

Interactions of asymmetric perfluorosubstituted β -diketones and carbamoyl amines.

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A cyclocondensation reaction of asymmetric perfluoro-substituted β -diketones with derivatives of guanidine and urea has been investigated. There have been determined conditions of the formation of functional derivatives of 6-perfluoro-substituted 1,3-diazines.

Organofluoric compounds are used for producing thermally and chemically stable polymers, medicines, pesticides, high-resistant dyes, refrigerants and heat carriers, lubricants and other important products. The creation of heterocycles whose side chain contains inert perfluorosubstituents with a large number of units is of a practical interest. This is caused by a well-known fact, that the series of perfluorocontaining carbon-chain and heterochain compounds (for example, perfluorocarbonic acids) possess pronounced surface-active properties enhanced with the growth of the alkyl chain length.

One of the widely used synthesis methods for pyrimidine derivatives is condensation of 1,3-diketones (or their analogues) with different derivatives of guanidine and urea. The range of compounds produced in such a way is extremely wide [1-3, 4-11]. Thus, condensation of guanidinium hydrochloride with acetylacetone at heating in a water-alcohol solution of sodium hydrocarbonate results in the formation of 2-amino-4-dimethylpyrimidine; 2-amino-4,5,6-trimethylpyrimidine is formed in sodium ethylate; 2-amino-4,6-dimethyl-5-phenylazopyrimidine is formed in an alcohol solution of sodium hydroxide guanidine nitrate with 3-phenylhydroazonoacetylacetone [3-5]. T.Nishivaki et al. [4,5] noted that melting guanidine carbonate with derivatives of 3,3,3-trifluoroacetylacetone [4] and its nonfluorinated analogue [5] at 140-150°C for 1 hour results in the formation of appropriate 4-substituted 2-aminopyrimidines (79-90%).

Another example [6] of synthesis of 6-trifluoromethyl derivatives and 6-heptafluoropropyl derivative of 4-alkylpyrimidine (Alk = C1-C5) may be ethylguanidine cyclization with corresponding 1,3-ketones in a mixture of ether and alcohol at room temperature for 14 hours (24.7-62.8%). Kreutzerberg et al. [10] also conducted condensation of 4-tolylguanidine with fluorine containing β -diketones in the presence of sodium carbonate (90-115°C, 8-12 hours) resulting in derivatives of 6-alkyl-4-trifluoromethyl-2-(4-toluidino)pyrimidine (Alk = C1-C5), yields reached 49-69%. In 1993 the same authors [11] synthesized a number of derivatives of 2-[N-(2-hydroxyethyl)methylamino]-4-trifluoromethylpyrimidine possessing physiological activity by a reaction of sulfate of N-(2-hydroxyethyl)-N-methylguanidine with various β -diketones with trifluoromethyl substituent in a water-alcohol solution of sodium bicarbonate.

Sareen et al. [12] reported on the synthesis of fluoro-substituted pyrimidines, in particularly on the condensation of asymmetric perfluoro-substituted 1,3-diketones ($R_F = CF_3, C_2F_5, C_3F_7$) with guanidinium carbonate at boiling in absolute alcohol with addition of catalytic amounts of hydrochloric acid during 10-14 hours, as a result 6-alkyl(perfluoroalkyl)-4-arylpyrimidines are formed in high yields (73-82%). Interaction of the mentioned 1,3-diketones with pentafluorophenylhydrazine under the same conditions leads to the formation of appropriate 5-perfluoroalkyl-3-fluoroaryl-1-pentafluoroarylpyrazoles (70-80%).

There are data [13] on the synthesis method to produce mono- and difluoromethyl- and *p*-fluoroaryl-substituted 2-aminopyrimidines by condensation of aminoguanidine derivatives with different fluorine containing β -diketones in the presence of sodium in an alcohol solution at heating for 12 hours (54-82%).

