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Catalytic Synthesis Of Polyfluoroalkylchloroformiates

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Abstract: Here the catalytic impact of trimethylamine, pyridine, N,N-dimethylformamide on the reaction of phosgenation of polyfluorinated alcohols and the yield of polyfluoroalkylchloroformiates is shown.

Keywords: polyfluorinated alcohol, phosgene, polyfluoroalkyl chloroformiate, trimethylamine, pyridine and N, N-dimethylformamide (DMF).

Introduction

The development of methods of microdoping of polyfluorinated fragments into macromolecular schemes is an important task as it allows significant improving of physical and chemical properties of polymer composition materials [1-11]. One of introduction methods of polyfluoroalkyl groups is application of polyfluoroalkylchloroformiates – reagents for obtaining polyfluoroalkyl-peroxydicarbonates used as initiators and modifiers for polymer materials for these purposes, they differ by their high resistance to impact of strong oxidizers and aggressive media, non-combustibility, thermal stability and necessary durability characteristics [12, 13].

The aim of present work is catalytic (using trimethylamine, pyridine, N,N-dimethylformamide) synthesis of polyfluoroalkylchloroformiates by phosgenation of polyfluorinated alcohols used to obtain peroxydicarbonates – initiators and modifiers of polymer compositions [13].

Results and Discussion

When studying kinetics of phosgene reaction with different alcohols in heptane, dioxane

and without solvent we have stated low values of enthalpy and entropy of activation [14], which can be explained by the simplicity of alcohol molecule oxygen atom attachment to carbon atom of phosgene with further detachment of hydrogen chloride molecule. The impact of alcohol structure on its reactivity is estimated by Taft equation [14].

We have studied the phosgenation of polyfluorinated alcohols which were catalyzed by trimethylamine, pyridine and N,N-dimethylformamide. The reaction is going according to the following scheme (Table 1):



Where: X = H or F, n = 1, 2, 4, 6, 8.

The introduction of electron seeking substituents (dimethyl groups) into the molecule of alcohol decreases electron density at oxygen atom of HO-group of alcohol molecule, what lowers its reactivity during the carbon atom's attack of phosgene molecule.

The participation of trimethylamine, pyridine and N, N-dimethylformamide in the association with HO-group of alcohol molecule is their special feature, it favors carbon atom's attack of phosgene molecule.

We have used trimethylamine, pyridine and N, N - dimethylformamide (Table 1) as alcohols phosphogenating catalysts. All catalyst differ by basic capacity. Triethylamine have a maximum basic capacity ($pK_b = 3.1$). Pyridine is also a typical basic capacity containing $pK_b = 8.8$ (unseparated electron pair of pyridine nitrogen at account of which the interaction of proton passes is at sp^2 - hybridized orbital).

However, base capacity of pyridine is significantly lower than the base capacity of ammonia and aliphatic amines (pK_b of ammonia equals 4.8, methylamine 2.3). Unseparated electron pair of pyridine nitrogen, at which account the interaction with proton is going is at sp^2 - hybridized orbital.

As opposed to trimethylamine and pyridine the nitrogen atom in DMF possesses such a weak basic properties that most likely is the association of oxygen atom of carbonyl group of DMF. As a result of interaction of associate with phosgene molecule the formation of six-membered complex is possible, which decomposition results in forming of chloroformate, isolation of hydrogen chloride and regeneration of catalyst - N,N-dimethylformamide:

In Table 1 you can see the impact of catalyst, conditions of polyfluorinated alcohol phosgenation (nature of alcohol, catalyst quantity, presence or absent of solvent, temperature and reaction time) on yield of polyfluoroalkylchloroformates.

The maximum yield was obtained for tetrafluoropropylchloroformate (93%). The phosgenation of tetrafluoropropanol carried out in the presence of DMF (0,01 mole) without of solvent. The temperature was 95 °C, reaction time 2 hours. The attempts to use benzene and ether as solvents leads to decreasing of chloroformates yield.

