QUATERNARY PYRIDINIUM KETOXIMES – NEW EFFICIENT MICELLAR HYDROLYTIC CATALYSTS

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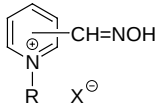
A series of quaternized alkyl pyridyl ketoximes was synthesized and tested as micellar hydrolytic catalysts. 2- And 4-[1-(hydroxyimino)tridecyl]-1-methylpyridinium bromides were surprisingly efficient, most probably due to the location of their nucleophilic hydroxyimino group below the micellar surface. Absorbance of the reaction mixture *vs* time plots exhibited remarkable positive deviation from the first-order kinetics when hydrolysis of 4-nitrophenyl phosphates was catalyzed by 1-dodecyl-3-[1-(hydroxyimino)ethyl]- or 3-[1-(hydroxyimino)tridecyl]-1-methylpyridinium bromide.

Key words: Micelles; Pyridinium salts; Oximes; Phosphates; Hydrolyses; Kinetics; Micellar catalysis.

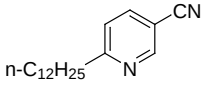
Functional cationic tensides possessing various nucleophilic functions have been widely studied as potential micellar hydrolytic catalysts[1] during the past decades.

Deprotonated hydroxyimino group in quaternary pyridinium aldoximes is known to be a powerful nucleophile readily attacking phosphorus atom in phosphoric and phosphonic acid derivatives. The 1-alkyl-[(hydroxyimino)methyl]pyridinium moiety, representing a leading structure in reactivators of acetylcholinesterase[2], inspired many authors[3] in synthesis of functional cationic surfactants of general formula **1** as micellar catalysts for hydrolysis of toxic derivatives of phosphoric and phosphonic acid. Compounds **1** (especially 2-substituted isomers) exhibit high activity towards 4-nitrophenyl diphenyl phosphate (PNPDPP) and other nervous gases simulants[3]. In continuation of our previous work concentrated on quaternary heteroarenium aldoximes[3d], we turned our attention to quaternary

pyridinium ketoximes **2**. General formula **2** comprises two series of cationic surfactants with inverse position of the hydrophobic alkyl chain. We decided to synthesize the following pyridinium bromides: 1-dodecyl-2-[1-(hydroxyimino)ethyl]- (**2a**), 1-dodecyl-3-[1-(hydroxyimino)ethyl]- (**2b**), 1-dodecyl-4-[1-(hydroxyimino)ethyl]- (**2c**), 1-methyl-2-[1-(hydroxyimino)-tridecyl]- (**2d**), 1-methyl-3-[1-(hydroxyimino)tridecyl]- (**2e**), and 1-methyl-4-[1-(hydroxyimino)tridecyl]- (**2f**). The aim of the present study was to evaluate the influence of the relative position of the hydrophobic alkyl chain, polar head and nucleophilic group on the hydrolytic activity of salts **2**.



1	position	R	X
a	2	n-$C_{12}H_{25}$	I
b	3	n-$C_{12}H_{25}$	Br
c	4	n-$C_{12}H_{25}$	Br

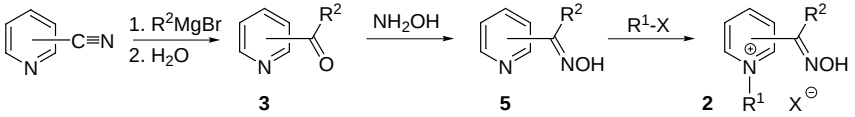


4

RESULTS AND DISCUSSION

*Syntheses of Quaternary Pyridinium Ketoximes **2***

Synthesis of the selected quaternary pyridinium ketoximes **2** from methyl pyridyl ketones **3a**–**3c** (salts **2a**–**2c**) or from pyridinecarbonitriles (salts **2d**–**2f**) is outlined in Scheme 1.



3,5	position	R^2
a	2	CH_3
b	3	CH_3
c	4	CH_3
d	2	n-$C_{12}H_{25}$
e	3	n-$C_{12}H_{25}$
f	4	n-$C_{12}H_{25}$

2	position	R^1	R^2	X
a	2	n-$C_{12}H_{25}$	CH_3	Br
b	3	n-$C_{12}H_{25}$	CH_3	Br
c	4	n-$C_{12}H_{25}$	CH_3	Br
d	2	CH_3	n-$C_{12}H_{25}$	Br
e	3	CH_3	n-$C_{12}H_{25}$	Br
f	4	CH_3	n-$C_{12}H_{25}$	Br
g	2	CH_3	n-$C_{12}H_{25}$	I
h	3	CH_3	n-$C_{12}H_{25}$	I
i	4	CH_3	n-$C_{12}H_{25}$	I

SCHEME 1

Addition of dodecylmagnesium bromide to pyridin-2- or pyridin-4-carbonitriles afforded the expected dodecyl pyridin-2- (**3d**) and -4-yl (**3f**) ketones in good yields. As expected, a longer reaction time at higher temperature was necessary to complete the reaction with the less reactive pyridin-3-carbonitrile. As a consequence, a small amount of the 6-dodecylpyridin-3-carbonitrile (**4**), product of the concurrent nucleophilic attack of the pyridine ring by Grignard reagent, was isolated from the reaction mixture.

Ketoximes **5a–5f** were readily prepared from the corresponding ketones **3a–3f**. Only one set of signals was observed in ^{1}H and ^{13}C NMR spectra of methyl pyridin-2- (**5a**), -3- (**5b**), and -4-yl (**5c**) ketoximes thus giving evidence of the presence of a single stereoisomer in each case. However, except for ketoxime **5a**, we were not able to ascertain the configuration at the C=N bond. In oxime **5a**, *E* configuration was confirmed by IR spectroscopy[4a]. Surprisingly, mixtures of *E* and *Z* isomers of dodecyl pyridin-2- (**5d**), -3- (**5e**), and -4-yl (**5f**) ketoximes resulted from the reactions of lipophilic ketones **3d–3f** with hydroxylamine although the reaction conditions used were similar as in our previous studies[4] where only single stereoisomers of alkyl heteroaryl ketoximes were obtained. So far, we have not been able to explain the factors controlling the configuration of the arising ketoximes. In the case of ketoxime **5d**, both stereoisomers were separated by column chromatography. Pure *E* isomers of ketoximes **5e** and **5f** were obtained by repeated crystallization from aqueous ethanol. Besides the purifying effect of the crystallization, irreversible conversion of *Z* to more stable *E* isomers was observed upon gentle heating of their ethanolic solutions or even upon standing for a long period. The configurations of ketoximes **5d–5f** were attributed according to the rule formulated by Roberts *et al.*[5]: on going from ketones to ketoximes, both α-carbon resonances in ^{13}C NMR shift upfield, with the effect for the α-*syn* carbon (relative to OH) being greater than that for the α-*anti* carbon. Chemical shifts of the α-CH_2 carbons in both isomers of ketoximes **5d–5f** are summarized in Table I. The *E*/*Z* ratio given in Table I was obtained from integrals of the corresponding α-CH_2 signals in ^{1}H NMR (in all cases, signals of α-*syn*-CH_2 protons, relative to OH, were downfield compared to those of α-*anti*-CH_2). With the isomer **5d**, the configuration on the C=N bond was confirmed independently by IR spectroscopy[4a]. Since the ^{13}C NMR spectra of ketoximes **5d–5f** were not taken immediately after their isolation, the *Z* isomers present were the minor components in mixtures of isomers. Therefore, we were able to find the most intensive signals only (see Experimental).

