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The Interaction of Polyfluorinated β-diimin Perfluorocarboxylic Acids' Fluoroanhydr

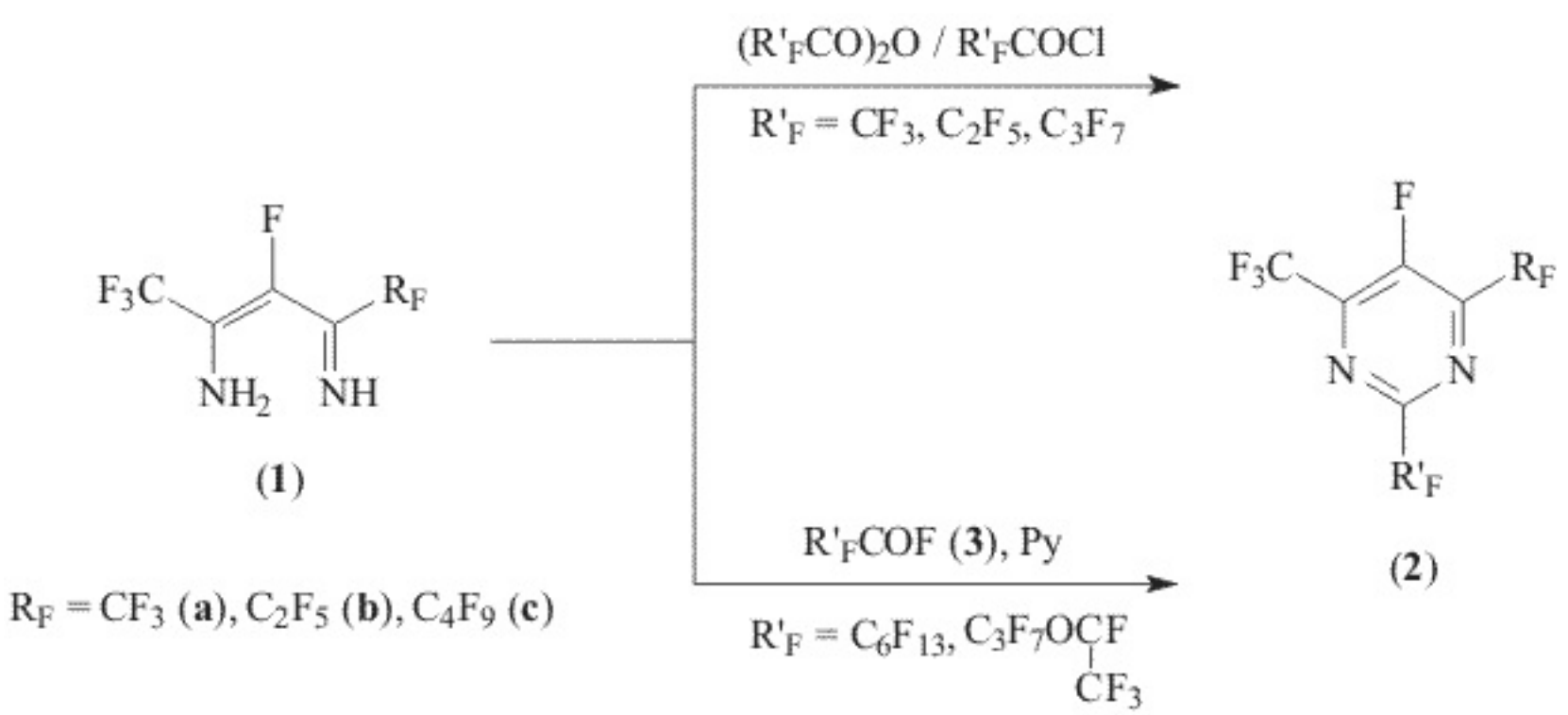
D. U. Verbitsky, * M. A. Kurikin

A.N.Nesmeyanov Institute of Organoelements Compounds RAS. 119991, Vavilova str.28, M Fax (499) 135 5085. E-mail: ***mak@ineos.ac.ru***

The tris-(perfluoroalkyl)pyrimidines synthesis methods based on the reaction of perfluorocarboxylic acids fluoroanhydrides has been developed

The condensation of polyfluorinated β-diimines (**1**) with acylhalogenides resulting in forming c [1] opens wide opportunities for synthesis of new biologically active compounds and monomers

Before [2] it was proved, that at interaction with perfluorocarboxylic acids' anhydrides and form 2,4,6-tris-(perfluoroalkyl)-5-fluoropyrimidines (**2**).



