THE ACYLATION-DEHYDRATION OF N'-(PERFLUOROACYLIMIDOYL)PERFLUOROALKYLAMIDINES BY CARBOXYLIC AND POLYFLUORO- AND PERFLUOROCARBOXYLIC ACID ANHYDRIDES

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UDC 542.951.1:547.298.5'161

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The properties of polyperfluorofluorotriazines, namely, their molecular weights, molecular weight distributions, thermal and chemical stabilities, depend on the completeness of the acylation-dehydration of N'-(perfluoroacylimidoyl)perfluoroalkylamidines (imidoylamidines). In order to explain the mechanism of the cyclization of imidoylamidines into triazines, it was interesting to follow the change in reactivity of imidoylamidines and carboxylic and polyfluoro- and perfluorocarboxylic acid anhydrides in relation to their structures. For the study, imidoylamidines were taken which were models for the monomer units of polyperfluoroalkenes and polyperfluorooxaalkylenimidoylamidines. Acid anhydrides whose polar and steric

 $\begin{array}{cccc} \mathbf{R_{f}-C-N=C-R_{f},} & \text{where } \mathbf{R_{f}=CF_{2}CF_{2}CF_{3}} \text{ (I) and } CFOCF_{2}CF_{2}CF_{3} \text{ (II),} \\ & \parallel & \parallel \\ & \mathbf{NH} & \mathbf{NH_{2}} & & \mathbf{CF_{3}} \end{array}$

substituent constants differed significantly were taken for the cyclization (Table 1).

Imidoylamidines (I) and (II) were subjected to acylation-cyclodehydration by an equimolar mixture of two anhydrides; the molar ratio of the imidoylamidine to the anhydride mixture was 1:6. The reaction was performed with stirring in a sealed, thermostated volume at 20°C. The imidoylamidine was introduced rapidly to the anhydride mixture. The increase in temperature upon stirring of the reagents was $\leq 0.5^{\circ}$.

The IR and NMR spectra showed that the imidoylamidine had completely entered the reaction over 1 h. Triazines, acids, and unreacted anhydrides were present in the reaction mixture (Figs. 1 and 2). The reaction mixture was analyzed by NMR spectroscopy after mixing of the reagents and maintaining for 3 h at a thermostated temperature. The fluorine content in the mixture was calculated from the integrated intensity of the triazine fluorine atom signals (Table 2).

Acetic anhydride and difluoroacetic anhydride do not react with imidoylamidines (I) and (II) under ordinary conditions; the system was heterogeneous. However, as soon as a few drops of CF_3CO_2H were added to the mixture, homogenization took place and the acylation-cyclodehydration reaction proceeded very rapidly. Triazines with methyl and trifluoro-methyl substituents were detected by NMR. Apparently, CF_3CO_2H interacts with acetic anhydride,

60 60 100 1600 1800 2000 3000 3000 3400 y, cm⁻¹

Fig. 1. IR spectrum of the cyclization products of imidoylamidine $C_3F_7C-N=CC_3F_7$ by a mixture of $\| \|$ NH NH_2

anhydrides $(CF_3CO)_2O$ and $(CHF_2CO)_2O$.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 580-585, March, 1979. Original article submitted October 3, 1977.

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TABLE 1. Polar and Steric Constants of R Substituents in Acid Anhydrides (RCO)₂O

R in anhydride	σI	Lit. ref.	Es	Lit. ref.	
CH ₃ CF ₂ H CF ₃ CF ₃ CF ₂ CF ₂ CF ₃ OCF ₂ CF ₂	-0,05 0,32 0,41 0,42 0,41	[1] [1] [1] *	0 -0,67 -1,16 -5,4 -4,5	[2] [2] [2] †	

*Determined from the refined equation for the polar constant σ_{I} as a function of the chemical shift δH_2 for substituted α -oxides: $\sigma_{I} = 0.791\delta H_2 -$ 2.371 [3].