The yield of polyfluoroalkyl esters of chlorocarbonic acid go down with increasing of length of perfluorocarbon chain (Table 2).

Polyfluoroalkylchloroformates are easy distilled colorless liquids, having high density, which gain with increasing of perfluorinated chain length from 1,4896 g/cm³ for CF₃CH₂OC(O)Cl till 1,7240 g/cm³ for H(CF₂)₆CH₂OC(O)Cl.

Experimental Part

Synthesis of 1,1,3- Trihydrotetrafluoropropylchloroformiate (CF₂)₂CH₂OC(O)Cl.

33.0 g (0.25 mole) of 1.1.3 trihydrotetrafluoropropanol containing 0.57 g (0.0078 mole) N,N-dimethylformamide at temperature -5 °C were loaded into reactor, 14.8 g (0.15 mole) of liquid phosgene were added. After that the reaction mass was heated up to 90°C and 14.85g (0.15 mole) of gaseous phosgene were passed through for more than 2.5 hours. Isolating hydrogen chloride and phosgene residue were removed by dry nitrogen introducing of. The product was distilled. B. p. 5°C at 32 mm Hg. Yield of 1.1.3-trihydrotetrafluoropropylchloroformiate equals 93%. n_d²⁰1.3510, d₄²⁰1.5179.

Table1. Polyfluoroalkylchloroformiates Synthesis, X(CF₂)_nCH₂OC(O)Cl

Alcohol X(CF ₂) _n CH ₂ OH			C(O)Cl ₂ mole	Catalyst, mole	Solvent	Temperature of Reaction, °C	Reacti Period,h
x	n	mole					
H	2	1	1,0	TEA 0,01	-	50	2,0
H	2	1	1,2	DMF 0,01	-	90	2,5
H	2	1	1,2	Pyridine 0,03	-	80	2,5
H	6	1	1,25	TEA 0,04	-	90	2,0
F	4	1	1,4	TEA 0,05	-	80	2,0
H	2	1	1,2	DMF 0,05	-	90	1,5
F	1	1	1,4	DMF 0,07	-	50	3,0
F	6	1	1,3	TEA 0,08	-	70	2,0
H	2	1	1,0	DMF 0,1	-	90	1,5
H	4	1	1,0	Pyridine	-	80	3,0

				0,1			
H	4	1	1,2	DMF 0,1	-	90	1,5
H	2	1	1,2	DMF 0,1	-	90	1,5
H	2	1	1,25	DMF 0,1	-	40	4,0
H	2	1	1,33	DMF 0,1	-	60	2,5
H	2	1	1,35	DMF 0,1	benzene	80	2,0
F	2	1	1,5	TEA 0,1	-	50	2,0
H	2	1	1,5	DMF 0,1	-	95	2,0
F	1	1	3,0	Pyridine 1,11	ether	4-12	3,0
H	2	1	3,0	Pyridine 1,11	ether	2-8	3,0

Table 2. Physical and Chemical Properties of polyfluoroalkyl esters of chlorocarbonic acid, $X(CF_2)_nCH_2OC(O)Cl$

#	$X(CF_2)_nCH_2OC(O)Cl$		Yield, %	Boiling Point, °C (mm Hg)	n_d^{20}	d_4^{20}
	X	n				
1	F	1	90	40 (165)	1.3210	1.4896
2	H	2	93	35 (32)	1.3510	1.5179
3	H	4	90	50 (11)	1.3376	1.6475
4	F	4	88	36 (15)	1.3182	1.6200

5	F	6	88	59 (13)	1.3188	1.7105
6	H	6	87	63 (3)	1.3338	1.7240

Conclusion

It has been stated, that out of studied catalysts of phosphogenation polyfluorinated alcohols (Triethylamine, Pyridine, DMF) the most effective is N,N-dimethylformamide allowing to obtain polyfluoroalkyl esters of chlorocarbonic acid with they of up to 93%. Mechanism of catalytic phosphogenation for polyfluorinated alcohol has been offered.

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