SYNTHESIS AND ANTISTATIC PROPERTIES OF SOME SURFACE-ACTIVE PERIMIDINE DERIVATIVES

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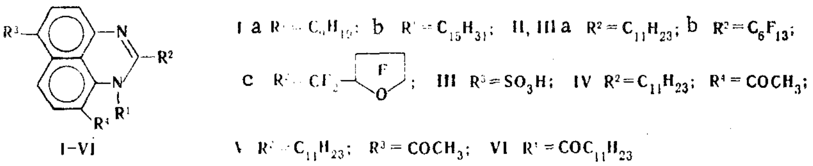
UDC 547.856.7'732.07

Perimidine derivatives containing as substituents high-molecular-weight alkyl, acyl, and perfluoroalkyl groups in positions 1, 2, 4(9) and 6(7) have been synthesized. The sulfonation of perimidines has been performed for the first time using 2-perfluoroalkyl- and 2-undecylperimidines as examples; it takes place exceptionally readily in this series. It has been shown that the best antistatic effect on application to the surface of polymers is given by 2-perfluoroalkylperimidine-6(7)-sulfonic acid).

It is known that imidazolinium salts containing high-molecular-weight alkyl groups in position 2 possess a high surface activity and are used as detergents, emulsifying agents, and antistatics [1-3]. In the present work we have synthesized a series of surface-active perimidine derivatives (I-VI) with the aim of studying their antistatic properties. As hydrophobic groups we introduced into the perimidine nucleus high-molecular-weight alkyl, acyl, and perfluoroalkyl substituents.

1-Nonyl- and 1-pentadecylperimidines (I) were obtained with yields of 50-70% by the standard method of alkylating perimidine in alkyl solution in an inert atmosphere [4]. Compounds (II) were synthesized by the reaction of equimolecular amounts of 1,8-naphthylenediamine and the chloride of the corresponding acids in benzene [5, 6]. With a twofold excess of lauroyl chloride, contrary to literature statements [5], we did not succeed in obtaining compound (IIa): in this case the main reaction product was 1,8-dilauroylaminonaphthylene. The acylation of 2-undecylperimidine with acetic acid in polyphosphoric acid under the conditions of kinetic (70-75°C) and thermodynamic (125-135°C) control [7] gave, respectively, its 6(7)- and 4(9)-acetyl derivatives (IV and V). It is interesting to note that the acylation of perimidine with lauric acid under the conditions of kinetic control does not take place, which is apparently due to the low activity of the lauroyl cation. With a rise in the temperature, the reaction is immediately directed to the 4(9) position and gives a 40% yield of 4(9)-lauroylperimidine (VI).



I-VI

I a $R^1 = C_9H_{19}$; b $R^1 = C_{15}H_{31}$; II, III a $R^2 = C_{11}H_{23}$; b $R^2 = C_6F_{13}$; c $R^2 = CF_2$–; III $R^3 = SO_3H$; IV $R^2 = C_{11}H_{23}$; $R^4 = COCH_3$; V $R^2 = C_{11}H_{23}$; $R^3 = COCH_3$; VI $R^4 = COC_{11}H_{23}$

It is known that potential antistatic agents should contain, in addition to a hydrophobic constituent, an ionogenic grouping [1]. Consequently, compounds (I, IIa, and IV-VI) were converted into hydrochlorides and compounds (IIa-c) into the 6(7)-sulfonic acids (III), since 2-perfluoroalkylperimidines do not form salts with acids. The sulfonation of perimidines has not been studied previously. Using compounds (II) as examples, we have established that sulfonation takes place exceptionally readily in this series: even at 20°C their treatment with concentrated sulfuric acid forms the sulfonic acids (III) in practically quantitative yield in 30 min. We also studied other possibilities for the production of salts from the perimidines synthesized. When compound (Ia) was fused with an equimolecular amount of adipic acid (160°C, 5 h), the adipate was obtained with a yield of only 22%. It was impossible to obtain adipates of compounds (IIa and IV-VI) under the same and more severe conditions. We were likewise unable to effect the quaternization of (Ia) with ethylene chlorohydrin (a β-hydroxyethyl group is favorable for antistatic activity [1-3]) when the components were heated

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Rostov State University, Rostov-na-Donu. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 550-553, April, 1980. Original article submitted February 14, 1979.