Quaternization of pyridin-3-yl ketoximes **5b**, **5e** and pyridin-4-yl ketoximes **5c**, **5f** afforded the desired pyridinium salts **2b**, **2c**, **2h**, and **2i** in satisfactory yields. On the other hand, quaternization of the pyridine-2-yl ketoximes **5a**, **5d** made a great problem. Due to the steric hindrance of the (hydroxyimino)alkyl group, alkylation of the ketoxime **5d** was very slow and the arising pyridinium salt **2g** was obtained only in a moderate yield. Quaternization of methyl pyridin-2-yl ketoxime (**5a**) with dodecyl bromide failed even on 100 h heating at 150 °C in a sealed tube and in the presence of potassium iodide (Finkelstein reaction)[6]. A complex mixture of compounds resulted from this reaction. Methyl pyridin-2-yl ketone (**3a**) was isolated as the major product and identified by ^{1}H NMR. The origin of the above-mentioned compound can be explained by N-alkylation of the deprotonated hydroxyimino group of the ketoxime **5a** followed by decomposition of the resulting nitrone[7].

Pyridinium salts **2b**, **2c**, **2g**–**2i** were isolated as single isomers. We assume that no isomerization occurred during the quaternization and therefore the prepared pyridinium ketoximes **2g**–**2i** should be of *E* configuration.

Kinetic Studies

Hydrolytic efficiency of the prepared salts **2** was evaluated by measuring the kinetics of the hydrolysis of model substrates (4-nitrophenyl esters in all cases). As usual in similar studies[3,4], kinetic experiments were performed under pseudo-first-order conditions with an excess of the catalyst. The reactions were followed spectrophotometrically by monitoring the appearance of 4-nitrophenoxide ion at 400 nm.

TABLE I
Configurations of ketoximes **5d**–**5f** from the ^{13}C NMR spectra

α-CH_2 chemical shift, ppm			*E*/*Z*
Ketone	(*E*)-oxime	(*Z*)-oxime	
3d 38.4	**5d** 32.7	**5d** 33.7	5 : 4
3e 39.6	**5e** 32.6	**5e** 35.7	4 : 1
3f 39.6	**5f** 32.6	**5f** 35.5	4 : 1

In the first series of experiments, 4-nitrophenyl diphenyl phosphate (PNPDPP) was employed as a toxic organophosphate simulant. The reactions were carried out at 25 °C under slightly basic conditions (pH 7.2). The obtained plots of the observed pseudo-first-order rate constant k_{obs} of the PNPDPP cleavage *vs* concentration *c* of salt **2** are shown in Fig. 1. However, we were not able to obtain these plots for 3-substituted salts **2b** and **2e**. As we have previously reported[8], considerable positive deviations from the expected first-order curves were observed in the absorbance *vs* time plots when the PNPDPP was hydrolyzed in micellar solutions of **2b** and **2e** (Fig. 2).

The plots given in Fig. 1 clearly demonstrate the difference between the reactivity of 1-dodecylpyridinium salt **2c** and 1-methylpyridinium salts **2d** and **2f** with the inverse position of the hydrophobic alkyl chain. The observed rate constants k_{obs} of the PNPDPP cleavage in the presence of 1-methylpyridinium salt **2d** and **2f** are comparable with those obtained with 1-dodecyl-2-[(hydroxyimino)methyl]pyridinium iodide (**1a**), the most efficient hydrolytic catalyst of the quaternary pyridinium aldoximes[3d], under the same conditions. This fact is surprising since the acidity of the hydroxyimino group in pyridinium ketoximes **2d**–**2f** is lower by more than one order of magnitude than that of the above-mentioned pyridinium aldoxime and, consequently, a lower concentration of the nucleophile (deprotonated hydroxyimino group) is present in solutions at the same pH. Although the anomalous absorbance *vs* time dependences in the case of the 3-substituted salts **2b** and **2e** do not allow to calculate the observed rate constants k_{obs} of the PNPDPP cleavage, it is evident that the hydrolysis of

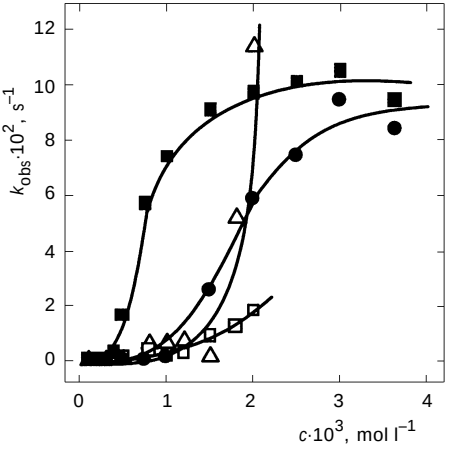


FIG. 1
Rate constant k_{obs} of the PNPDPP hydrolysis *versus* surfactant concentration: **2c** (❑), **2d** (●), **2f** (■), and **1a** (Δ) (ref.[3d]). Conditions: 25 °C, pH 7.2 (0.05 M HEPES buffer and 0.04 M Tris-HBr buffer for ketoximes **2** and aldoxime **1a**, respectively)

PNPDPP is much faster in the presence of 1-methylpyridinium salt **2e** than in the presence of its 1-dodecylpyridinium isomer **2b** (Fig. 2).

A question appears about the source of the high reactivity of 1-methylpyridinium salts **2d**–**2f** towards PNPDPP. No doubt, a low critical micelle concentration (below $1.5 \cdot 10^{-3}$ and $5 \cdot 10^{-4}$ mol l^{-1} for salts **2d** and **2f**, respectively, as follows from the k_{obs} *vs* concentration plots shown in Fig. 1) affords the kinetic benefit of micellar catalysis even at low concentrations of salts **2d**–**2f**. Nevertheless, the remarkable reactivity of 1-methylpyridinium salts **2d**–**2f** could also be explained as follows: PNPDPP (similarly to other lipophilic compounds) is solubilized in the micellar interior in solutions of surfactants. As evident from Fig. 3 (using salts **2c** and **2f** as examples), if the nucleophilic group is located beneath the micellar surface (1-methylpyridinium salt **2f**), the probability of the attack of PNPDPP shall

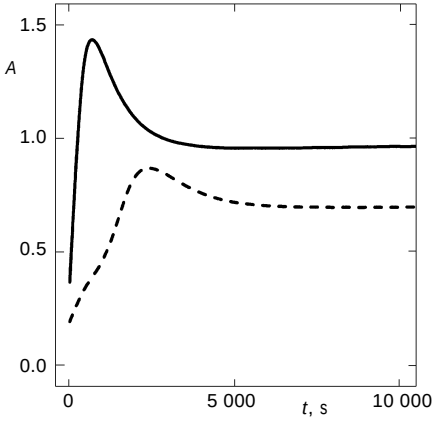


FIG. 2
Anomalous absorbance *versus* time plot of the PNPDPP hydrolysis in micelles of **2b** (dashed) and **2e** (full). Conditions: [oxime] = $3.6 \cdot 10^{-3}$ mol l^{-1}, 25 °C, pH 7.2 (0.05 M HEPES buffer)

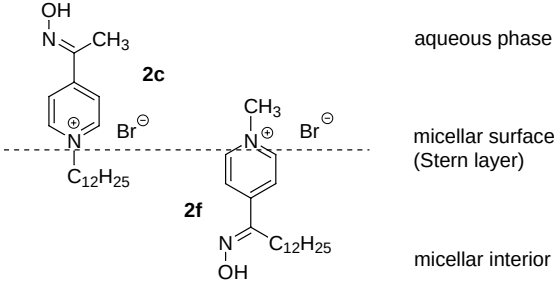


FIG. 3
Orientation of the hydrophobic alkyl chain, polar head and nucleophilic group at the aqueous/micellar interface

be higher compared with micelles of isomeric 1-dodecylpyridinium salt **2c** with the hydroxyimino group orientated into aqueous phase. Figure 3 also explains high solubilities and low critical micelle concentrations of salts **2d**–**2f**: all hydrophobic parts of their molecules are "hidden" in the micellar interior and only *N*-methyl group "sticks out" from the Stern layer into the aqueous phase.