+Determined in our earlier work [4] from the equation for the steric constant E_S as a function of the flexibility parameter of polyethers of the type $(CH_2CHR_fO)_n$, $E_S = 3.4 - 2.0\sigma$.







forming a mixed anydride which acylates the starting imidoylamidine:

 $(MeCO)_2O + CF_3COOH \rightarrow CF_3COOCOMe + MeCOOH$

TABLE 2. Results of the Competing Acylation-Cyclodehydration of Imidoylamidines (I) and (II) by Carboxylic Acid Anhydrides

				Ν		Ν	
R _f C—N NH	=CR _f + $ $ NH ₂	2(R′CO) ₂ O 2(R _f ′CO) ₂ O	3R'COOH 3Rf 'COOH		$CR_{f} + \frac{\ }{N}$		CRr II N (5)

			Content of triazines in mixture, ^{of,}			
Run No.	R'	Rf	$\begin{array}{l} \text{series} \text{I}, \\ \text{R}_{\text{f}} = \text{C}_3\text{F}_7 \end{array}$		series II, $R_f = CF(CF_2)OC_3F_7$	
			(A)	(B)	(A)	(B)
1234567890	CH_{3} CH_{3} CH_{3} CH_{5} CHF_{2} CHF_{2} CHF_{2} CHF_{2} CHF_{3} CHF_{3}	$\begin{array}{c} CF_{3} \\ C_{3}F_{7} \\ C_{2}F_{4}OCF_{3} \\ CF(CF_{3})OC_{3}F_{7} \\ CF_{3} \\ C_{3}F_{7} \\ C_{2}F_{4}OCF_{3} \\ CF(CF_{3})OC_{3}F_{7} \\ CF_{7} \\$	10 9 44 36 55 50 68 65	90 91 56 64 45 50 32 35	10 8 10 	90 92 90 .65 44 50 - 36
10 11 12	CF_3 CF_3 C_3F_7	$C_2F_4OCF_3$ $CF(CF_3)OC_3F_7$ $C_2F_4OCF_3$ $CECF_4OCF_3$	84 46	50 16 54	82 46	50 18 54
15 14	$C_2F_4OCF_3$	$ CF(CF_3)OC_3F_7 $	67	55 33		_

Transacylation reactions are known for ordinary anhydrides and acids [5]. CF_3CO_2H and $(CF_3OC_2F_4CO)_2O$ were taken as starting compounds for their proof in the case of perfluorinated analogs. Three separate signals were seen in the NMR spectrum of perfluoromethoxypropionic acid anhydride: 55 (OCF_3), 87.3 (OCF_2), and 120.9 (CF_2) ppm relative to CFCl_3. Upon mixing of the anhydride and acid, all the signals belonging to the original anhydride are split, which is characteristic for a mixture of the anhydride and the corresponding acid. Methoxypropionic acid appears in this system; the presence of this compound is clearly indicated by the increase in the corresponding signals in the NMR spectrum upon its introduction into the mixture. The NMR spectrum of CF_3CO_2H has a single signal, while there is yet another signal in this system which belongs to the CF_3CO group of the mixed anhydride (Fig. 3).

The formation of the mixed anhydride cannot significantly affect the results of the competing acylation-dehydration because the anhydride formed is equivalent to a mixture of the initial anhydrides in terms of concentrations and direction of the process, though the reaction rate constants may differ somewhat.

The data in Table 2 were plotted in terms of the equation: $\log k/k_0 - bE_S = a\sigma_I + c$, where k/k_0 is the relative rate of acylation-cyclodehydration which is equal to the ratio of the yield of the given triazine to the yield of the triazine taken as the standard (in our case, triazines with the trifluoromethyl group served as the standard); E_S and σ_I are the Taft steric and inductive constants of the R group in the acylating anhydride; and a, b, and c are coefficients. The coefficients a and b characterize the sensitivity of the transition state towards polar and steric effects of the R group in the anhydride-imidoylamidine system. They indicate that the structure of the R' and Rf' groups in the acid anhydrides significantly affects the yield of triazines. Both polar and steric effects of these substituents are clearly seen. Runs 1, 5, 9, and 10 in Table 2 in both series permit establishment of the quantitative effects of these factors.