0009-3122/80/1604-0429$07.50

TABLE 1. Specific Surface Electrical Resistance of Polymers Treated with Perimidine Derivatives

Compound	ρ_s, Ω				
	application to the surface of the following polymers*				added to the bulk polymer†
	low-density polyethylene	polypropylene	block polystyrene	poly(methyl methacrylate)	low-density polyethylene
Ia HCl	$9,5\cdot10^{13}$	$2,6\cdot10^{14}$	$4,0\cdot10^{13}$	$6,2\cdot10^{13}$	$4,2\cdot10^{15}$
Ib·HCl	$1,9\cdot10^{13}$	$6,0\cdot10^{12}$	$1,2\cdot10^{13}$	$1,6\cdot10^{13}$	$4,3\cdot10^{13}$
IIa·HCl	$4,2\cdot10^{15}$	$4,2\cdot10^{15}$	$4,2\cdot10^{15}$	$1,8\cdot10^{14}$	$1,1\cdot10^{11}$
IV·HCl	$4,0\cdot10^{14}$	$1,7\cdot10^{14}$	$1,1\cdot10^{14}$	$4,4\cdot10^{14}$	$1,8\cdot10^{14}$
V·HCl	$4,2\cdot10^{15}$	$2,4\cdot10^{15}$	$4,2\cdot10^{15}$	$4,2\cdot10^{15}$	$6,0\cdot10^{13}$
VI·HCl	$1,3\cdot10^{14}$	$3,0\cdot10^{14}$	$1,2\cdot10^{14}$	$1,7\cdot10^{14}$	$1,4\cdot10^{10}$
Perfluoro(tetrahydrofuryl acetate)	$4,2\cdot10^{15}$	$4,2\cdot10^{15}$	$4,2\cdot10^{15}$	$2,5\cdot10^{15}$	$4,2\cdot10^{15}$
IIIb	$1,1\cdot10^{10}$	$2,1\cdot10^{10}$	$2,3\cdot10^{10}$	$3,9\cdot10^{11}$	$8,4\cdot10^{13}$—$4,2\cdot10^{15}$
IIIc	$3,2\cdot10^{8}$	$1,1\cdot10^{8}$	$7,1\cdot10^{9}$	$8,9\cdot10^{8}$	$6,3\cdot10^{12}$—$4,2\cdot10^{15}$
Blank experiment	$4,2\cdot10^{15}$	$4,2\cdot10^{15}$	$4,2\cdot10^{15}$	$4,2\cdot10^{15}$	$4,2\cdot10^{15}$

*Concentration of the solution 2 wt.%.

†Concentration 4 wt.%.

at 100-150°C for several hours: the reaction took place slowly and was accompanied by the formation of a complex mixture of substances difficult to separate. The reaction between compound (VI) and ethylene chlorohydrin took place very slowly at 100-160°C in a sealed tube.

The antistatic effect of the preparations obtained was evaluated from the lowering of the specific surface electrical resistance [8]. The compounds tested were deposited on the surface of the polymer or were added to the bulk polymer [8, 9].

It can be seen from the results given in Table 1 that the sulfo derivatives of perimidine when applied to the surface of polymers showed a high antistatic effect. Attention is attracted by the fact that the antistatic action of the sulfo group is higher when the molecule contains a perfluorotetrahydrofurfuryl substituent in position 2 ($\rho_s = 10^8$ Ω) as compared with a perfluorohexyl group ($\rho_s = 10^{10}$-10^{11} Ω). However, these compound exhibited only a weak antistatic action when added to the bulk polymer. Thus, the perimidines (IIb, c) are good antistatics on the surface treatment of polymers. The other compounds investigated had a low efficiency ($\rho_s = 10^{12}$-10^{13} Ω) or showed practically no antistatic action ($\rho_s = 10^{14}$-10^{15} Ω). Only the hydrofluoride of (IIa) was capable of reducing ρ_s of the polymer to 10^{11}Ω when introduced within the polymer.

EXPERIMENTAL

1-Nonylperimidine (Ia). With stirring and the continuous passage of nitrogen, a solution of 0.62 g (0.011 mole) of caustic potash in 5 ml of ethanol and then, dropwise, 2.49 g (0.012 mole) of nonylbromide were added to a suspension of 1.68 g (0.01 mole) of perimidine in 25 ml of ethanol. The mixture was boiled in an inert atmosphere for 3 h, after which the ethanol was distilled off and the residue was extracted with benzene. The extract was evaporated to a volume of 25 ml and was chromatographed on a column of alumina the first fraction being collected (the eluent was chloroform). Red-brown oil. Yield 1.5 g (51%). Found: C 81.5; H 8.4; N 9.3%. $C_{20}H_{26}N_2$. Calculated: C 81.6; H 8.8; N 9.5%. The hydrochloride of (Ia) was obtained by passing a current of dry hydrogen chloride into a benzene solution of the base (Ia). The yellow-brown oil that deposited was dissolved in the minimum amount of ethanol and by the addition of ether the hydrochloride was precipitated in the form of dark green crystals. Yield ~50%, mp 152-153°C. Found: C 72.4; H 8.5; Cl 10.2; N 8.3%. $C_{20}H_2N_2 \cdot HCl$. Calculated: C 72.6; H 8.2; Cl 10.7; N 8.5%. Adipate of (Ia). A mixture of 2.94 g (0.01 mole) of the perimidine (Ia) and 0.73 g (0.005 mole) of adipic acid was fused at 160°C for 5 h. The reaction product was washed free from (Ia) with acetone. Yield 0.8 g (22%), yellow-green crystals with mp 187-188°C (from ethanol). Found: C 75.0; H 8.2; N 6.9%. $C_{40}H_{52}N_4 \cdot C_6H_{10}O_4$. Calculated: C 75.2; H 8.5; N 7.6%.

