PERFLUORO-BIS-1, 3, 4 OXADIAZOLES

(UDC 542.91 + 547.7 + 546.16)

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Continuing work on the synthesis of derivatives of perfluorocarboxylic acids [1], we produced hydrazides of perfluoroglutaric, perfluoroadipic, perfluorosebacic, and perfluorododecamethylenedicarboxylic acids by the action of hydrazine hydrate on the diethyl esters of the acids in alcohol solution.

C₂H₅OCO (CF₂)_nCOOC₂H₅ $\xrightarrow{\text{NH}_2\text{NH}_2}$ NH₂NHCO (CF₂)_nCONHNH₂ n=3, 4, 8, 12 n=3, 4, 8, 12

In the acylation of the hydrazides of perfluorodicarboxylic acids with perfluorobutyryl chloride or perfluorobutyric anhydride, we obtained the corresponding N,N'-perfluorobutyryl hydrazides of dicarboxylic acids.

 $\begin{array}{c|c} \text{NH}_{2}\text{NHC} (\text{CF}_{2})_{n}\text{CNHNH}_{2} \xrightarrow{\text{ClCOC}_{3}F_{7}}{(\text{C}_{2}\text{H}_{3})_{3}\text{N}} \xrightarrow{\text{C}_{3}\text{F}_{7}\text{CNHNHC} (\text{CF}_{2})_{n}\text{CNHNHCC}_{3}\text{F}_{7}} \\ \parallel & \parallel & \parallel & \parallel \\ \text{O} & \text{O} & \text{O} & \text{O} \\ n=3, 4, 8 & n=3, 4, 8 \end{array}$

The hydrazide of perfluoroglutaric acid was acylated at room temperature. For the acylation of hydrazides of perfluoroadipic and perfluorosebacic acids by perfluorobutyryl chloride, heating in dioxane solution for two and four hours, respectively, was required. N,N'-Perfluorobutyryl hydrazides of perfluoroadipic and perfluorosebacic acids are formed under rather mild conditions in the reaction of the dichlorides of these acids with perfluorobutyryl hydrazide

CICO (CF₂)_n COC1
$$\xrightarrow{\text{H}_2\text{NHNCOC}_3\text{F}_7}_{\text{CHCl}_3, \sim 50^\circ} \rightarrow \text{C}_3\text{F}_7\text{CONHNHCO} (\text{CF}_2)_n\text{CONHNHCOC}_3\text{F}_7$$

 $n=4, 8$ $n=4, 8$

Acylation of the hydrazides of perfluorodicarboxylic acids by chlorides of perfluorinated carboxylic acids proceeds at room temperature; in the acylation we obtained N,N'-butyryl and N,N'-benzoyl hydrazides of perfluorodicarboxylic acids. The perfluoroacyl derivatives of hydrazides of perfluorodicarboxylic acids which we obtained were converted to corresponding bis-1,3,4-oxadiazoles by heating with P_2O_5 [2, 3]. In the case of 10-hour heating of N,N'-perfluorobutyryl hydrazides of perfluoroglutaric, perfluoroadipic, and perfluorosebacic acids with excess P_2O_5 at a temperature of 250-300°, a cyclodehydration of the latter occurred, with the formation of 2,2', perfluoropropyl-5,5'polydifluoromethylene-bis-1,3,4-oxadiazoles.



				0	Ö		0		Ö				
•		R	Wield the	В. р.,		Fou	nd , %		Calculated,%				
	п		rieu, w	°C	C	Н	F	N	C	H	F	Ν	
	3	CoF-	90	182-183	23,91	0,61	57,64	8,26	23,63	0,606	57,57	8,18	
	3.	C_3H_7 C_6H_5	75 88	144—146 177—178	38,30 47,90	4,43 3,08	28,02 23,98	$13,70 \\ 11,76$	38,23 47,87	4,41 2,91	27,94 23,95	$ \begin{array}{c} 13,72 \\ 11,76 \end{array} $	
	4 4	C_3F_7 C_3H_7	89 66	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	23,84	0,72 3,92	58,86 33,14	8,00 12,16	23,66	0,56 3,93	58,87 33,18	7,88 12,22	
	8 8	C_3F_7 C_3H_7	72 82	198-202 206-208	23,93 32,66	0,39 2,81	62,58 46,30	$6,18 \\ 8,58$	23,74 32,82	0,44	$ \begin{array}{r} 62,63 \\ 46,20 \end{array} $	6,15 8,51	
	12	C_6H_5	80	220-223	36,33	1,74	49,83	6,21	36,28	1,51	49,24	6,04	

 $\begin{array}{c} \mathbf{R} - \mathbf{C} - \mathbf{N} \mathbf{H} \mathbf{N} \mathbf{H} - \mathbf{C} - (\mathbf{C} \mathbf{F}_2)_n - \mathbf{C} - \mathbf{N} \mathbf{H} \mathbf{N} \mathbf{H} - \mathbf{C} - \mathbf{R} \\ \parallel & \parallel & \parallel \\ \mathbf{O} & \mathbf{O} & \mathbf{O} & \mathbf{O} \end{array}$