To verify our hypothesis of the influence of the nucleophilic group position on hydrolytic efficiency of salts **2**, we decided to investigate the activity of both types of pyridinium ketoximes **2** towards a series of substrates of different lipophilicity. If our assumption was correct, both types of salts **2** should differ in the log k_{obs} *vs* log *P* profiles where *P* stands for the partition coefficient of the substrate between octan-1-ol and water. In an extreme case, the increase in the model substrate lipophilicity should decrease the rate of its hydrolysis in micellar solutions of 1-dodecylpyridinium salts **2b** and **2c** and *vice versa* in micellar solutions of 1-methyl- pyridinium salts **2d**–**2f**. 4-Nitrophenyl alkanoates were chosen as substrates for this study since they are a homologous group of substances with the lipophilicity dependent only on the alkyl chain length. Moreover, hydrolysis of 4-nitrophenyl alkanoates in the presence of 3-substituted pyridinium salts **2b** and **2e** did not exhibit the above-mentioned anomaly in the absorbance *vs* time plots and, therefore, salts **2b** and **2e** could be involved in this study as well. The following esters were hydrolyzed in micellar solutions of salts **2b**–**2f** (25 °C, pH 6.3, concentration of salt **2** $2.0 \cdot 10^{-3}$ mol l^{-1} in all cases): 4-nitrophenyl acetate (PNPA), 4-nitrophenyl propanoate (PNPP), 4-nitrophenyl butanoate (PNPB), 4-nitrophenyl pentanoate (PNPV), 4-nitrophenyl hexanoate (PNPH), and 4-nitrophenyl octanoate (PNPO). Compared with the above-mentioned hydrolyses of PNPDPP, pH of the reaction mixtures was kept lower since alkanoates are hydrolyzed too fast in micelles of salts **2** at pH 7.2. All experiments were performed above the critical micelle concentration of each of the salts **2**. The partition coefficients *P* of the substrates between octan-1-ol and water were calculated using the software Pallas 1.2 (ref.[9]). To check the calculated partition coefficient values, log *P* was determined in several cases (PNPA, PNPB, and PNPO). The calculated and found values of log *P* are given in Table II.

The obtained log k_{obs} *vs* log *P* profiles for all the synthesized salts **2** are shown in Fig. 4. Unfortunately, the plots are more complicated than expected and, at first sight, they do not give unequivocal evidence that the nucleophilic group position (above or below the micellar surface) influences hydrolytic efficiency of salts **2**. Regardless of the structure of salt **2**, the increase in the substrate lipophilicity also increases the rate of its hy-

drolysis when log *P* value is higher than 3 (pentanoate and higher carboxylic acid esters). Most probably, formation of comicelles with salts **2** occurs in the case of substrates with longer alkyl chains and deforms the simple partition between the aqueous and micellar phase. Thus, relevant information can be obtained only if less lipophilic substrates of log $P < 3$ are employed. Increasing the lipophilicity of these esters (PNPA, PNPP, and PNPB), the rates of their hydrolysis (log k_{obs}) are invariant or rather decreasing in micelles of 1-dodecyl salts **2b** and **2c**. On the other hand, in the case of micellar solutions of 1-methyl salts **2e** and **2f**, the rates of the substrate hydrolysis slightly increase with the increasing lipophilicity of the above-mentioned 4-nitrophenyl esters. As expected, the slopes of the log k_{obs} *vs* log *P* plots differ depending on the type of micellar catalyst em-

TABLE II
Calculated and found octan-1-ol : water partition coefficient *P* values of selected 4-nitrophenyl alkanoates

Substrate	log *P*	
	calculated	found
PNPA	1.53	1.54
PNPB	2.73	2.67
PNPO	4.77	4.27

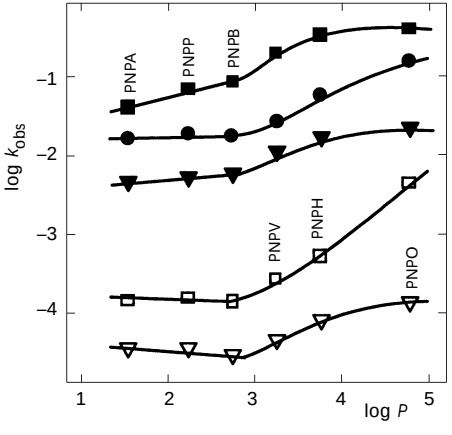


FIG. 4
Rate constant k_{obs} of the hydrolysis of various 4-nitrophenyl alkanoates *versus* their lipophilicity in micelles of **2b** (▽), **2c** (❑), **2d** (●), **2e** (▼), and **2f** (■). Conditions: [oxime] = $2.0 \cdot 10^{-3}$ mol l^{-1}, 25 °C, pH 6.3 (0.05 M MES buffer)

ployed (1-dodecyl salts **2b** and **2c** or 1-methyl salts **2e** and **2f**), nevertheless, the differences are very small. Surprisingly, the slope of the log k_{obs} *vs* log *P* profile of the 2-substituted 1-methyl salt **2d** is almost the same as those of 1-dodecyl salts **2b** and **2c**. Most probably, the proximity of the nucleophilic hydroxyimino group to quaternary nitrogen and to micellar surface is responsible for this behaviour.

CONCLUSION

Kinetic studies performed with quaternary pyridinium ketoximes **2** revealed that the activity of the hydrolytic micellar catalysts might be strongly influenced by the position of their nucleophilic group relative to the micellar surface. Most likely, location of the nucleophilic function beneath the micellar surface (given by relative arrangement of hydrophobic alkyl chain, head and functional group of the surfactant) is the source of the unusual activity of 1-methylpyridinium salts **2d**–**2f**. Similar influence of the hydrophobic alkyl chain and functional group position on the reactivity of amphiphilic compounds was observed by Richmond *et al.*[10] in the case of Cu^{2+} chelation by isomeric lipophilic β-hydroxyketoximes. Nevertheless, to our knowledge, none of the hydrolytic micellar or metallomicellar catalyst so far investigated[1] has been of analogous structure as our pyridinium ketoximes **2d**–**2f**, *i.e.* with the nucleophilic group located in the micellar interior. Therefore, salts **2d**–**2f** represent a new and promissing type of hydrolytic catalysts. Nevertheless, further studies (with surfactants of a longer distance between the polar head and nucleophilic groups) are necessary to verify undoubtedly our hypothesis of the influence of the nucleophilic function position on the hydrolytic activity of micellar catalysts.

