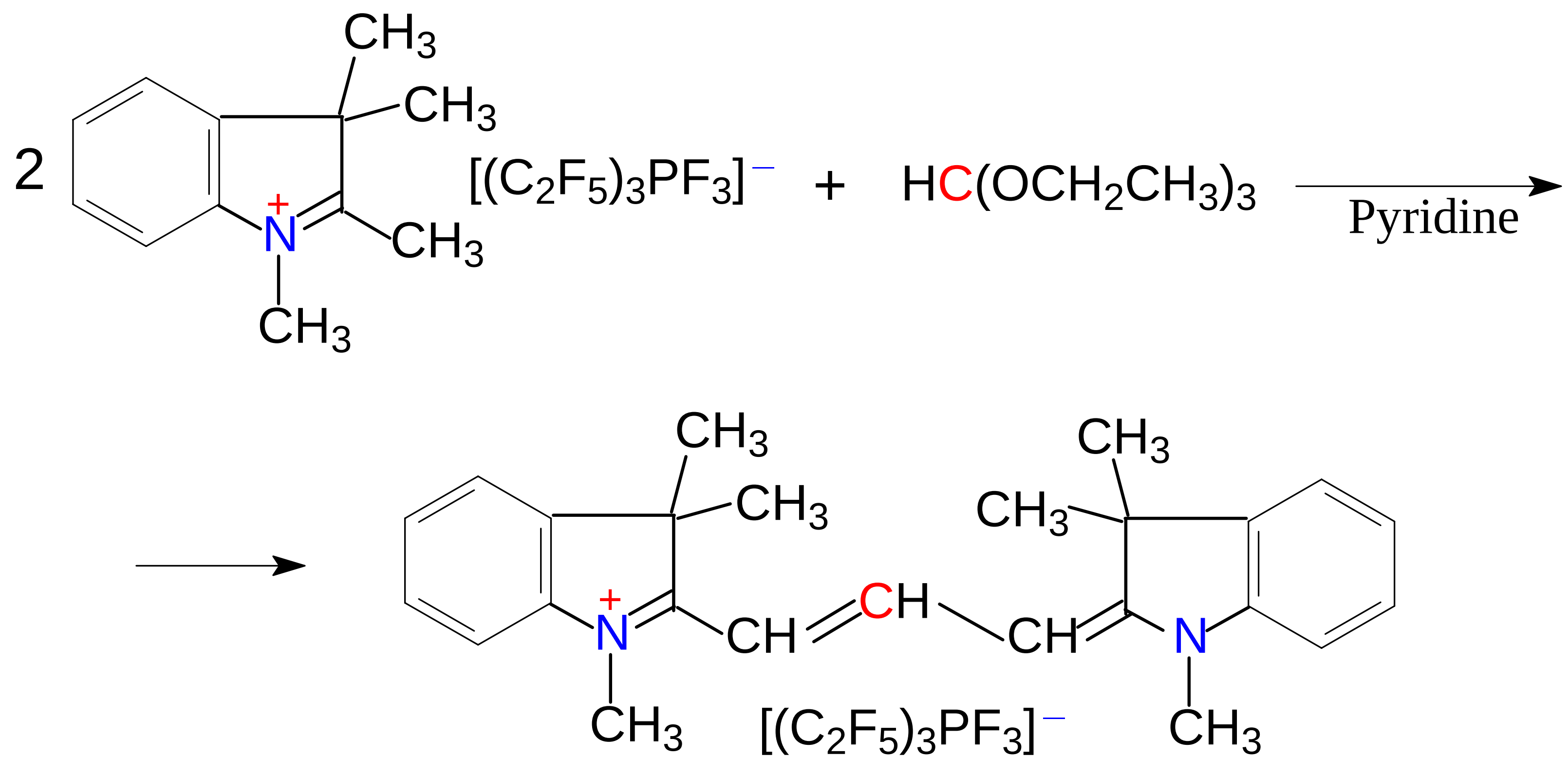
3-Ethyl-2-methyl-benzthiazolium FAP



N. Ignatiev, U. Welz-Biermann, M. Weiden, A. Kucheryna, H. Willner,
DE 10338933.4, Merck Patent GmbH, Darmstadt, Germany

Synthesis of cationic dyes with FAP-anion

Cyanine dyes



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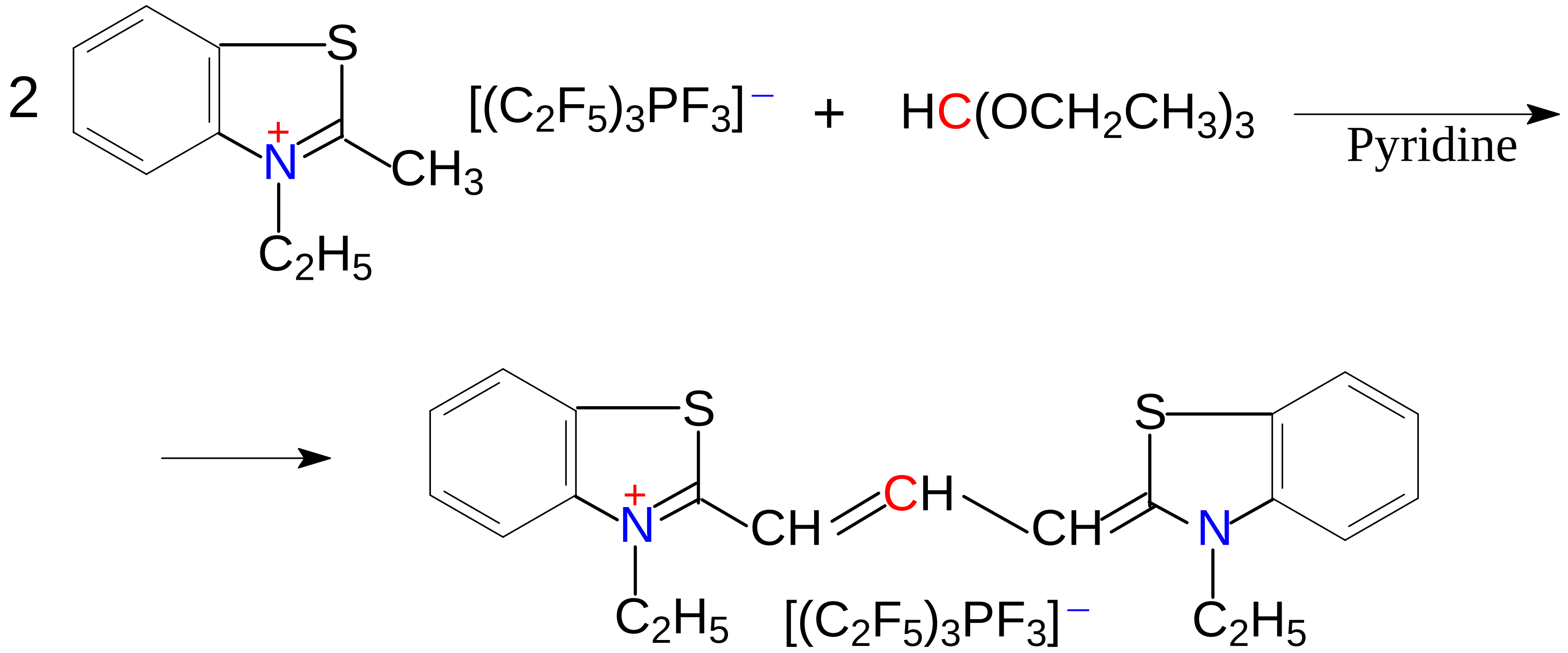
Synthesis of cationic dyes with FAP-anion

Cyanine dyes



N. Ignatiev, U. Welz-Biermann, M. Weiden, A. Kucheryna, H. Willner,
DE 10338933.4, Merck Patent GmbH, Darmstadt, Germany

Salts of Bis(perfluoroalkyl)phosphinic Acids

$$(C_2F_5)_2P(O)OH + (C_2H_5)_4N^+ \ ^-OH \longrightarrow (C_2H_5)_4N^+ [(C_2F_5)_2P(O)O]^- + H_2O$$

M. p. = 100-102° C

$$2\,(C_2F_5)_2P(O)OH + H_2N(CH_2)_6NH_2 \longrightarrow [H_3N(CH_2)_6NH_3]^{+2} [(C_2F_5)_2P(O)O]_2^-$$

M. p. = 208-210° C

$$(C_4F_9)_2P(O)OH + (C_6H_{13})_3N \longrightarrow [(C_6H_{13})_3NH]^+ [(C_4F_9)_2P(O)O]^-$$