Least-squares treatment of the experimental results indicates a clear linear relationship of the reactivity of these anhydrides to the polar and steric constants of the R' and R_f ' substituents (Fig. 4). In analytical form, they may be given as the equations

$\lg k/k_0 = 2.31\sigma_I + 0.081E_s - 0.86$ (series I) *

^{*}The correlation coefficient is 0.995 with 95% confidence; the mean-square error does not exceed 10%.



Fig. 3. The ¹⁹F NMR spectrum of the mixture of $(CF_3OCF_2CF_2-CO)_2O + CF_3CO_2H$.



Fig. 4. Dependence of the relative rate of acylation-cyclodehydration of imidoylamidines (I) and (II) $R_f C - N = CR_f$, where $R_f = C_3 H_7$ (I) and $C_3 F_7 -$ $\| M + NH_2$

 $OCF(CF_3)$ (II) on the inductive and steric effects of the substituents in the acylating reagent (see equation in text).

 $\lg k/k_0 = 2.29\sigma_I + 0.075E_s - 0.86$ (series II) *

An increase in the electronegativity of the R group leads to an increase in the rate of acylation. This indicates that the transition state is favored by the appearance of an additional positive charge at the reaction center of the anhydride in the rate-limiting step of the process. The structure of the imidoylamidine has only a slight effect on the rate of acylation: the values of the coefficients which determine the sensitivity of the transition state towards polar and steric effects of the substituents hardly vary.

Hence, the acylation-cyclodehydration of imidoylamidines by perfluorocarboxylic acid anhydrides may be represented by the scheme

^{*}The correlation coefficient is 0.993 for the 95% confidence level; the mean-square error does not exceed 10%.



The rate-limiting step of the reaction is apparently step 1. Steps 2 and 4 cannot be rate-limiting because an increase in the electronegativity of the R_{f} ' group for them should have led to a decrease in the relative rate of acylation, which is opposite to the experimental findings. The rates of steps 3 and 4 (cyclodehydration) should be especially great as a consequence of the formation of the energetically favorable triazine ring.

EXPERIMENTAL

The IR spectra were recorded on a UR-10 spectrometer and the NMR spectra were taken on an RS-56 M spectrometer (Special Design Shop, Institute of Organic Chemistry, Academy of Sciences of the USSR) with $CFCl_3$ as an external standard.

The imidoylamidines were synthesized from the corresponding nitriles and amidines of perfluorocarboxylic acids according to Brown and Schuman [6]. N'-(Perfluorobutyroimidoyl)-perfluoropropylamidine (I), bp 40-41°C (2 mm Hg). Found: C 23.62; H 0.75; F 65.36; N 10.30%. Calculated for $C_8H_3F_{14}N_3$: C 23.59; H 0.73; F 65.69; N 10.32%. N'-(Perfluoro- α -propoxy-propioimidoyl)perfluoro- α -propoxyethylamidine (II), bp 70°C (3 mm Hg). Found: C 22.54; H 0.38; F 65.51; N 6.73%. Calculated for $C_{12}H_3F_{22}N_3O_2$: C 22.53; H 0.47; F 65.41; N 6.5%.

The anhydrides of the carboxylic, fluorocarboxylic, and perfluorocarboxylic acids were synthesized from the corresponding acids by heating with P_2O_5 and had the following boiling points: Ac₂O 140°C [7], (CHF₂CO)₂O 125-127°C, (CF₃CO)₂O 39.5-40.5°C [8], (C₃H₇CO)₂O 106-107.5°C [9], (CF₃OC₂F₄CO)₂O 112°C, and (C₃F₇CF(CF₃)OCO)₂O 152°C.

CONCLUSIONS

1. The reactivities of a series of anhydrides of alkane, fluoroalkane, and perfluoroalkane carboxylic acids were determined using the method of competing acylation-cyclodehydration and the cyclization process was shown to be subject to polar and steric effects of the groups at the reaction centers of the anhydrides.

2. Carboxylic acid anhydrides react with perfluorocarboxylic acids with the formation of the mixed anhydride and the corresponding carboxylic acid.

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