EXPERIMENTAL

Temperature data were uncorrected. ^{1}H NMR spectra were recorded on spectrometers Bruker AMX3 and Varian Gemini 300 at 400 and 300 MHz, respectively. ^{13}C NMR spectra were recorded on a spectrometer Bruker AMX3 at 100 MHz. Chemical shifts are reported in ppm relative to tetramethylsilane as an internal standard, coupling constants *J* are in Hz. Elemental analyses were performed on Perkin–Elmer 240 analyser. IR spectra were taken on an FTIR spectrometer Nicolet 740; the wavenumbers are given in cm^{-1}. TLC analyses were carried out on DC Alufolien Kieselgel 60 F254 (Merck). Preparative chromatographic separations were performed on Kieselgel 60H, 40–63 μm (Merck) or on Silpearl (Kavalier).

Methyl pyridin-2-yl (**3a**), pyridin-3-yl (**3b**) and pyridin-4-yl ketone (**3c**), pyridine-2-, -3- and -4-carbonitrile, dodecyl bromide and 1 M ethereal solution of dodecylmagnesium bromide (all purum) were obtained from Fluka. 2-(Morpholin-4-yl)ethane-1-sulfonic acid (MES), 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethane-1-sulfonic acid (HEPES), 4-nitrophenyl propanoate

(PNPP), 4-nitrophenyl hexanoate (PNPH), and 4-nitrophenyl octanoate (PNPO) (analytical grade) were purchased from Sigma. 4-Nitrophenyl acetate[11a] (PNPA), 4-nitrophenyl butanoate[11b] (PNPB), 4-nitrophenyl pentanoate[11b] (PNPV), and 4-nitrophenyl diphenyl phosphate[11c] (PNPDPP) were prepared and purified according to described methods.

Dodecyl Pyridyl Ketones **3d**–**3f**

Ketones **3d**–**3f** were prepared using the procedure described in our previous communications[4] from the corresponding pyridinecarbonitrile (3.00 g, 28.8 mmol) in dry ether (135 ml). In the case of the 3-isomer, refluxing the reaction mixture for 1 h was necessary to complete the reaction. Crude products were purified by column chromatography (chloroform–methanol, 100 : 2).

Dodecyl pyridin-2-yl ketone (**3d**). Pure ketone **3d** was obtained by distillation of the product resulting from column chromatography. Yield 2.75 g (35%), b.p. 128–132 °C/40 Pa. For $C_{18}H_{29}NO$ (275.3) calculated: 78.49% C, 10.61% H, 5.08% N; found: 78.50% C, 10.69% H, 4.30% N. ^{1}H NMR ($CDCl_3$): 0.87 t, 3 H, *J*(12′,11′) = 7.0 (H-12′); 1.23 bs, 18 H (H-3′–H-11′); 1.73 tt, 2 H, *J*(2′,1′) = *J*(2′,3′) = 7.7 (H-2′); 3.21 t, 2 H, *J*(1′,2′) = 7.6 (H-1′); 7.46 ddd, 1 H, *J*(5,4) = 7.5, *J*(5,6) = 4.3, *J*(5,3) = 0.9 (H-5); 7.83 td, 1 H, *J*(4,5) = *J*(4,3) = 7.7, *J*(4,6) = 1.6 (H-4); 8.04 d, 1 H, *J*(3,4) = 7.8 (H-3); 8.68 d, 1 H, *J*(6,5) = 4.5 (H-6). ^{13}C NMR ($CDCl_3$): 14.8 s (C-12′); 23.4 s (C-11′); 24.7 s (C-10′); 28.0 s (C-9′); 30.1 s (C-8′); 30.21 s (C-7′); 30.25 s (C-6′); 30.35 s (C-5′); 30.38 s (C-4′); 30.4 s (C-3′); 32.6 s (C-2′); 38.4 s (C-1′); 122.5 s (C-3); 127.6 s (C-5); 137.5 s (C-4); 149.6 s (C-6); 154.3 s (C-2); 202.9 s (C=O).

Dodecyl pyridin-3-yl ketone (**3e**). Yield 5.41 g (68%), m.p. 46–48 °C. For $C_{18}H_{29}NO$ (275.3) calculated: 78.49% C, 10.61% H, 5.08% N; found: 78.36% C, 10.41% H, 5.02% N. ^{1}H NMR ($CDCl_3$): 0.87 t, 3 H, *J*(12′,11′) = 6.6 (H-12′); 1.25 bs, 18 H (H-3′–H-11′); 1.74 tt, 2 H, *J*(2′,1′) = *J*(2′,3′) = 7.1 (H-2′); 2.97 t, 2 H, *J*(1′,2′) = 7.3 (H-1′); 7.42 dd, 1 H, *J*(5,4) = 7.9, *J*(5,6) = 4.7 (H-5); 8.23 dt, 1 H, *J*(4,5) = 7.9, *J*(4,6) = *J*(4,2) = 1.8 (H-4); 8.76 dd, 1 H, *J*(6,5) = 4.5, *J*(6,2) = 1.6 (H-6); 9.16 s, 1 H (H-2). ^{13}C NMR ($CDCl_3$): 14.8 s (C-12′); 23.4 s (C-11′); 24.8 s (C-10′); 30.0 s (C-9′); 30.2 m (C-4′–C-8′); 30.3 s (C-3′); 32.6 s (C-2′); 39.6 s (C-1′); 124.4 s (C-5); 133.0 s (C-3); 136.1 s (C-4); 150.3 s (C-6); 154.0 s (C-2); 199.9 s (C=O).

6-Dodecylpyridine-3-carbonitrile (**4**). Yield 0.13 g (2%), m.p. 40–43 °C. For $C_{18}H_{28}N_2$ (272.4) calculated: 79.36% C, 10.36% H, 10.28% N; found: 79.68% C, 10.52% H, 9.31% N. ^{1}H NMR ($CDCl_3$): 0.88 t, 3 H, *J*(12′,11′) = 6.6 (H-12′); 1.26 bs, 18 H (H-3′–H-11′); 1.73 tt, 2 H, *J*(2′,1′) = *J*(2′,3′) = 7.6 (H-2′); 2.56 t, 2 H, *J*(1′,2′) = 7.6 (H-1′); 7.27 d, 1 H, *J*(5,4) = 8.0 (H-5); 7.85 dd, 1 H, *J*(4,5) = 8.1, *J*(4,2) = 2.2 (H-4); 8.80 d, 1 H, *J*(2,4) = 1.7 (H-2). ^{13}C NMR ($CDCl_3$): 14.8 s (C-12′); 23.4 s (C-11′); 30.2 m (C-3′–C-10′); 32.6 s (C-2′); 39.4 s (C-1′); 107.8 s (C-3); 117.7 s (C≡N); 123.5 s (C-5); 139.9 s (C-4); 152.8 s (C-2); 168.0 s (C-6).