Interaction of urea, its methyl-N,N'-dimethyl derivative and also thiocarbamide with pentane-2,4-dione and its trifluoromethyl analogues in the presence of hydrochloric acid results in the formation of appropriate derivatives of 2-hydroxy- and 2-mercaptopyrimidines [14]. Condensation of benzylthiocarbamide with a number of asymmetric β -diketones containing trifluoromethyl and heptafluoropropyl groups at heating (aqueous K_2CO_3 , ethanol, ether, 96 hours) led to the formation of appropriate perfluoroalkyl-2-benzylthiopyrimidines (31-53%) with the exception of 2-benzylthio-4,6-di(trifluoromethyl)pyrimidine whose yield was 0.3% [7].

Koukhar' et al. [15] have shown that β -alkoxyvinyltrifluoromethylketones are suitable reagents for the synthesis of 4-trifluoromethylpyrimidines unsubstituted in 5 and 6 positions. The interaction of β -ethoxyvinyltrifluoromethylketone with ammonium chloride in formamide (160°C, 2 hours) leads to the formation of 4-trifluoromethylpyrimidine (23%). A treatment of organofluoric substrate with *gemdiamino* compounds allows to obtain 4-trifluoromethylpyrimidines containing various functional groups (OH, SH, NH₂) in position 2. 2-hydroxypyrimidine is formed at heating butenon with carbamide (120-130°C). Its yield is increasing from 35 to 75% in the course of the reaction during 2 days at 205°C, similarly 2-mercaptopyrimidine (65%) is formed

in the reaction with thiocarbamide (H⁺, 20°C, 2 days). 2-amino-pyrimidines are formed by condensation of butenon with guanidine and its sulfoderivative (NSO₂C₆H₄NHCOCH₃-4). In the reaction with guanidinium chloride (EtOH, NaOEt, 60°C, 2 hours), pyrimidine yields in 45% and heating with guanidinium carbonate in benzene (120°C, 6 hours) increases the yield to 60%.

The aim of the study was to develop technologically acceptable synthesis ways and study the physicochemical properties of the new group of functional derivatives of 6-perfluoro-substituted pyrimidines.

Given the interaction of asymmetric perfluoro-substituted β -diketone(1) with thiocarbamide under conditions of acid catalysis as an example, kinetic evaluation of the cyclocondensation reaction was performed by spectrophotometric method by means of registration of the running values of the optic density index of solutions (D). To measure the optic density of 1,1,1,3,3-pentahydroperfluorodecane-2,4-dione (1) there were used water-alcohol (isopropanol) solutions of hydrochloric acid due to low solubility of the diketone (1) in water. The condensation reaction was carried out at fixed values of temperature of 20 and 30°C in a 50% vol. of thiocarbamide (at a ratio of the reagents diketone/thiocarbamide of 1:50) in a 0.1 M solution of HCl (pH 3). The experimental results are presented in **Fig.1**.

The reaction of cyclocondensation is known to proceed in two stages with subsequent removal of two water molecules [14]. A strong electron-deficient effect of the perfluoroalkyl substituent causes prevalence of the enol form of the diketone (up to 100%) [16,17]. In the first stage, thiocarbamide is added to the *enolized* carbon atom of β -diketone. The removing water molecule is [18] a good leaving group. Further as a result of intramolecular condensation, a cyclic product is formed (20).

Under these conditions in all the cases considered the dependence of the concentration of 2-mercapto-4-methyl-6-perfluoropyrimidine (20) on time of cyclization was satisfactorily approximated with the first order kinetic equation. The calculation of the cyclization rate was performed according to the first order equation [19]:

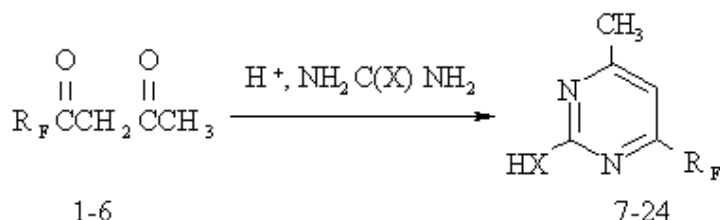
$$k = \frac{1}{\tau} \ln \frac{c_{\infty}}{c_{\infty} - c_i}$$

Here c_{∞} is the concentration of pyrimidine at reaction completion, c_i is the concentration of pyrimidine at instant τ .