TABLE 2



										· · · · · · · · · · · · · · · · · · ·	Name and Address of the Owner, which the Owner, which the	
20	R	Yield, %	в. р., °С	F	Found,	%		Calculated, %				
16				С	Ĥ	F	Ν	С	H	F	N	
3 3 4	$\begin{vmatrix} C_3 F_7 \\ C_6 H_5 \\ C_3 F_7 \end{vmatrix}$	68 60 81	35-37 95-97 51-52	25,02 51,54 24,73	0,07 2,35	60,85 26,30 61,74	9,11 12,92 8,34	25,00 51,81 24,92	2,27	60,89 25,90 62,017	8,97 12,72 8,31	
4 8 8	C_3H_7 C_3F_7 C_3H_7	82 60 80	75-77 42-43 76-78	39,78 24,64 34,70	3,36	36,20 65,32 49,20	$ \begin{bmatrix} 13, 12 \\ 6, 55 \\ 9, 00 \end{bmatrix} $	39,81 24,71 34,72	2,25	65,21 48,87	13,27 6,40 9,00	

The bis-oxadiazoles formed were distilled under vacuum and purified by recrystallization. They represented low-melting crystalline substances, investigation of the IR spectra of which indicated the presence of absorption bands characteristic of the 1,3,4-oxadiazole ring [4]. Cyclodehydration of N,N'-acylhydrazides of perfluorodi-carboxylic acids, with the formation of 2,2'-alkyl-5,5'-polydifluoromethylene-bis-1,3,4-oxadiazoles was carried out by boiling with POCl₃.



EXPERIMENTAL

Hydrazides of Perfluorodicarboxylic Acids. To a solution of 0.03 mole of the diethyl ester of the perfluorodicarboxylic acid in 25 ml of abs. alcohol, we added with mixing 0.06 mole of hydrazine hydrate. The reaction mixture was mixed for 1-1.5 h at room temperature. We obtained: 1) hydrazide of perfluoroglutaric acid with m. p. 168-169°, yield 85%. Found: C 22.22; H 2.21; F 42.43; N 21.16%. $C_5H_6O_2F_6N_4$. Calculated: C 22.34; H 2.23; F 42.54; N 20.80%. 2) Hydrazide of perfluoroadipic acid with m. p. 188-189° (in alcohol). Found: C 22.82; H 1.67; F 47.64; N 17.21%. $C_2H_6O_2F_8N_4$. Calculated: C 22.61; H 1.88; F 47.71; N 17.61%. 3) Hydrazide of perfluorosebacic acid with m. p. 202-204° (from alcohol). Found: C 22.87; H 1.28; F 58.56; N 10.68%. $C_{10}H_6O_2F_{16}N_4$. Calculated: C 23.16; H 1.15; F 58.68; N 10.81%. 4) Hydrazide of perfluoroddecamethylenedicarboxylic acid with m. p. 282-285° Found: C 23.20; H 0.80; F 63.35; N 8.03%. $C_{14}H_6O_2F_2AN_4$. Calculated: C 23.39; H 0.83; F 63.64; N 7.79%.

N,N'-Acylhydrazides of Perfluorodicarboxylic Acids. The hydrazide of the perfluorodicarboxylic acid (0.03 mole) was dissolved in 70 ml of dioxane, 0.06 mole of triethylamine was added, and then a solution of 0.06 mole of RCOClin 10 ml of dioxane. The reaction mixture was mixed at room temperature for 2-4 h or while heating on a boiling water bath from one to four hours (in the case of the reaction with $C_{3}F_{7}COCl$). After treatment of the reaction mixture with water and, when necessary, extraction with ether, N,N'-acylhydrazides of perfluorodicarboxylic acid were obtained and were crystallized from aqueous alcohol (Table 1).

2,2'-Perfluoropropyl-5,5'-polydifluoromethylene-bis-1,3,4-oxadiazoles. A mixture of 0.01 mole of the N,N'-perfluorobutyryl hydrazide of the perfluorodicarboxylic acid and 0.1-0.15 mole of P₂O₅ was heated in a round-bottomed flask with reflux condenser on a bath of Wood's metal at a temperature of 300° for 10 h. Then, at the same temperature, the reaction products were distilled off under vacuum (10 mm). The liquid or slightly cry-stallizing substances collected in the receiver were subjected to further purification by repeated distillation and cry-stallization from alcohol and benzene; yield of the oxadiazoles from 60 to 80%.

2,2' - Alkyl - 5,5' - polydifluoromethylene-bis - 1,3,4 - oxadiazoles. The N,N'-alkylhydrazide of the perfluorodicarboxylic acid (0.01 mole) was dissolved in 50 ml of POCl₃, and the solution was boiled with a reflux condenser for 10 h. Most of the POCl₃ was distilled off; the remainder was treated with water and extracted with ether. Bis-1,3,4-oxadiazoles were isolated from the ether solution and purified by recrystallization (Table 2).

CONCLUSIONS

1. The hydrazides of perfluorodicarboxylic acids of the general formula $NH_2NHCO(CF_2)_nCONHNH_2$ (n = 3,4, 8, 12) were produced by the action of hydrazine hydrate on the diethyl esters of the perfluorodicarboxylic acids in alcohol solutions.

2. Acylation of hydrazides of perfluorodicarboxylic acids by chlorides of carboxylic and perfluorocarboxylic acids produced N,N'-acyl derivatives of the hydrazides RCONHNHCO(CF₂)_nCONHNHCOR (n = 3,4,8, R = C₃F₇, C₃H₇; n = 3, 12, R = C₆H₅).

3. Cyclodehydration of the N,N'-perfluoroacyl hydrazides of perfluorodicarboxylic acids with phosphoric anhydride at 300° yielded 2,2'-perfluoroalkyl-5,5'-polydifluoromethylene-bis-1,3,4-oxadiazoles.

4. 2, 2' - Alkyl- 5, 5' - polydifluoromethylene-bis-1, 3, 4-oxadiazoles were produced by heating the N, N' - acyl hydrazides of perfluorodicarboxylic acids with POCl₃.

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