Dodecyl pyridin-4-yl ketone (**3f**). Yield 4.97 g (63%), m.p. 56–60 °C. For $C_{18}H_{29}NO$ (275.3) calculated: 78.49% C, 10.61% H, 5.08% N; found: 78.13% C, 10.51% H, 4.77% N. ^{1}H NMR ($CDCl_3$): 0.88 t, 3 H, *J*(12′,11′) = 7.0 (H-12′); 1.26 bs, 18 H (H-3′–H-11′); 1.74 tt, 2 H, *J*(2′,1′) = *J*(2′,3′) = 7.3 (H-2′); 2.96 t, 2 H, *J*(1′,2′) = 7.3 (H-1′); 7.72 dd, 2 H, *J*(3,2) = *J*(5,6) = 4.6, *J*(3,5) = *J*(5,3) = 1.2 (H-3, H-5); 8.81 d, 2 H, *J*(2,3) = *J*(6,5) = 4.4 (H-2, H-6). ^{13}C NMR ($CDCl_3$): 14.8 s (C-12′); 23.4 s (C-11′); 24.6 s (C-10′); 30.2 m (C-3′–C-9′); 32.6 s (C-2′); 39.6 s (C-1′); 121.8 s (C-3, C-5); 143.6 s (C-4); 151.7 s (C-2, C-6); 200.5 s (C=O).

Alkyl Pyridyl Ketoximes **5a**–**5f**

Ketoximes **5a**–**5f** were prepared from ketones **3a**–**3f** using the procedure described in our previous communications[4]. Pure products were obtained either by crystallization from ethanol–water, 1 : 1 (ketoximes **5a**–**5c**) or by precipitation with water from their ethanolic solutions followed by column chromatography (chloroform–methanol, 100 : 2) and crystallization from ethanol–water (**5d**–**5f**).

(E)-Methyl pyridin-2-yl ketoxime (**5a**). Prepared from ketone **3a** (4.00 g, 0.033 mol). Yield 2.96 g (64%), m.p. 122–123 °C (ref.[12a] 121 °C). ^{1}H NMR ($CDCl_3$): 2.43 s, 3 H (CH_3); 7.28 ddd, 1 H, *J*(5,4) = 7.5, *J*(5,6) = 4.9, *J*(5,3) = 1.1 (H-5); 7.70 td, 1 H, *J*(4,5) = *J*(4,3) = 7.8, *J*(4.6) = 1.8 (H-4); 7.85 dt, 1 H, *J*(3,4) = 8.0, *J*(3,5) = *J*(3,6) = 0.9 (H-3); 8.66 ddd, 1 H, *J*(6,5) = 4.9, *J*(6,4) = 1.6, *J*(6,3) = 0.9 (H-6); 9.90 s, 1 H (OH). ^{13}C NMR ($CDCl_3$): 11.4 s (CH_3); 121.3 s (C-3); 124.4 s (C-5); 137.1 s (C-4); 149.6 s (C-6); 155.1 s (C-2); 157.6 s (C=NOH). IR (CCl_4): ν(OH) 3 240 (bridged), ν(OH) 3 580 (free).

Methyl pyridin-3-yl ketoxime (**5b**). Prepared from ketone **3b** (4.00 g, 0.033 mol). Yield 3.73 g (83%), m.p. 114–118 °C (ref.[12a] 116 °C, ref.[12b] 111–113 °C). ^{1}H NMR ($CDCl_3$): 2.30 s, 3 H (CH_3); 7.32 dd, 1 H, *J*(5,4) = 7.9, *J*(5,6) = 4.9 (H-5); 7.95 d, 1 H, *J*(4,5) = 8.2 (H-4); 8.61 d, 1 H, *J*(6,5) = 4.5 (H-6); 8.91 s, 1 H (H-2). ^{13}C NMR ($CDCl_3$): 12.4 s (CH_3); 124.1 s (C-5); 133.7 s (C-3); 134.4 s (C-4); 147.8 s (C-6); 150.0 s (C-2); 153.3 s (C=NOH).

Methyl pyridin-4-yl ketoxime (**5c**). Prepared from ketone **3c** (4.00 g, 0.033 mol). Yield 3.91 g (87%), m.p. 160–161 °C (ref.[12a] 157.5 °C). ^{1}H NMR ($CDCl_3$): 2.31 s, 3 H (CH_3); 7.56 d, 2 H, *J*(5,6) = *J*(3,2) = 6.0 (H-3, H-5); 8.64 d, 2 H, *J*(6,5) = *J*(2,3) = 6.0 (H-2, H-6). ^{13}C NMR ($CDCl_3$): 11.9 s (CH_3); 121.1 s (C-3, C-5); 145.3 s (C-4); 150.4 s (C-2, C-6); 154.0 s (C=NOH).

Dodecyl pyridin-2-yl ketoxime (**5d**). Prepared from ketone **3d** (2.70 g, 9.8 mmol). Yield 2.59 g (91%), m.p. 55–63 °C (*E*/*Z* ratio *ca* 5 : 4 by ^{1}H NMR). Both stereoisomers were separated by column chromatography (chloroform–methanol, 100 : 2).

(E)-Dodecyl pyridin-2-yl ketoxime. M.p. 60–63 °C (ref.[4a] 58–63 °C). For $C_{18}H_{30}N_2O$ (290.5) calculated: 74.44% C, 10.41% H, 9.64% N; found: 74.58% C, 10.23% H, 9.63% N. ^{1}H NMR ($CDCl_3$): 0.87 t, 3 H, *J*(12′,11′) = 6.8 (H-12′); 1.24 bs, 18 H (H-11′–H-3′); 1.58 tt, 2 H, *J*(2′,1′) = *J*(2′,3′) = 7.7 (H-2′); 2.98 t, 2 H, *J*(1′,2′) = 7.7 (H-1′); 7.26 m, 1 H (H-5); 7.69 td, 1 H, *J*(4,5) = *J*(4,3) = 7.6, *J*(4,6) = 1.7 (H-4); 7.79 d, 1 H, *J*(3,4) = 8.0 (H-3); 8.22 s 1 H (OH); 8.63 d, 1 H, *J*(6,5) = 4.3 (H-6). ^{13}C NMR ($CDCl_3$): 14.8 s (C-12′); 23.4 s (C-11′); 25.3 s (C-10′); 27.0 s (C-9′); 30.0–30.6 m (C-8′–C-2′); 32.6 s (C-1′); 121.6 s (C-3); 124.2 s (C-5); 136.9 s (C-4); 149.7 s (C-6); 154.7 s (C-2); 161.6 s (C=NOH). IR (CCl_4): ν(OH) 3 257 (bridged), ν(OH) 3 594 (free).

(Z)-Dodecyl pyridin-2-yl ketoxime. M.p. 55–59 °C. For $C_{18}H_{30}N_2O$ (290.5) calculated: 74.44% C, 10.41% H, 9.64% N; found: 74.09% C, 10.23% H, 9.31% N. ^{1}H NMR ($CDCl_3$): 0.87 t, 3 H, *J*(12′,11′) = 6.8 (H-12′); 1.24 bs, 18 H (H-11′–H-3′); 1.62 tt, 2 H, *J*(2′,1′) = *J*(2′,3′) = 7.7 (H-2′); 2.67 t, 2 H, *J*(1′,2′) = 7.7 (H-1′); 7.41 dd, 1 H, *J*(5,4) = 7.4, *J*(5,6) = 4.4 (H-5); 7.51 d, 1 H, *J*(3,5) = 8.1 (H-3); 7.91 td, 1 H, *J*(4,3) = *J*(4,5) = 7.5, *J*(4,6) = 1.6 (H-4); 8.57 d, 1 H, *J*(6,5) = 4.9 (H-6). ^{13}C NMR ($CDCl_3$): 33.7 s (C-1′).