The least-square procedure was used to calculate the values of the pseudomonomolecular (apparent) rate constants of the cyclization reaction, their logarithms and half-lives as follows: at 298K $k = 0.745 \cdot 10^{-3} \text{ s}^{-1}$ ($\ln k$ 6.613), $\tau_{1/2}$ 930 c, at 303K $k = 0.239 \cdot 10^{-3} \text{ s}^{-1}$ ($\ln k$ 7.779), $\tau_{1/2}$ 300 .

The kinetic evaluation of the reactivity of β -diketone (1) allows to determine the conditions of cyclization with carbomoyl amines.

As a result of the study, a large number of functional derivatives of pyrimidine was synthesized by the reaction of cyclocondensation of asymmetric perfluoro-substituted β -diketones (1-6) with guanidinium carbonate, carbamide and thiocarbamide under conditions of acid catalysis. As a result, the appropriate 6-perfluoro-substituted 2-amino- (7-12), 2-hydroxy- (13-18) and 2-mercapto-(19-24)-4-methylpyrimidines were found to be formed:



$\text{R}_F = \text{C}_6\text{F}_{13}$ (1,7,13,19), C_8F_{17} (2,8,14,20), $\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ (3,9,15,21),
 $\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ (4,10,16,22),
 $\text{CF}(\text{CF}_3)[\text{OCF}_2\text{CF}(\text{CF}_3)]_2\text{OC}_3\text{F}_7$ (5,11,17,23),
 $\text{CF}(\text{CF}_3)[\text{OCF}_2\text{CF}(\text{CF}_3)]_n\text{OC}_3\text{F}_7$ ($n = 9$) (6,12,18,24),
 $\text{X} = \text{NH}$ (7-12), O (13-18), S (19-24).

Asymmetric perfluoro-substituted β -diketones (1-6) were used as a dicarbonyl fragment.

The reaction was carried out in a polar solvent (alcohol) in the equimolar ratio of β -diketone (1-6) and carbomoyl amine in the presence of an acid catalyst at heating (70-100°C) for 3-5 h. The yields of 6-perfluoro-substituted 4-methylpyrimidines (7-24) attained 68-95%. An increase in the yield is connected with partial solubility of some 6-perfluoro-substituted pyrimidines in a water-alcohol solution.

Also, 2-amino-, 2-hydroxy- and 2-mercapto-4-methyl-6-perfluorohexylpyrimidine (7,13,19) were produced in isopropanol at room temperature after 3 days, the yields of the polycondensation products (7,13,19) were 68, 72 and 72% respectively. The course of the reaction was controlled by TLC procedure according to the starting diketone disappearance. Under the conditions of cyclocondensation of β -diketones with guanidinium carbonate, carbamide and thiocarbamide, attempts to record chromatographically the formation of the reaction products by only one ketonic group failed.

Separation of the synthesized compounds was carried out after addition of alkali or soda solutions (13-24) by distillation of the solvent with subsequent reprecipitation from water (7,8), vacuum sublimation (13,14), extraction by ether (19-24), recrystallization from alcohol (9-12, 15-18, 21-24) or from acetone (7,8,19,20). Perfluoro-substituted functional derivatives of pyrimidine are separated as crystals (7,9,13,15,19,21), amorphous (10,11,16,20,22) and viscous oily substances (8,12,17,18,23,24) (Tables 1-3). An attempt to crystallize compound (20) via fractional vacuum distillation resulted in the product decomposition. All synthesized 2-mercaptopyrimidines (19-24) possess a specific odor.

