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ELECTROCHEMICAL FLUORINATION (ECF) OF TOLUENE AND BENZOT THE PRESENCE OF TRIALLYLAMINE

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Electrochemical fluorination (ECF) in anhydrous hydrogen fluoride on nickel anodes is a freque converting hydrocarbons or partly fluorinated organics into their perfluorinated analogues tho functional groups or structure of the original substance that involves some heteroatom. For th was described in the late 1940th by J.Simons, and then further developed by many researche the fluorination of organics soluble and conductive in HF, with molecules containing C-O, C-N, C-

Among numerous practically useful perfluorinated substances synthesized by ECF method amines and ethers, derivatives of perfluorocarbonic acids and sulfoacids, they usu perfluorocycloalkanes as all attempts to produce those substances by the electrolysis of their insoluble in electrolytes mostly failed.

However, the development of a method for perfluorocycloalkanes manufacture is an im because those fluorocarbons are known for quite unusual combination of their physico-chemica large molecular masses they have low boiling points, critical temperatures and pressures; t expansion and compressibility coefficients provide very low sonic speed in those media. refraction indices of those substances are much lower than those of any other liquid. They ar excellent insulation properties and their unique chemical and biochemical stability makes them

The synthesis of perfluoromethylcyclohexane (PFMCH) through ECF of toluene with very low [2], while in the case of benzotrifluoride when the yield was 47% [3] the arrangement of non was hindered by electrolyte gumming in the process of electrolysis.

Earlier it has been shown [4] that those effects are suppressable by adding some depolar stationary electrolysis regime. It is particularly important in the case when ECF chemicals are non-conductive, because such additive provides both conductivity of electrolyte and solubility c in it.

In this our study we attempted to apply ECF in the synthesis of perfluorinated cycled paraf electrolyte additive that undergoes electrolysis without electrolyte gumming and its fluorir products of practical significance.

In this connection we conducted a comparative study of the function of the yield of PFMCH benzotrifluoride using n-triallylamine (TAA) ($(CH_2=CHCH_2)_3N$) for a depolarizing additive, as its E mode at the conditions of continuous electrolysis and results in a mixture of perfluorotripropyl propyl-5- or -6-member heterocycles with high yields [5].

Experimental procedure

To produce perfluoromethylcyclohexane by ECF method we applied the electrolysis of ber mixed with triallylamine used for electrolytic additive.

Electrochemical fluorination was conducted in a carbon steel Simons electrolyser of volume water-cooled coil and a stack of nickel electrodes with the surface of anodes 500cm^2. The ele with a reflux condenser for condensation and recycling of hydrogen fluoride carried with ele those experiments the current load was 15A permanently, and the current density was 0.03A/

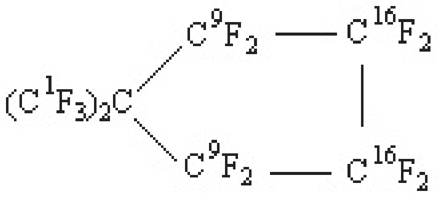
For electrolyte we used a solution that contained 5% (mass.) benzotrifluoride or toluen triallylamine in liquid anhydrous hydrogen fluoride. To keep the concentration of organics in ele initial organic blend was being fed 1-2 times hourly in amounts appropriate to their consumptio toluene/triallylamine mixture the designed electricity consumption Q, was much higher than in

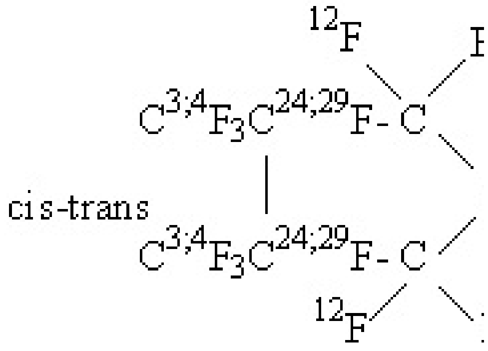
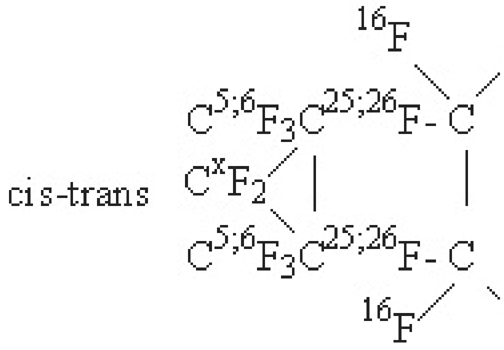
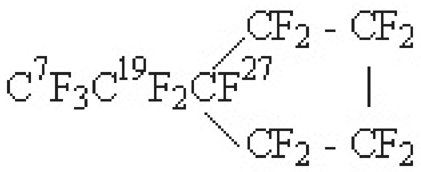
The ECF products with densities exceeding that of electrolyte were collected at the bottom drained over equal time periods. Crude product was pour off under water and neutralized wit product was cleaned from non-fluorinated products with water-alcohol alkaline solution and silicagel. Dried crude product was directed to rectification in order to separate into three fract $t_{boiling}$ 52-54 ^oC, target fraction with $t_{boiling}$ 76-78 ^oC and heavy fraction with $t_{boiling}$ 129-131

The fraction components were identified by their NMR F^{19} at Bruker Spectrospin AM-500 at in C_6F_6 solution used for the internal standard. The composition was analyzed by GL-chro equipped with a katharometer and a column charged with silochrome-80 with 20% α,α,α-tris- GCL composition is in good agreement with the signal intensities in NMR ^{19}F spectra.