Dodecyl pyridin-3-yl ketoxime (**5e**). Prepared from ketone **3e** (2.10 g, 7.5 mmol). Crude product (*E*/*Z* ratio *ca* 4 : 1 by ^{1}H NMR) was purified by crystallization from ethanol.

(E)-Dodecyl pyridin-3-yl ketoxime. Yield 1.84 g (86%), m.p. 81.5–83 °C. For $C_{18}H_{30}N_2O$ (290.5) calculated: 74.44% C, 10.41% H, 9.64% N; found: 74.76% C, 10.51% H, 10.10% N. ^{1}H NMR ($CDCl_3$): 0.88 t, 3 H, *J*(12′,11′) = 7.0 (H-12′); 1.25 bs, 18 H (H-11′–H-3′); 1.57 tt, 2 H, *J*(2′,1′) = *J*(2′,3′) = 7.3 (H-2′); 2.82 t, 2 H, *J*(1′,2′) = 7.6 (H-1′); 7.32 dd, 1 H, *J*(5,4) = 7.9, *J*(5,6)

= 4.8 (H-5); 7.94 d, 1 H, *J* (4,5) = 8.0 (H-4); 8.61 d, 1 H, *J*(6,5) = 4.3 (H-6); 8.91 d, 1 H, *J*(2,6) = 1.2 (H-2); 9.75 s, 1 H (OH). ^{13}C NMR ($CDCl_3$): 14.8 s (C-12′); 23.4 s (C-11′); 26.5 s (C-10′); 27.0 s (C-9′); 30.0–30.5 m (C-8′–C-2′); 32.6 s (C-1′); 124.1 s (C-5); 132.7 s (C-3); 134.5 s (C-4); 148.3 s (C-6); 150.3 s (C-2); 157.9 s (C=NOH).

(Z)-Dodecyl pyridin-3-yl ketoxime. This compound was not isolated and the spectral characteristics were deduced from the spectra of an *E*/*Z* mixture. ^{1}H NMR ($CDCl_3$): 0.88 t, 3 H, *J*(12′,11′) = 7.0 (H-12′); 1.25 bs, 18 H (H-11′–H-3′); 1.46 m, 2 H (H-2′); 2.58 t, 2 H, *J*(1′,2′) = 7.8 (H-1′); 7.37 dd, 1H, *J*(5,4) = 8.2, *J*(5,6) = 4.3 (H-5); 7.83 d, 1 H, *J*(4,5) = 8.2 (H-4); 8.56 d, 1 H, *J*(6,5) = 4.3 (H-6); 8.73 s, 1 H (H-2); 9.29 s, 1 H (OH).^{13}C NMR ($CDCl_3$): 31.5 s (C-2′); 35.7 s (C-1′).

Dodecyl pyridin-4-yl ketoxime (**5f**). Prepared from ketone **3f** (0.98 g, 3.6 mmol). Crude product (*E*/*Z* ratio *ca* 4 : 1 by ^{1}H NMR) was purified by crystallization from ethanol.

(E)-Dodecyl pyridin-4-yl ketoxime. Yield 0.48 g (46%), m.p. 92–94 °C. For $C_{18}H_{30}N_2O$ (290.5) calculated: 74.44% C, 10.41% H, 9.64% N; found: 74.78% C, 10.58% H, 9.39% N. ^{1}H NMR ($CDCl_3$): 0.88 t, 3 H, *J*(12′,11′) = 6.8 (H-12′); 1.25 bs, 18 H (H-11′–H-3′); 1.55 tt, 2 H, *J*(2′,1′) = *J*(2′,3′) = 7.9 (H-2′); 2.79 t, 2 H, *J*(1′,2′) = 7.8 (H-1′); 7.52 d, 2 H, *J*(3,2) = *J*(5,6) = 5.9 (H-3, H-5); 8.63 d, 2 H, *J*(2,3) = *J*(6,5) = 5.9 (H-2, H-6); 9.15 s, 1 H (OH). ^{13}C NMR ($CDCl_3$): 14.8 s (C-12′); 23.4 s (C-11′); 26.0 s (C-10′); 26.5 s (C-9′); 27.1–30.5 m (C-8′–C-2′); 32.6 s (C-1′); 121.3 s (C-3, C-5); 144.9 s (C-4); 150.4 s (C-2, C-6); 157.8 s (C=NOH).

(Z)-Dodecyl pyridin-4-yl ketoxime. This compound was not isolated and the spectral characteristics were deduced from the spectra of an *E*/*Z* mixture. ^{1}H NMR ($CDCl_3$): 0.88 t, 3 H, *J*(12′,11′) = 6.8 (H-12′); 1.25 bs, 18 H (H-11′–H-3′); 1.44 tt, 2 H, *J*(2′,1′) = *J*(2′,3′) = 7.5 (H-2′); 2.52 t, 2 H, *J*(1′,2′) = 7.6 (H-1′); 7.33 d, 2 H, *J*(3,2) = *J*(5,6) = 6.0 (H-3, H-5); 8.57 s, 1 H (OH); 8.63 d, 2 H, *J*(2,3) = *J*(6,5) = 5.9 (H-2, H-6). ^{13}C NMR ($CDCl_3$): 14.8 s (C-12′); 23.4 s (C-11′); 26.0 s (C-10′); 26.9 s (C-9′); 27.1–30.5 m (C-8′–C-2′); 35.5 s (C-1′); 123.4 s (C-3, C-5); 142.4 s (C-4); 150.6 s (C-2, C-6); 157.4 s (C=NOH).

Quaternization of Methyl Pyridyl Ketoximes **5a**–**5c**

Methyl pyridyl ketoximes **5b** and **5c** (3.00 g, 22.0 mmol) and dodecyl bromide (9.22 g, 37.0 mmol) were heated in refluxing acetonitrile (100 ml) for 8 h. Evaporation of the solvent under reduced pressure afforded crude products which were purified by crystallization from ethanol. Methyl pyridin-2-yl ketoxime (**5a**) did not react under the above-mentioned conditions. The reaction in the sealed glass tube at 150 °C for 50 h led to a complex mixture of products. Unreacted starting compounds and methyl pyridin-2-yl ketone (**3a**) were isolated by column chromatography (chloroform–methanol, 10 : 1) from the reaction mixture. Similar results were also obtained with oxime **5a** and dodecyl bromide in the presence of an equimolar amount of potassium iodide[6] in acetone.

Methyl pyridin-2-yl ketone (**3a**). Isolated by column chromatography (chloroform–methanol, 10 : 1). ^{1}H NMR ($CDCl_3$): 2.95 s, 3 H (CH_3); 7.45 m, 1 H (H-5); 7.81 td, 1 H, *J*(4,3) = *J*(4,5) = 7.7, *J*(4,6) = 1.6 (H-4); 7.98 d, 1 H, *J*(3,4) = 8.2 (H-3); 8.63 dm, 1 H, *J*(4,3) = 5.5 (H-6).

