
Reactions of 3-Substituted 1,2-Epoxypropanes with Pyridinium Salts. N-Alkylpyridinium Salts and Their Synthetic Potential

A. N. Karaseva, V. F. Mironov, V. V. Karlin, A. I. Konovalov, O. V. Tsepaeva, and E. R. Yunusov

Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, Kazan, Tatarstan, Russia

Received August 2, 2000

Abstract—1-Chloro-2,3-epoxypropane and 2,3-epoxypropyl carboxylates react with pyridinium carboxylates and phosphonates, yielding *N*-alkylated pyridinium salts.

2-Hydroxy-3-ammoniopropyl alkyl (or aryl) ethers and esters of the general formula **I** exhibit diverse pharmacological activity and are widely used in medicine. Pyridiniopropyl ethers and esters **II** are structural analogs of **I**, which combine hydroxypropyl and pyridinium salt fragments and are promising from the viewpoint of searching for new pharmacologically active compounds.

$$\begin{array}{c} \operatorname{ROCH_2-CH-CH_2-\mathring{\hspace{-.07cm} \text{N}}} \swarrow X^- \\ \operatorname{OH} \\ \operatorname{I} \\ \operatorname{RCOCH_2-CH-CH_2-\mathring{\hspace{-.07cm} \text{N}}} \searrow X^- \\ \operatorname{OH} \\ \operatorname{II} \end{array}$$

The present communication describes the synthesis of compounds **II** starting from 1-chloro-2,3-epoxypropane and 2,3-epoxypropyl carboxylates. Hayes *et al.* [1] reported on the preparation of pyridinium salts on the basis of epoxy derivatives [1]. *N*-(2-Hydroxycyclohexyl)pyridium salts **V** were obtained from 1,2-epoxycyclohexane (**III**) and pyridium perchlorates and *p*-toluenesulfonates. It was presumed that the reaction involves intermediate formation of oxonium ion like **IV** (Scheme 1).

We have studied the possibility of involving in this reaction substituted epoxy derivatives and pyridine salts with substituted carboxylic and phosphonic acids in order to extend its synthetic potential.

As substrates we used 1-chloro-2,3-epoxypropane (VI) and 2,3-epoxypropyl carboxylates, and the reagents were pyridine salts with 2-hydroxybenzoic, perfluoropentanoic, and α -hydroxyphenylacetic (mandelic) acids and 6-chloro-2-hydroxy-4-phenyl-2H-1,2 λ ⁵-benzoxaphosphinine 2-oxide (compounds VIIa–VIId).

Scheme 1.

Variation of the reaction conditions showed that the optimal temperature of the reaction of pyridinium salts VIIa–VIId with chloromethyloxirane VI is 18–20°C. In this case longer reaction time is compensated by the absence of by-products which could be formed at elevated temperature, and the yield of target products VIIIa–VIIId is nearly quantitative (Scheme 2). The structure of salts VIIIa–VIIId was proved by IR spectroscopy. The IR spectra of VIIIa–VIIId contained bands typical of hydroxy group and pyridinium ring (see Experimental).

Atom	Chemical shifts $\delta_{\mathbb{C}}$, ppm	Coupling constants J, Hz
C^o C^m C^p CH_2Cl $CHOH$ CH_2N^+ $COO^ CF_3$	146.68 br.s (br.d.m) 128.96 s (d.d.d.d) 147.08 s (d.m) 46.37 s (t.m) 71.01 s (d.m) 65.25 br.s (t.m) 162.36 br.t (br.t) 118.82 q.t (q.t)	191.2 (HC°) 175.6 (HC ^m), 7.5 (HC ^m 'CC ^m), 3.4 (HC°C ^m), 1.3 (HC°C ^m) 171.8 (HC°), 5.9–6.1 (HC°CC°) 151.8 (HC), 1.5 (HCC) 147.1 (HC), 3.0 (HOC), 3.0 (HCC) 145.6 (HC), 4.5 (HCC) 23.9 (FCC) 288.0 (FC), 33.6 (FCC)
CF ₂ COO ⁻ CF ₃ CF ₂ CF ₂ CCOO	110.72 br.t.t (br.t.t) 110.22 br.t.q.t (br.t.q.t) ^b 112.05 br.t.t (br.t.t) ^c	265.7–266.5 (FC), 36.0 (FCC) 268.5 (FC), 35.0–38.0 (FCC), 35.0–38.0 (FCC) 266.0 (FC), 32.5 (FCC), 32.5 (FCC)