Two structures were identified in the head fraction: perfluorocyclohexane and perfluoromet isomers resulting from its cycle contraction. The target fraction at 76-78^oC conta perfluoromethylcyclohexane CF_3-c-C_6F_{11} (with well-known NMR ^{19}F spectrum [6]) and its iso cycle contraction identified as perfluoro-1,1-dimethylcyclopentane and its stereois dimethylcyclopentanes, perfluoro-1,3-dimethylcyclopentanes and perfluoroethylcyclopentane, t signals in NMR ^{19}F spectra being shown in Table 1.

Table 1

N	CCl_3, m.d	multiplet	J_{F-F} , Hz	Number of F atoms	Structure substance
Perfluoro-1,1-dimethylcyclopentane					
1	-59.6	q,q (m)	^1F-^9F 12;^1F- ^xF 7	6F	
9	-114,6		^9F-^1F , 12	4F	
16	-123,3	m		4F	
Perfluoro-*cis* -1,2-dimethylcyclopentane and perfluoro-trans-1,2-dimethylcyclop					
3	-70,6	t		6F	

4	-70,8	m		6F	
12	-119,4	d	^{12}F-^{15}F 277	4F	
15	-123,3	d.m.	^{15}F-^{12}F 277	4F	
18	-124,2	d	^{18}F-^{19}F 274	2F	
19	-128,2	d	^{19}F-^{18}F 274	2F	
24	-183,0	s		2F	
24	-183,0	s		2F	
Perfluoro-*cis*-1,3-dimethylcyclopentane and perfluoro-*trans*-1,3-dimethylcyclop					
5	-71,4	t	^{5}F-^{x}F , 15	6F	
6	-71,6	Cê	^{6}F-^{x}F , 7,6	6F	
16	-122,4	D.m.	^{16}F-^{x}F , 271	4F	
17	-124,0	d	^{16}F-^{x}F , 271	4F	
25	-183,3	s		2F	
26	-184,0	s		2F	
Perfluoroethylcyclopentane					
7	-80,0	t	^{7}F-$^{\tilde{o}}$F , 11	3F	
19	-127,3	s		2F	
27	-184,4	s		1F	

The heavy fraction was a blend of perfluoroalkyl- and cycloalkylamines with its composition (%
- perfluorotri(n-propyl)amine, 41.2 - perfluoro-N-(n-propyl)-*cis*-3,4-dimethyl-, 18.7 - perflu
dimethyl- pyrrolidine [n-C_3F_7-N<*c*-C_4F_6(-3,4-CF_3)$_2$] and 19.3 perfluoro-N-(n-propyl)-3-methyl
C_5F_9-3-CF_3), their spectra being well known [5].

Experimental results and discussion

The experimental conditions and results of ECF of toluene and benzotrifluoride mixtures with in table 2.

Table 2

Charged, g(mole)		Q, A*h	Obtained in fractions, g(mole)			Yield,
$CH_3C_6H_5$	$N(CH_2CHCH_2)_3$		Light c-C_6F_{12}	Target c-C_7F_{14}	Heavy $C_9F_{21}N$+c-$C_9F_{19}N$	c-C_6F_1 +c-C_6
62,0(0,68)	75,0(0,55)	788	2,5(0,013)	5,0(0,021)	32,2(0,081)	**5,1(**
$CF_3C_6H_5$	$N(CH_2CHCH_2)_3$	Q, A*h	C_6F_{12}	C_7F_{14}	$C_9F_{21}N+C_9F_{21}N$	c-C_6F_1 +c-C_6F_1
127,4(0,87)	121,0(0,89)	440	41,4(0,14)	236(0,67)	82,2(0,21)	**93(0,**

The observed yields-by-substance and yields-by-current do not contradict those shown in liter usage of n-triallylamine for electrolyte additive allows increasing of the yield of useful fluorinatior

The target ECF fraction contains up to 20% of the products that due to cyclohexane ring con forming eutectic with PFMCH, decrease the mixture freezing point by 30?C (to compare with 65^{o}C.

Electrolysis being stable in time, this study opens technological opportunities for the high- number of organofluorochemicals for medical and technical applications in the uni benzotrifluoride/triallylamine mixture.

Conclusions

The possibility is shown to produce PFMCH with rather good yield in the presence of TAA additive. The process may be depicted as combined fluorination of two classes of substance with good yield-by-current, it is stable in time and technologically applicable.

Among the main electrolysis products are perfluorinated tertiary amines widely applied in indu industry, etc.

Thanks to its process peculiarities the proposed method allows improving of some characteri synthesis of perfluoromethylcyclohexane from benzotrifluoride and cut down its prime cost manufacture of some other marketable reaction products, namely perfluorinated tertiary amine

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