pound was obtained from 51.0 g (0.25 mole) of VIb, 23 ml of $POCl_3$, and 92 ml (1.0 mole) of aniline by a procedure similar to that used to prepare XVIb. The yield was 25 g.

1-(4-Methoxyphenyl)-3-methyldihydrouracil (XVIIIa). A) An 11.4-ml (0.12 mole) sample of dimethyl sulfate was added with stirring to a mixture of 10.3 g (0.05 mole) of VIa, 50 ml of 10% NaOH, and 150 ml of dioxane, and the mixture was stirred at 20-25°C for 30 min. It was then allowed to stand at 20°C for 6 h, after which the liquid fractions were removed by distillation, the residue was treated with water, and the mixture was filtered to give 9.4 g of XVIIIa.

B) A 7.8-ml (0.125 mole) sample of methyl iodide was added to a mixture of 5.15 g (0.025 mole) of dihydrouracil VIa and 6.0 g of powdered KOH in 50 ml of DMF at such a rate that the temperature of the reaction mixture did not exceed 40°C, after which the mixture was stirred for 2 h, and the product was isolated as in method A. The yield was 4.5 g.

1-(4-Methoxyphenyl)-3,5-dimethyldihydrouracil (XVIIIb) and 1-(4-Methoxyphenyl)-3,6-dimethyldihydrouracil (XVIIIc). These compounds were obtained from VIb,c by method A for the synthesis of XVIIIa.

1-(4-Ethoxyphenyl)-3-ethyl-5-methyldihydrouracil (XIXb) and 1-(4-Ethoxyphenyl)-3-ethyl-6-methyldihydrouracil (XIXc). These compounds were obtained from VIb,c and ethyl iodide by a procedure similar to that used to prepare XVIIIa.

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SYNTHESIS AND REACTIONS OF 2-CHLOROHEXAFLUOROCYCLOPENTENE- AND 2-CHLOROOCTAFLUOROCYCLOHEXENE-1-CARBONITRILES

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UDC 547.514.7'539.16.18'859.1.07:543.422

2-Chlorohexafluorocyclopentene- and 2-chlorooctafluorocyclohexene-1-carbonitriles were synthesized. Products of substitution of the chlorine atoms by a phenylamino group and the fluorine atoms in the α position by a phenylimino group were obtained by reaction of the products with aniline. The reactions with amidines of trifluoro- and trichloroacetic acids, as well as with 2-aminopyridine, lead to pyrimidine derivatives with condensed perfluorinated five- and six-membered rings.

We have previously developed a general method for the preparation of perfluoroalkyl-substituted 1-cyano-2-chloroethylenes, studied their reactions with nucleophilic reagents, and demonstrated that these compounds have high reactivities and are convenient reagents for the preparation of various heterocyclic compounds [1-4]. In the present paper we describe the synthesis of 2-chlorohexafluorocyclopentene- and 2-chlorooctafluorocyclohexene-1-carbonitriles IIa,b that contain a 1-cyano-2-chloroethylene fragment included in a perfluorinated ring.

For the preparation of nitriles IIa,b, 1,2-dichlorohexafluorocyclopentene and 1,2-dichlorooctafluorocyclohexene were converted to the corresponding carboxylic acids by the action of butyllithium and carbon dioxide gas [5]. The indicated cyano compounds were synthesized

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252600. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1407-1409, October, 1982. Original article submitted December 28, 1981.

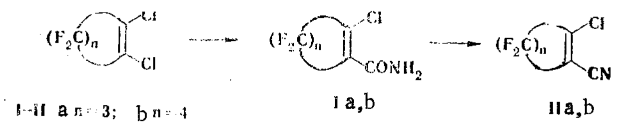
0009-3122/82/1810-1095$07.50

TABLE 1. Characteristics of the Synthesized Compounds

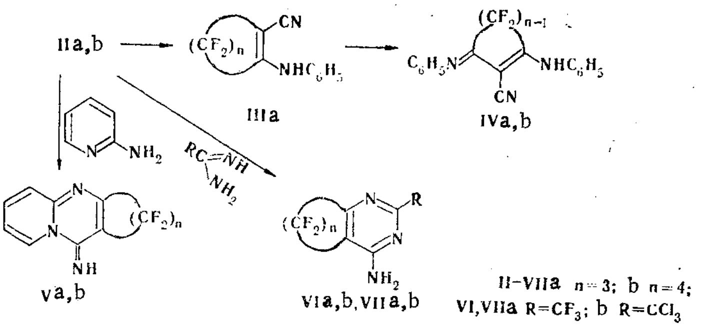
Compound	mp, °C	IR spectrum, cm^{-1}				Found, %				Empirical formula	Calc., %				Yield, %
		C≡N	C=C	C=N	N—H	C	H	F	N		C	H	F	N	
IIIa	177—118	2235	1598	1648	3098, 3160, 3205, 3243, 3270	49,3	2,1	39,5		$C_{12}H_6F_6N_2$	49,3	2,1	39,0		86
IVb	185—187	2230	1590	1660	3070, 3140, 3250	57,9	2,7	28,7		$C_{19}H_{11}F_6N_3$	57,7	2,8	28,9		83
IVa	172—173	2225	1607	1658	3025, 3130, 3180, 3205	62,5	3,1	22,3		$C_{18}H_{11}F_4N_3$	62,6	3,2	22,0		98
Va	182—184			1660	3076, 3150, 3310	45,1	1,6		14,3	$C_{11}H_5F_6N_3$	45,1	1,7		14,3	52
Vb	142—143			1650	3050, 3070, 3120, 3395	41,7	1,5		12,1	$C_{12}H_5F_8N_3$	42,0	1,5		12,2	83
VIa	106—107			1670	3230, 3290, 3360, 3400, 3505	30,6	0,8		13,6	$C_8H_2F_9N_3$	30,9	0,6		13,5	76
VIb	128			1650	3180, 3235, 3320, 3510	26,8	0,5		11,8	$C_8H_2Cl_3F_6N_3$	26,6	0,6		11,7	81
VIIa	94—95			1660	3220, 3240, 3280, 3355, 3485, 3520	29,7	0,6		11,6	$C_9H_2F_{11}N_3$	29,9	0,6		11,6	90
VIIb	106			1630	3195, 3220, 3253, 3350, 3470, 3510	26,5	0,4		10,5	$C_9H_2Cl_3F_8N_3$	26,3	0,5		10,2	84