The composition and structure of compounds (7-12) have been confirmed by the data of elemental analysis, and also by IR, UV and PMR spectroscopy (Tables 4-6).

IR spectra of compounds (7-12) in many respects are similar to those of 2-amino-substituted pyrimidines [3,15] for which the bands of valence vibrations of the aminogroup in a range of $3480-3330\text{ cm}^{-1}$ are typical. In the spectra of 2-hydroxypyrimidines (13-18) an absorption band of $3500-3300\text{ cm}^{-1}$ corresponds to valence vibrations of the hydroxyl group and a band of $1780-1770$ is probably related to the tautomeric form of hydroxypyrimidine-pyrimidine-2-one. The spectra of 2-mercapto derivatives (19-24) contain a band of valence vibrations of middle intensity of S-H group at $2600-2500\text{ cm}^{-1}$ and valence vibrations of C-S at 665 cm^{-1} . For all 6-perfluoro-substituted derivatives (7-24), valence vibrations of the methyl group in a range of $3220-2310\text{ cm}^{-1}$, vibrations of the pyrimidine ring ($\nu_{\text{C}=\text{C}}$, $\nu_{\text{C}=\text{N}}$, δ_{NH}) at $1680-1440\text{ cm}^{-1}$ (skeletal vibrations of the cycle), $1340-900\text{ cm}^{-1}$ (valence vibration of C-F bond) were recorded [20] (Tables 4-6).

The UV spectra of 6-perfluoro-substituted 2-aminopyrimidines (7-12) in a water-alcohol solution exhibit one (compounds 7,8,10,11) or two absorption maxima (9,12) associated with $I\pi\pi\rightarrow\pi^*$ transition (compounds 7-12) in a range of $217-228\text{ nm}$ ($\lg\epsilon$ 3.04-3.15) and with $II\pi\pi\rightarrow\pi^*$ transition (compounds 9,12) at $202-205\text{ nm}$ ($\lg\epsilon$ 3.98-3.05) which confirm the presence of multiple bonds in the hetero ring [21] (Tables 4-6). In a strong acid medium (0.01M HCl solution), electron spectra of the products (7,10) exhibit a hypsochromic shift of the absorption bands by 22 nm (7) and 17 nm (10) with an absorption maximum of 206 nm ($\lg\epsilon$ 3.23) and ($\lg\epsilon$ 3.38). In an alkali medium (pH 14) for compounds (7,10) a hypsochromic shift of the absorption bands was observed by 20 nm (7) and 14 nm (10), with a maximum at 208 nm ($\lg\epsilon$ 2.72) and 209 nm ($\lg\epsilon$ 3.00). The *isosbestic* point (230 nm) at different values of pH is an evidence of the presence of two equilibrium forms of the every investigated compounds (7,10)[22]. Two absorption bands are observed in the spectra of compounds (13,15,16,18) recorded in aqueous isopropanol at pH7: $202-218\text{ nm}$ ($\lg\epsilon$ 2.72-3.30) and a range of $217-270\text{ nm}$ ($\lg\epsilon$ 3.00-3.32) while compounds (14,17) have only the first absorption band. An addition of a concentrated acid (0.01M HCl) also leads to hypsochromic and hyperchromic shifts of the maximum absorption band by 11 nm ($\lg\epsilon$ 3.40 and 3.42) (13,16) at 206 nm . An addition of an alkali (pH 14) also causes the hypsochromic shift of the maximum of the absorption band by 8 nm at 209 nm . ($\lg\epsilon$ 3.15 and $\lg\epsilon$ 3.31) (13 and 16 respectively). At the wave length of 230 nm and various values of pH similarly to the case of 2-aminopyrimidines (7,10), an *isosbestic* point also is observed allowing to consider such systems (13,16) as two-component ones [22]. The spectra of mercapto-derivatives of pyrimidine (19,24) show two absorption maxima at 202 nm ($\lg\epsilon$ 2.74-3.14) and 217 nm ($\lg\epsilon$ 3.01 and 3.35) (23,24), one maximum at 235 nm ($\lg\epsilon$ 3.92-4.29) (19,21) and for compound (20) a maximum as a shoulder at 212 nm (Tables 4-6).