The distribution of this reaction over industrially available perfluorocarboxylic acids fluoroanh from the practical point of view.

The present work is dedicated to the topic. The β-diimines (**1**) appeared to interact wit temperature in the solution of absolute diethyl ether. However the yields of isolated required very low (~40%). Along with that the products of acidic decomposition of initial diimine (for F trifluoroacetic acid) were detected in the reaction mass.

The condensation discussed in this review is followed by the isolation of by-products - water the initial diimine (**1**) results in its destruction. This process is likely to be put into practice i reagent (anhydride, chloro- or fluoroanhydride). If condensation is being realized in a quick w then the decomposition of -diimine (**1**) will occur at an insignificant grade.

In case of fluoroanhydrides (**3**) differing from corresponding chloroanhydrides by their processes [3], the acidic decomposition of β-diimines (1) starts to compete with the main rea the condensation of diimines (**1**) and fluoroanhydrides (**3**) over acid acceptor (pyridine) the s hydrolysis of compounds (**1**) was managed to put down and pyrimidines (**2**) were isolated with

Experimental

NMR ^{19}F spectra were registered at "Bruker AC-200F" spectrometer (188,3 MHz). Chem CF_3COOH as standard, the coupling constants reported in Hz.

Perfluoro-2-hexyl-4-butyl-6-methylpyrimidine (2c, $R'_F = n\text{-}C_6F_{13}$)

1. In the absence of pyrimidine.

The solution of 7.0g (18.7 mmole) of diimine (**1c**) in 100 ml of absolute ether was put into backflow condenser and drop funnel. Afterwards during mixing (magnetic stirrer) 16.4 g (44.8 dropwise (~ 2 hours). The reaction mass was neutralized by aqueous solution of $NaHCO_3$, t flashed out with water (2X150 ml), dried over $CaCl_2$. 5.5 g (42%) (**2c**), boiling point 110-113^o distillation.

2. Over pyrimidine.

The solution of 15.5 g (41.4 mmole) of diimine (**1c**) and 12.8 g (162.0 mmole) of dried pyrim was put into two-heck flask equipped with the backflow condenser and drop funnel. Afterwards 34.7 g (94.8 mmole) n-$C_6F_{13}COF$ (~ 2 hours) were added dropwise. The reaction mass wa layer was separated, washed with the water (2X150 ml) and dried over $CaCl_2$. 19.5g (67%) (**2**

Analogously other perfluoropyrimidines were synthesized (**2**); the details of experiments as and physical constants of obtained compounds are listed in Table 1.

References

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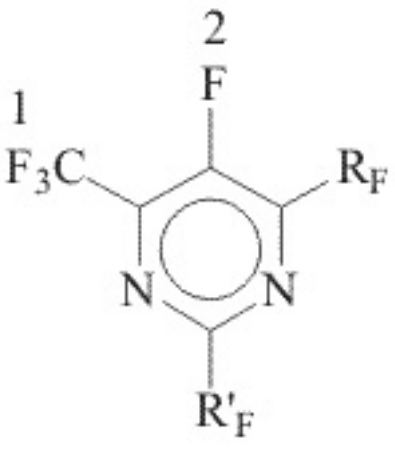

Table 1.

#	R_F	R'_F	Py	DI / R'_FCOF	BP/ ^{o}C (p mm Hg)	Yie

1	$CF_3{}^3$	$CF_3{}^7CF_2{}^8CF_2{}^9CF_2{}^{10}CF_2{}^{11}CF_2{}^{12}$	+	1 : 2.3	86 – 89 (21)	87
2	$CF_3{}^3CF_2{}^4$	—— // ——	–	1 : 2.2	93 – 96 (21)	33

#	R_F	R'_F	Py	DI / R'_FCOF	BP/ ^oC (p mm Hg)	Y
3	$CF_3{}^3CF_2{}^4CF_2{}^5CF_2{}^6$	—— // ——	–	1 : 2.4	110 – 113 (22)	4

4	$CF_3^3CF_2^4$	—— // ——	+	1 : 2.3	95 – 97 (21)	7
5	$CF_3^3CF_2^4CF_2^5CF_2^6$	—— // ——	+	1 : 2.3	110 – 113 (22)	6
6	CF_3^3	$CF_3^{13}CF_2^{14}CF_2^{15}OCF^{16}(CF_3^{17})$	+	1 : 2.4	61 – 64 (21)	5