1-Pentadecylperimidine (Ib). This was obtained in a similar manner to (Ia) with a yield of 68%. Viscous brown pasty mass. Found: N 7.1%. $C_{26}H_{38}N_2$. Calculated: N 7.4%. Hydrochloride of Ib. A current of dry hydrogen chloride was passed into a solution of 1 g of the base (Ib) in the minimum amount of benzene. After evaporation of the solvent, 1.1 g (100%) of brown crystals of the salt were obtained with mp 131-132°C (from ethanol with ether). Found: C 74.8; H 9.1; Cl 8.3; N 6.2%. $C_{26}H_{38}N_2 \cdot HCl$. Calculated: C 75.3; H 9.4; Cl 8.6; N. 6.6%.

2-Undecylperimidine (IIa). This was obtained as described by Paragamian et al. [5], using one equivalent of lauroyl chloride instead of two. Yield 96%, mp 85-86°C, which corresponds to literature information [5]. Hydrochloride of (IIa). Dry hydrogen chloride was passed through a hot benzene solution of the perimidine (IIa). After cooling, the precipitate was filtered off, washed with benzene, and dried. The yield was quantitative. Light yellow crystals with mp 192-194°C (from aqueous ethanol). Found: C 72.3; H 8.7; Cl 9.1; N 7.7%. $C_{22}H_{30}N_2 \cdot HCl$. Calculated: C 73.6; H 8.7; Cl 9.9; N 7.8%.

General Procedure for Obtaining the Sulfonic Acids (III). A compound (IIa-c) (1 g) was added in small portions with stirring into 3 ml of concentrated H_2SO_4 at such a rate that the temperature of the mixture did not exceed 30°C. After this, stirring was continued for 30 min at room temperature and the mixture was poured on to 20 g of crushed ice. The resulting precipitate was filtered off, washed with 10 ml of ice water, and dried. Compound (IIIa) was repurified by recrystallization from a large volume of ethanol, and (IIIb and c) by reprecipitation of their hydrochlorides from hot ammoniacal solutions that had been boiled with activated carbon.

2-Undecylperimidine-6(7)-sulfonic Acid (IIIa). Yellow-green crystals decomposed without melting above 180°C, sparingly soluble in water and the majority of organic solvents. Readily soluble in alkalis and moderately in ethanol on heating. UV spectrum (paraffin oil) cm^{-1}: 3470, 3415, 3290, 3190, 1665, 1590, 1255, 1165, 1030. UV spectrum, λ_{max} (log ε), cm^{-1}; (in CH_3OH): 324 (3.88); (in 0.1 NaOH): 342 (3.49). Found: C 65.0; H 7.5; N 6.9%. $C_{22}H_{30}N_2O_3S$. Calculated: C 65.7; H 7.5; N 7.0%.

2-Perfluorohexylperimidine-6(7)-sulfonic acid (IIIb). Orange crystals with mp 129-133°C, soluble in alkalis, ethanol, and DMFA. Found: C 36.8; H 1.0, N 4.8%. $C_{17}H_7F_{13}N_2O_3S$. Calculated: C 37.2; H 1.2; N 4.9%.

2-Perfluorotetrahydrofurfurylperimidine-6(7)-sulfonic Acid (IIIc). Orange crystals with mp 150-156°C with solubility properties similar to those of the sulfonic acid (IIIb). Found: C 39.2; H 1.1; N 5.5%. $C_{16}H_7F_9N_2O_4S$. Calculated: C 38.9; H 1.4; N 5.7%.