The PMR spectra of compounds (7, 9-11) in a range of $10.25-10.90\text{ ppm}$. show a broadened signal of NH protons pointing to the presence of two tautomeric forms of pyrimidine derivatives : amine and imine ones. The spectra of products (15,16) exhibit a broadened signal at $8.95-9.2\text{ ppm}$ assigned to the proton bonded with the nitrogen of the pyrimidine ring, that also confirms the presence of tautomeric form: pyrimidine-2-one. The spectra of pyrimidines (19,21,23) recorded a broadened proton signal assigned to the cyclic nitrogen of the ring in a range of $8.45-8.88\text{ ppm}$. Moreover, for compounds (7, 9-11, 15, 16,19,21,23) the proton signal at C5 at the pyrimidine ring as a singlet (7,10,19,21,23) with a chemical shift of $6.90-7.47\text{ ppm}$ and a doublet with δ (ppm.) are typical: $7.00\text{ J}_{\text{FH}}\text{ 50Hz}$ (11), $7.47\text{ J}_{\text{FH}}\text{ 34.4Hz}$ (15), $7.70\text{ J}_{\text{FH}}\text{ 50Hz}$ and $7.75\text{ J}_{\text{FH}}\text{ 34.4Hz}$ (Tables 4-6). The proton signal of the S-H group at $4.75-4.92\text{ ppm}$ was observed in the spectra of compounds (19,21,23). Integral intensities of the signals, their multiplicity and upfield chemicals shifts ($1.20-3.34\text{ ppm}$) point to the presence of the methyl group in the pyrimidine molecules.

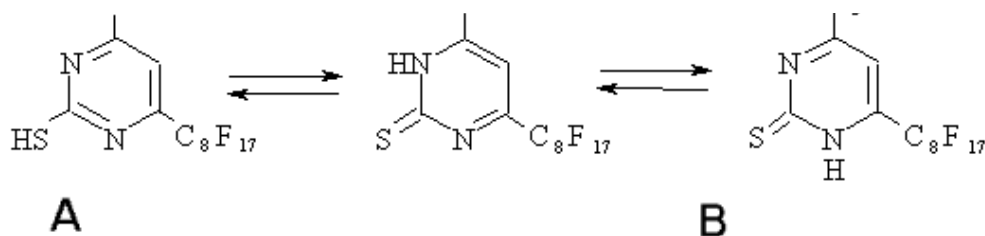
The signals of fluorine atoms of the trifluoromethyl-2-undecafluoroxapentyl fragment were observed in the ^{19}F NMR spectra of 2-amino- (9) and 2-hydroxy-4-methyl-6-perfluoro(1-methyl-2-oxapentyl) pyrimidine (15) in a range of $34-83.19\text{ ppm}$ (relatively C_6F_6).

IR spectroscopy was used to evaluate *thione-thiol* equilibrium in ethanol solutions of 2-mercapto-4-methyl-6-perfluorooctylpyrimidine (20) ($1\cdot 10^{-1}\text{ mol/l}$) in carbon tetrachloride (ϵ 2.238) and in different mixtures of CCl_4 and CH_3CN (ϵ 36.02) [15], the thickness of the recorded layer was 1.08 mm . The spectra of ethanol solutions of pyrimidine(20) in carbon tetrachloride and also alcohol solutions of (20) in a mixture of carbon tetrachloride and acetonitrile at different contents of the latter (20,60,90%) were analyzed.