1-Dodecyl-3-[1-(hydroxyimino)ethyl]pyridinium bromide (**2b**). Yield 6.33 g (75%), m.p. 118–120 °C. For $C_{19}H_{33}BrN_2O$ (385.3) calculated: 59.21% C, 8.63% H, 7.27% N; found: 59.16% C, 8.58% H, 7.22% N. ^{1}H NMR ($CDCl_3$): 0.86 t, 3 H, *J*(12′,11′) = 6.8 (H-12′); 1.23 bs, 18 H (H-11′–H-3′); 2.04 tt, 2 H (H-2′); 2.26 s, 3 H (CH_3-C=N); 4.96 t, 2 H, *J*(2′,1′) = 7.2 (H-1′); 8.15 m, 1 H (H-5); 8.63 d, 1 H, *J*(4,5) = 8.1 (H-4); 9.17 d, 1 H, *J*(6,5) = 5.5 (H-6); 9.39 s, 1 H (H-2); 11.12 s, 1 H (OH). ^{13}C NMR ($CDCl_3$): 12.7 s (CH_3C=NOH); 14.8 s (C-12′); 23.4 s

(C-11′); 26.9 s (C-10′); 29.9 s (C-9′); 30.2 s (C-8′–C-4′); 32.6 s (C-3′); 32.7 s (C-2′); 63.1 s (C-1′); 128.9 s (C-5); 138.5 s (C-3); 142.1 s (C-4); 142.5 s (C-6); 144.5 s (C-2); 149.6 s (C=NOH). pK_a = 10.1.

1-Dodecyl-4-[1-(hydroxyimino)ethyl]pyridinium bromide (**2c**). Yield 5.86 g (69%), m.p. 128–131 °C. For $C_{19}H_{33}BrN_2O$ (385.3) calculated: 59.21% C, 8.63% H, 7.27% N; found: 58.52% C, 8.77% H, 6.91% N. ^{1}H NMR ($CDCl_3$): 0.86 t, 3 H, *J*(12′,11′) = 7.0 (H-12′); 1.32 bs, 18 H (H-11′–H-3′); 2.03 m, 2 H (H-2′); 2.17 s, 3 H (CH_3-C=N); 4.83 t, 2 H, *J*(2′,1′) = 7.2 (H-1′); 8.15 d, 2 H, *J*(3,2) = *J*(5,6) = 6.6 (H-3, H-5); 9.24 d, 2 H, *J*(2,3) = *J*(6,5) = 6.5 (H-2, H-6); 11.68 s, 1 H (OH). ^{13}C NMR ($CDCl_3$): 11.8 s (CH_3C=NOH); 14.8 s (C-12′); 23.4 s (C-11′); 26.9 s (C-10′); 29.8 s (C-9′); 30.2 s (C-8′–C-4′); 32.4 s (C-3′); 32.6 s (C-2′); 62.1 s (C-1′); 124.5 s (C-3, C-5); 145.3 s (C-2, C-6); 150.6 s (C-4); 152.9 s (C=NOH). pK_a = 9.3.

Quaternization of Dodecyl Pyridyl Ketoximes **5d**–**5f**

Dodecyl pyridyl ketoximes **5d**–**5f** and methyl iodide (5–6 molar excess) were heated in ethanol to 45 °C. Evaporation of the solvent under reduced pressure afforded crude products which were purified by crystallization from acetone–ether. In the case of 2-[1-(hydroxyimino)tridecyl]-1-methylpyridinium iodide (**2g**), unreacted ketoxime **5d** was separated by column chromatography (chloroform–methanol–acetone–water, 30 : 5 : 5 : 1) before crystallization. Iodides **2g**–**2i** were converted to corresponding bromides **2d**–**2f** by anion exchange on Amberlite IRA-400 using the previously described procedure[3d].

2-[1-(Hydroxyimino)tridecyl]-1-methylpyridinium iodide (**2g**). Prepared from oxime **5d** (1.0 g, 3.5 mmol). Reaction time 70 h. Yield 0.39 g (23%), m.p. 80–85 °C. For $C_{19}H_{33}IN_2O$ (432.3) calculated: 52.78% C, 7.69% H, 6.48% N; found: 53.00% C, 7.64% H, 6.30% N. ^{1}H NMR ($CDCl_3$): 0.87 t, 3 H, *J*(12′,11′) = 6.5 (H-12′); 1.24 bs, 18 H (H-11′–H-3′); 1.44 tt, 2 H, *J*(2′,1′) = *J*(2′,3′) = 7.7 (H-2′); 2.82 t, 2 H, *J*(1′,2′) = 7.8 (H-1′); 4.46 s, 3 H (CH_3-N^+); 8.05 m, 2 H (H-5, H-4); 8.68 d, 1 H, *J*(3,4) = 7.6 (H-3); 9.55 d, 1 H, *J*(6,5) = 6.0 (H-6); 10.51 s, 1 H (OH). ^{13}C NMR ($CDCl_3$): 14.8 s (C-12′); 23.4 s (C-11′); 26.5 s (C-10′); 30.2 m (C-9′–C-2′); 32.6 s (C-1′); 49.5 s (CH_3-N^+); 128.4 s (C-3); 129.6 s (C-5); 146.9 s (C-4); 148.9 s (C-6); 151.5 s (C-2); 153.1 s (C=NOH).

3-[1-(Hydroxyimino)tridecyl]-1-methylpyridinium iodide (**2h**). Prepared from oxime **5e** (1.3 g, 4.5 mmol). Reaction time 20 h. Yield 1.4 g (68%), m.p. 98–101.5 °C. For $C_{19}H_{33}IN_2O$ (432.3) calculated: 52.78% C, 7.69% H, 6.48% N; found: 51.65% C, 7.52% H, 6.49% N. ^{1}H NMR ($CDCl_3$): 0.87 t, 3 H, *J*(12′,11′) = 6.5 (H-12′); 1.24 bs, 18 H (H-11′–H-3′); 1.46 m, 2 H (H-2′); 2.81 t, 2 H, *J*(1′,2′) = 7.9 (H-1′); 4.64 s, 3 H (CH_3-N^+); 8.11 dd, 1 H, *J*(5,4) = 8.0, *J*(5,6) = 6.2 (H-5); 8.54 d, 1 H, *J*(4,5) = 8.2 (H-4); 9.06 d, 1 H, *J*(6,5) = 5.9 (H-6); 9.24 s, 1 H (H-2); 9.93 s 1 H (OH). ^{13}C NMR ($CDCl_3$): 14.8 s (C-12′); 23.4 s (C-11′); 26.2 s (C-10′); 30.4 m (C-9′–C-2′); 32.6 s (C-1′); 51.1 s (CH_3-N^+); 129.0 s (C-5); 137.4 s (C-3); 142.2 s (C-4); 143.6 s (C-6); 145.3 s (C-2); 154.1 s (C=NOH).

4-[1-(Hydroxyimino)tridecyl]-1-methylpyridinium iodide (**2i**). Prepared from oxime **5f** (0.37 g, 1.28 mmol). Reaction time 40 h. Yield 0.25 g (63%), m.p. 117–120.5 °C. For $C_{19}H_{33}IN_2O$ (432.3) calculated: 52.78% C, 7.69% H, 6.48% N; found: 52.61% C, 7.49% H, 6.19% N. ^{1}H NMR ($CDCl_3$): 0.87 t, 3 H, *J*(12′,11′) = 6.6 (H-12′); 1.24 bs, 18 H (H-11′–H-3′); 1.41 tt, 2 H, *J*(2′,1′) = *J*(2′,3′) = 7.3 (H-2′); 2.71 t, 2 H, *J*(1′,2′) = 7.3 (H-1′); 4.58 s, 3 H (CH_3-N^+); 8.09 d, 2 H, *J*(3,2) = *J*(5,6) = 6.7 (H-3, H-5); 9.14 d, 2 H, *J*(2,3) = *J*(6,5) = 6.6 (H-2, H-6); 10.24 s, 1 H (OH). ^{13}C NMR ($CDCl_3$): 14.8 s (C-12′); 23.4 s (C-11′); 25.7 s (C-10′); 30.3 m (C-9′–C-2′); 32.6 s

(C-1′); 49.7 s (CH_3-N^+); 124.6 s (C-3, C-5); 146.2 s (C-2, C-6); 152.5 s (C-4); 154.9 s (C=NOH).