4(9)-Acetyl-2-undecylperimidine (IV). A mixture of 3.2 g (0.01 mole) of the perimidine (IIa), 0.9 ml (0.015 mole) of acetic acid, and 30 g of PPA was stirred vigorously at 125-135°C for 2 h, after which it was cooled to 70-80°C and was poured in a thin stream into 200 ml of a 3-5% solution of ammonia. Where necessary, the mixture was made alkaline to pH 9 and the resinous precipitate that had deposited was stirred in the alkaline medium for 30 min. The precipitate was extracted with chloroform (3 × 50 ml) and the extract was dried with sodium sulfate. The chloroform was distilled off and the residue was dissolved in 30 ml of benzene and chromatographed on a column of alumina. The first fraction, characterized by yellow-green fluorescence, was collected. Yield 2.3 g (64%), yellow crystals with mp 61-62°C (from petroleum ether). Found: C 79.2; H 9.0; N 7.4%. $C_{24}H_{32}N_2O$. Calculated: C 79.1; H 8.8; N 7.7%. Hydrochloride of (IV). When a current of dry hydrogen chloride was passed through a solution of the base (IV) in the minimum amount of benzene, a gel-like precipitate was deposited. Evaporation of the benzene gave yellow crystals of the hydrochloride with mp 170-171°C (decomp.). Found: C 72.1; H 8.6; Cl 8.6; N 7.4%. $C_{24}H_{32}N_2O \cdot HCl$. Calculated: C 72.0; H 8.3; Cl 8.9; N 7.0%.

6(7)-Acetyl-2-undecylperimidine (V). A mixture of 3.2 g (0.01 mole) of the perimidine (IIa), 0.9 ml (0.015 mole) of acetic acid, and 30 g of PPA was stirred at 70-75°C for 8 h, after which it was poured in a thin stream into 200 ml of a 3-5% solution of ammonia. The semicrystalline precipitate that separated out in the form of a clot was separated off and treated with 50 ml of chloroform and, by adding a 22% solution of ammonia in small portions with stirring, its complete dissolution in the chloroform was achieved. The extract was washed three times with water and was dried with sodium sulfate. After all the chloroform had been distilled off under reduced pressure, the residual oil was treated with 40 ml of petroleum ether. On trituration, a dark yellow precipitate of compound (V) deposited. Yield 2 g (56%), dark yellow crystals with mp 127-129°C (from benzene with petroleum ether). Found: C 79.3; H 8.5; N 7.5%. $C_{24}H_{32}N_2O$. Calculated: C 79.1; H 8.8; N 7.7%. The hydrochloride of (V) was obtained in a similar manner to the hydrochloride of (IV). Yellow crystals with mp 215-216°C. Found: C 71.1; H 8.1; Cl 8.6; N 7.4%. $C_{24}H_{32}N_2O \cdot HCl$. Calculated: C 72.0; H 8.3; Cl 8.9; N 7.0%.

The petroleum ether was distilled off completely from the filtrate remaining after the removal of compound (V), and after chromatographic purification on alumina 0.5 g (14%) of the perimidine (IV) was obtained.

6(7)-Acetyl-2-undecylperimidine Perfluoro(tetrahydrofurylacetate). With gentle warming and stirring, 3.64 g (0.01 mole) of the perimidine (V) and 2.92 g (0.01 mole) of perfluoro(tetrahydrofurylacetic) acid were mixed. The viscous mass formed was triturated with ether, giving a yellow powder of the salt. It was impossible to select a solvent for recrystallizing the salt. Found: N 3.8%. $C_{24}H_{32}N_2O \cdot C_6HF_9O_3$. Calculated: N 4.0%.

4(9)-Lauroylperimidine (VI). A mixture of 1.7 g (0.01 mole) of pyrimidine, 3 g (0.015 mole) of lauric acid, and 25 g of PPA was stirred at 130-135°C for 3 h 30 min, after which the hot mass was poured with stirring into 200 ml of cold water and was neutralized with ammonia. The precipitate that deposited was filtered off, washed with water, and dried. For purification, the product was treated with 50 ml of chloroform, the solution filtered, and the filtrate was transferred to a column of alumina and chloroform—petroleum ether (1:1), which eluted a first fraction colored yellow. The yield of compound (I) was 1.4 g (40%), yellow crystals with mp 103-104°C (from benzene with petroleum ether). Found: C 78.5; H 8.5; N 7.6%. $C_{23}H_{30}N_2O$. Calculated: C 78.9; H 8.6; N 8.0%. The hydrochloride of (VI) was obtained in a similar manner to the hydrochloride of (IV). Bright yellow crystals with mp 183-185°C. Found: C 72.0; H 8.4; Cl 9.0; N 7.5%. $C_{23}H_{30}N_2O \cdot HCl$. Calculated: C 71.5; H 8.1; Cl 9.2; N 7.3%.

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