Usually the vibration range of C=S group in heterocyclic systems coincides with the range of deformation ring vibrations [20]. Based on the data of calculations made for thiopyrimidines, we assume that the band of middle intensity at $1195-1205\text{ cm}^{-1}$ is assigned to the vibration component $\nu_{\text{C}=\text{S}} + \delta_{\text{C-H}}$.

An absorption band at 1200 cm^{-1} related to vibrations $\nu_{\text{C}=\text{S}}$ is observed in the spectra of alcohol solution of compound (20) (Fig.2). Its intensity is minimal in CCl_4 probably due to the presence of *thiol* form (A).





Along with an increase in polarity of the solvent (in our case an increase in the acetonitrile share) , the concentration of the *thione* form (B) is increasing causing a growth of the band intensity at 1200 cm^{-1} . The effect of the solvent polarity on the ratio of tautomeric forms (A) and (B) is determined by the differences in solvation energies of heterocycle π -system [15]. Besides, at acetonitrile addition, a band in a zone of 1180cm^{-1} appears that is associated with deformation ring vibrations. The change in the heterocycle electronic structure at transition from the thiol form to thione one leads to a significant decrease in its intensity.

An effect of electron-deficient trifluoromethyl group in the 4 position on the heteroring π -system was reported in paper [15]. Probably, the conjugation of lone-pair electrons of the sulfur atom with the aromatic system is strengthened in comparison with the unfluorinated pyrimidine, that leads to S=H bond strengthening. In contrast to the data of paper [15] , a significant shift of the vibration band of 1230 cm^{-1} to the direction of high frequencies was not observed though its intensity increased. This band is a summary one and includes vibrations $\nu_{\text{C=S}} + \delta_{\text{C-H}} + \delta_{\text{NH}}$.

The increase in the intensity may be explained by an increase in the *thione* form (B) concentration ($\nu_{\text{C=S}}$ component). A negligible shift of this band at transition to a more polar solvent depends on displacement δ_{NH} as a result of the formation of the hydrogen bond with proton-deficient molecules of acetonitrile for example. In this case, absorption bands of bond vibrations $\nu_{\text{C=S}}$ and $\delta_{\text{C-H}}$ appear as low-frequency shoulders on the new band of 1220 cm^{-1} . **(Fig. 2)**

Thus, the interaction of the asymmetric perfluoro-substituted β -diketones (1-6) with guanidinium carbonate, carbamide and thiocarbamide under different conditions has been investigated. It has been shown that the appropriate 6-perfluoro-substituted 2-amino- (7-12), 2-hydroxy- (13-18) and 2-mercapto- (19-24) 4-methylpyrimidines are formed as a result of the cyclocondensation in alcohol or benzene (in case of guanidine) in the presence of catalytic amounts of hydrochloric acid.

Experimental.

IR spectra were recorded on a IKS-29 and a Shimadzu IR-470 (Japan) instrument (film, KBr pellets).

UV spectra of aqueous and alcohol solutions of substances were performed on a SF-26 spectrophotometer at a concentrations of the compounds of 10^{-4} mol/l , a thickness of the absorption layer of 1 cm .

PNR spectra of solutions of compounds in CD_3OD were measured on a WM-250 (250MHz), a Tesla-BS 487C (80 MHz) and a WF-200 (200 MHz) spectrometers, with *GMDs* as internal standard .

^{19}F NMR spectra were recorded on a WF-200 (200MHz) instrument, with C_6F_6 as external standard.

The control over the reaction course and purity of the compounds produced was performed by *TLC* method on Sulifol UV-254 plates.

Perfluoro-substituted β -diketones (1-6) were synthesized by the condensation according to the method [23,25].

2-amino-4 methyl-6-perfluorohexylpyrimidine (7). 32.3 grams (0.08 mole) of 1,1,1,3,3-pentahydroperfluorodecane-2,4-dione (1) were added to 7.04 grams (0.04 mole) of a suspension of guanidinium carbonate in isopropanol and heated for 3 h. The solvent was distilled, a dry residue was dissolved in acetone and transferred into water. The precipitated residue was filtered, dried over P_2O_5 . The yield was 17.0g (50%), colorless crystals, melting point of $126\text{-}128^\circ\text{C}$ (from acetone).