M. p. = 74-75° C

Possible applications: Salts for Super-Capasitors ; Ionic Liquids ; Surfactants

U. Welz-Biermann, N. V. Ignatyev, M. Weiden, U. Heider, A. Kucheryna,
H. Willner, P. Sartori, **WO 03/087110**, Merck Patent GmbH, Darmstadt, Germany

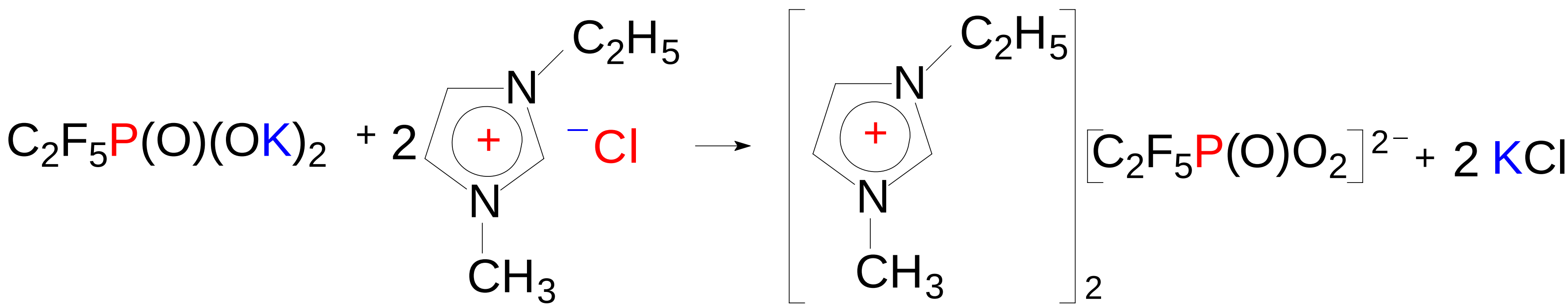
Salts of Perfluoroalkylphosphonic Acids

$$C_2F_5P(O)(OH)_2 + 2(C_2H_5)_4N^+\ {}^-OH \longrightarrow [(C_2H_5)_4N^+]_2[C_2F_5P(O)O_2]^{2-} + 2\,H_2O$$

M. p. = 93-95 ° C

$$C_4F_9P(O)(OH)_2 + 2(C_2H_5)_4N^+\ {}^-OH \longrightarrow [(C_2H_5)_4N^+]_2[C_4F_9P(O)O_2]^{2-} + 2\,H_2O$$

M. p. = 103-105 ° C



Possible applications: Salts for Super-Capasitors ; Ionic Liquids ; Surfactants

U. Welz-Biermann, N. V. Ignatyev, M. Weiden, U. Heider, A. Kucheryna, H. Willner, P. Sartori, **WO 03/087110**, Merck Patent GmbH, Darmstadt, Germany

FAP Chemistry

Phosphines

ECF (Merck KGaA Technology)

Perfluoroalkylphosphoranes

\+ Perfluoroalkanes (Side product;0.3 - 0.7 kg per kg of phosphorane)

Applications: Refrigerant composition
Etching agents
Cleaning gas
Blowing agents
Fire extinguisher
Contrast agent (diagnostic)

LiFAP
KFAP

Applications:
Li-Batteries;
Source of FAP anion

HFAP

Applications:
Replacement of HPF_6; Starting material for Ionic-Liquids, salts and acids production

Perfluorophosphinic Acids

Applications:
Conducting salts, Ionic-Liquids

Perfluoroalkylphosphines; Perfluoroalkylphosphazenes

Applications: Perfluoroalkylation of organic compounds; Fine chemicals

Monohydro-perfluoroalkanes (side products)

Applications:
Refrigerant composition,
Etching agents, Blowing agents,
Fire extinguisher, Anesthetics

Perfluorophosphonic Acids

Applications:
Conducting salts

New Cationic Dyes
(water insoluble)

Perfluoroalkylphosphineoxides

Applications:
New technology for alkylation of organic compounds with alcohols;
Ionic Liquids and conducting salts production

Acknowledgments

Merck KGaA, Darmstadt, Germany

Mrs. A. Amann

Dr. O. Korbut

Mrs. I. Skupch-Martinez

Dr. M. Schmidt

Dr. U. Welz-Biermann

and whole Merck KGaA Ionic Liquids Team

Syntheses were carried out in the Laboratory at the University of Wuppertal (Germany) and University Duisburg-Essen by Dipl.-Ing. A. Kucheryna in the co-operation with Prof. H. Willner and Prof. P. Sartori.