2-[1-(Hydroxyimino)tridecyl]-1-methylpyridinium bromide (**2d**). Prepared from iodide **2g** (0.34 g, 0.8 mmol). Yield 0.30 g (78%), m.p. 126–127 °C. For $C_{19}H_{33}BrN_2O$ (385.3) calculated: 59.22% C, 8.63% H, 7.27% N; found: 58.77% C, 8.76% H, 6.90% N. ^{1}H NMR ($CDCl_3$): 0.87 t, 3 H, *J*(12′,11′) = 6.6 (H-12′); 1.24 bs, 18 H (H-11′–H-3′); 1.43 tt, 2 H, *J*(2′,1′) = *J*(2′,3′) = 7.9 (H-2′); 2.79 t, 2 H, *J*(1′,2′) = 7.8 (H-1′); 4.49 s, 3 H (CH_3-N^+); 8.00 m, 2 H (H-5, H-4); 8.65 d, 1 H, *J*(3,4) = 7.9 (H-3); 9.78 d, 1 H, *J*(6,5) = 6.1 (H-6); 11.70 s, 1 H (OH). ^{13}C NMR ($CDCl_3$): 14.8 s (C-12′); 23.4 s (C-11′); 26.4 s (C-10′); 30.2 m (C-9′–C-2′); 32.6 s (C-1′); 48.8 s (CH_3-N^+); 128.0 s (C-3); 129.5 s (C-5); 146.1 s (C-4); 149.6 s (C-6); 151.8 s (C-2); 152.4 s (C=NOH). pK_a = 9.6.

3-[1-(Hydroxyimino)tridecyl]-1-methylpyridinium bromide (**2e**). Prepared from iodide **2h** (0.35 g, 0.8 mmol). Yield 0.37 g (84%), m.p. 106–108 °C. For $C_{19}H_{33}BrN_2O$ (385.3) calculated: 59.22% C, 8.63% H, 7.27% N; found: 59.20% C, 8.83% H, 7.01% N. ^{1}H NMR (DMSO-d_6): 0.85 t, 3 H, *J*(12′,11′) = 6.5 (H-12′); 1.23 bs, 18 H (H-11′–H-3′); 1.44 m, 2 H (H-2′); 2.79 t, 2 H, *J*(1′,2′) = 6.5 (H-1′); 4.41 s, 3 H (CH_3-N^+); 8.12 t, 1 H, *J*(5,4) = *J*(5,6) = 6.6 (H-5); 8.75 d, 1 H, *J*(4,5) = 7.9 (H-4); 8.98 d, 1 H, *J*(6,5) = 5.1 (H-6); 9.19 s, 1 H (H-2); 12.09 s, 1 H (OH). ^{13}C NMR (DMSO-d_6): 13.9 s (C-12′); 22.0 s (C-11′); 24.3 s (C-10′); 28.7 m (C-9′–C-2′); 31.4 s (C-1′); 48.2 s (CH_3-N^+); 127.5 s (C-5); 135.6 s (C-3); 140.9 s (C-4); 142.7 s (C-6); 144.8 s (C-2); 152.7 s (C=NOH). pK_a = 9.4.

4-[1-(Hydroxyimino)tridecyl]-1-methylpyridinium bromide (**2f**). Prepared from iodide **2i** (0.37 g, 0.9 mmol). Yield 0.34 g (98%), m.p. 134–135 °C. For $C_{19}H_{33}BrN_2O$ (385.3) calculated: 59.22% C, 8.63% H, 7.27% N; found: 59.02% C, 8.32% H, 7.29% N. ^{1}H NMR ($CDCl_3$): 0.88 t, 3 H, *J*(12′,11′) = 7.0 (H-12′); 1.24 bs, 18 H (H-11′–H-3′); 1.40 m, 2 H (H-2′); 2.68 t, 2 H, *J*(1′,2′) = 7.9 (H-1′); 4.61 s, 3 H (CH_3-N^+); 8.02 d, 2 H, *J*(3,2) = *J*(5,6) = 6.3 (H-3, H-5); 9.19 d, 2 H, *J*(2,3) = *J*(6,5) = 5.9 (H-2, H-6); 11.28 s, 1 H (OH). ^{13}C NMR ($CDCl_3$): 14.8 s (C-12′); 23.4 s (C-11′); 25.5 s (C-10′); 30.3 m (C-9′–C-2′); 32.6 s (C-1′); 49.2 s (CH_3-N^+); 124.3 s (C-3, C-5); 146.2 s (C-2, C-6); 152.7 s (C-4); 154.5 s (C=NOH). pK_a = 9.9.

Determination of pK_a

pK_a values were determined spectrophotometrically at two wavelengths (maxima of the =NOH and =NO^- form) using the described procedure[13].

Determination of log *P*

4-Nitrophenyl alkanoate was dissolved in octan-1-ol saturated with water. This solution (of known ester concentration) was shaken with redistilled water at 20 °C for 1 h. Then, the concentration of the 4-nitrophenyl ester in both phases was determined as follows: an aliquot amount of each phase was transferred into the spectrophotometric cell. An appropriate amount of water (with the aqueous phase) or methanol (with the organic phase) was added to obtain 1 500 µl of homogeneous solution. The excess of sodium hydroxide (500 µl of 4 M aqueous solution) was added to hydrolyze the 4-nitrophenyl ester; the reaction was over immediately. Concentration of the released 4-nitrophenoxide ion was determined spectrophotometrically at 400 nm. Four different ratios of water : octan-1-ol were used for the determination of partition coefficient *P* of each ester. The partition coefficient was obtained from the calculated ratios of the ester concentration in both phases using Horn procedure[14].

Kinetic Measurements

Solutions of salts **2** of the desired concentrations were prepared in an appropriate 0.05 M buffer. No changes in pH were observed during kinetic runs. The reactions were followed on a spectrophotometer Hewlett–Packard HP8452 equipped with a thermostatted multicell transport cell holder HP89075C maintaining the reaction temperature at 25.0 ± 0.1 °C. The reactions were initiated by injection of $8.0 \cdot 10^{-4}$ M PNPDPP solution in acetonitrile (50 µl) into the spectrophotometric cell containing 1 950 µl of the buffered solution of catalyst or by injection of $6.0 \cdot 10^{-3}$ M 4-nitrophenyl alkanoate solution in acetonitrile (5.5 µl) into the spectrophotometric cell containing 1 600 µl of the buffered solution of catalyst, the resulting concentration of the substrate being $2.0 \cdot 10^{-5}$ M in both cases. The reactions were monitored at the wavelength 400 nm (maximum of 4-nitrophenoxide absorption). The kinetics followed a first-order law in each case at least up to 95% conversion. The pseudo-first-order rate constants k_{obs} were obtained by non-linear regression analysis of the absorbance *vs* time data using software package Enzfitter[15]. The fit error of the rate constant did not exceed 5%.

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