2-amino-4-methyl-6-perfluorooctylpyrimidine (8), 2-amino-4-methyl-6-perfluoro(1-methyl-2-oxapentyl) pyrimidine (9), 2-amino-4-methyl-6-perfluoro(1,4-dimethyl-2,5-dioxaoctyl)pyrimidine (10), 2-amino-4-methyl-6-perfluoro(1,4,7-trimethyl-2,5,8-trioxaundecanyl)pyrimidine (11) and 2-amino-4-methyl-6-perfluoro(1,4,7,10,13,16,19,22,25,28-decamethyl-2,5,8,11,14,17,20,23,26,29-decaoxaditriacontyl)pyrimidine (12) were produced in much the same way as compound (7). The analytical and spectral characteristics are given in **Tables 1 and 4**.

4-methyl-6-perfluorohexylpyrimidine-2(1H)-one (13). 15.0 g (0.04 mole) of 1,1,1,3,3-pentahydroperfluorodecane-2,4-dione (1) were added to a mixture of 2.23g (0.04 mole) of carbamide in isopropanol and 1 ml of HCl. The reaction mass was kept at $80\text{-}100^\circ\text{C}$ for 3-5 hours. The solvent was distilled, the dry residue was sublimated under vacuum. The yield was 10.0g (68%), colorless crystals, melting point of $98\text{-}100^\circ\text{C}$.

4-methyl-6-perfluorooctylpyrimidine-2(1H)-one (14), 4-methyl-6-perfluoro (1-methyl-2-oxapentyl)pyrimidine-2(1H)-one (15), 4-methyl-6-perfluoro(1,4 -dimethyl-2,5-dioxaoctyl)-pyrimidine-2(1H)-one (16), 4-methyl-6-perfluoro(1,4,7-trimethyl-2,5,8-trioxaundecanyl)-pyrimidine-2(1H)-one (17) and 4-methyl-6-perfluoro (1,4,7,10,13,16,19,22,25,28-decamethyl-2,5,8,11,14,17,20,23,26,29-decaoxaditriacontyl)pyrimidine-2(1H)-one (18) were produced in much the same way as(13). The analytical and spectral data are given in **Tables 2 and 5**.

4-methyl-2-mercapto-6-perfluorohexylpyrimidine (19) 28.28g (0.07 mole) of 1,1,1,3,3-pentahydroperfluorodecane-2,4-dione

4-methyl-2-mercapto-6-perfluorooctylpyrimidine (19). 20.20g (0.07 mole) of 1,1,1,3,3,3-pentafluorooctanoic acid (1) were added to 6.08g (0.08 mole) of a solution of thiocarbamide in isopropanol and 2 ml of concentrated HCl. The reaction mass was kept at 70°C for 10-12h. The oily product was extracted, dried, the solvent was distilled, the product was recrystallized from acetone. The yield was 33.0g (60%), pink crystals, melting point of 114-116°C.

Similarly the following substances were produced: 4-methyl-2-mercapto-6-perfluorooctylpyrimidine (20), 4-methyl-2-mercapto-6-perfluoro(1-methyl-2-oxapentyl)pyrimidine (21), 4-methyl-2-mercapto-6-perfluoro (1,4-dimethyl-2,5-dioxaoctyl)pyrimidine (22), 4-methyl-2-mercapto-6-perfluoro(1,4,7-trimethyl-2,5,8-trioxadecanyl)pyrimidine (23) and 4-methyl-2-mercapto-6-perfluoro(1,4,7,10,13, 16,19,22,25,29-decamethyl-2,5,8,11,14,17,20,23,26,29-decaoxaditriacontyl)pyrimidine (24). The analytic and spectral data are given in **Tables 3 and 6**.

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