from the latter by the usual method [6, 7].

Since an attempt at direct replacement of the chlorine atom by a cyano group in 1,2-dichlorohexafluorocyclopentene was unsuccessful [8], we selected the following synthetic scheme:



Compound IIa reacts readily with aniline to give amine IIIa. A product of replacement of the α-fluorine atoms by a phenylimino group (IVa) was isolated upon further heating with aniline in benzene. In the case of six-membered IIb the reaction takes place immediately at the chlorine and fluorine atoms to give IVb. 2-Aminopyridine reacts with nitriles IIa,b to give pyrimidines Va,b. The reaction evidently proceeds through a step involving the formation of an intermediate similar to IIIa.



The IR spectra of III and IV contain vibrations at 3140-3270 (NH) and 2225-2235 cm^{-1} (CN), as well as frequencies of C=N bonds at 1650-1660 cm^{-1}. Vibrations at 3320-3400 (NH) and 1635-1640 cm^{-1} (C=N) are observed in the IR spectra of pyrimidines Va,b.

4-Aminopyrimidine derivatives condensed with a perfluorinated five-membered or six-membered ring (VI, VII) were obtained in the reaction of nitriles IIa,b with amidines of trifluoro- and trichloroacetic acids.

According to the IR spectral data, VI and VII exist in the form of amino compounds rather than in the form of tautomeric imino forms.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer.

2-Chlorohexafluoro-1-cyclopentene-1-carboxamine (Ia). A solution of 6.15 g (22.5 mmole) of 1-chloro-2-chloroformylhexafluoro-1-cyclopentene [6] in 40 ml of anhydrous ether was cooled to −70°C and the calculated amount of ammonia was passed through the mixture with stirring. The precipitate was removed by filtration, and the filtrate was evaporated *in vacuo* with a water aspirator to give 3.6 g (63%) of a product with mp 117°C (from CH_2Cl_2) (mp 116-118°C [8]).

2-Chlorooctafluoro-1-cyclohexene-1-carboxamide (Ib). This compound was similarly obtained at 0°C in 88% yield and had mp 125°C (from CH_2Cl_2). Found: N 4.6%. $C_7H_2ClF_8NO$. Calculated: N 4.6%.

2-Chlorohexafluorocyclopentene-1-carbonitrile (IIa). This compound was obtained from 1.4 g (5.5 mmole) of amide Ia and 5 g (0.035 mole) of phosphoric anhydride. Workup gave 1.1 g (85%) of a product with bp 107°C. Found: C 30.6%. C_6ClF_6N. Calculated: C 30.6%.

2-Chlorooctafluorocyclohexene-1-carbonitrile (IIb). This compound was similarly obtained from 3.35 g (0.011 mole) of amide Ib and 10 g (0.07 mole) of phosphorus pentoxide. Workup gave 2.84 g (90%) of a product with bp 124.5-125°C. Found: Cl 12.1%. C_7ClF_8N. Calculated: Cl 12.4%.

General Method for the Preparation of IIIa, IVb, and Va,b-VIIa,b. A 0.005-mole sample of IIa,b was added dropwise with stirring to a solution of 0.01 mole of aniline (2-aminopyridine or the corresponding amidine) in 15 ml of diethyl ether, after which the mixture was stirred for 1 h. The precipitated hydrochloride was removed by filtration, and the ether was removed by distillation *in vacuo* with a water aspirator. Compounds IIIa, IVb, and Vb were purified by recrystallization from heptane, IVa and Va were recrystallized from heptane–benzene, and pyrimidines VIa,b and VIIa,b were purified by sublimation. The yields, melting points, results of analysis, and data from the IR spectra are presented in Table 1.

2-Anilino-6-phenylaminotetrafluorocyclopentene-1-carbonitrile (IVa). A 0.4-g (1.4 mmole) sample of IIIa and 0.25 g (2.8 mmole) of aniline were refluxed in 10 ml of benzene for 1 h, after which the precipitate was removed by filtration, and the benzene was removed by distillation to give 0.46 g (98%) of IVa.

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