Table 1. ¹³C–{¹H} and ¹³C NMR spectra of N-(3-chloro-2-hydroxypropyl)pyridinium perfluoropentanoate (VIIIb)

The structure of products **VIIIa–VIIId** was also confirmed by 13 C NMR spectroscopy using salt **VIIIb** as an example (Table 1). Its 13 C NMR spectrum contains signals corresponding to the opened oxirane ring, whose multiplicities are consistent with the proton environment. The relatively downfield position of the CH₂N⁺ signal ($\delta_{\rm C}$ 65.25 ppm against usual value 44.6–60.8 ppm [2]) should be noted, which may be explained by joint deshielding effect of the β -hydroxy group and pyridinium fragment. Signals from carbon nuclei of the perfluoropentanoate ion appear in a weak field and are split due to coupling with fluorine through one ($^1J_{\rm C,F}=260$ –290 Hz) and two bonds ($^2J_{\rm C,F}=26$ –34 Hz). Signals from carbon atoms of the pyridine ring were identified on the basis of published

Scheme 2.

 $X = 2\text{-HOC}_6H_4COO$ (a), C_4F_9COO (b), PhCH(OH)COO (c),

data [2–4]. The chemical shifts and coupling constants were in full agreement with those reported for *N*-alkyl-pyridinium derivatives.

Pyridinium salts VIIIa-VIIId possess a fairly labile chlorine atom and are therefore convenient reagents for preparation of carboxylic acid esters via alkylation of the corresponding potassium carboxylates. By reactions of potassium pyridine-3-carboxylate (IX) with compounds VIIIa, VIIIb, and VIIId on moderate heating in DMF (50-70°C) we obtained novel esters Xa-Xc in quantitative yield (Scheme 3). Their structure was confirmed by IR spectroscopy and also by the ¹³C NMR spectra of products Xa and Xc (Tables 2, 3). Compounds Xa-Xc showed in the IR spectra a strong band at 1730-1740 cm⁻¹, which is typical of ester carbonyl. The ¹³C NMR spectra were interpreted with account taken of the above data, signal multiplicities, and also published data on derivatives of pyridine, nicotinic acid, salicylic acid [2-4], and 6-chloro-2-hydroxy-4phenyl-2H-1, $2\lambda^5$ -benzoxaphosphinine 2-oxide [5], including the corresponding anions. Mild conditions of the reaction shown in Scheme 3 allowed us to effect esterification of carboxylic acids having labile functional groups in the carbon chain. In such a way, from sodium (Z)-12-hydroxy-9-octadecenoate (XI) we synthesized ester XIIa (Scheme 4).

Another group of epoxy derivatives examined in the present work included 2,3-epoxypropyl carboxylates. As with chloromethyloxirane VI, opening of the epoxy ring in 2,3-epoxypropyl esters occurs under mild conditions, and the products were formed in quantitative yields. No tarring of the reaction

^a Hereinafter, the splitting mode in the ¹³C NMR spectrum is given in parentheses.

^b Apparent triplet of quintets; approximate values of ²J_{F,C} are given because of signal overlap.

Apparent triplet of sextets.

Scheme 3.

$$\begin{array}{c} \longrightarrow & \text{CH}_3(\text{CH}_2)_5 - \text{CH} - \text{CH}_2\text{CH} = \text{CH}(\text{CH}_2)_7\text{COOCH}_2 - \text{CH} - \text{CH}_2 - \overset{\dagger}{\text{COO}} \\ \text{OH} & \text{OH} \\ \end{array}$$

Scheme 5.

XIIa, XIIb, XIId

mixtures was observed. Starting from ester **XIII** and pyridinium salts **VIIa**, **VIIb**, and **VIId**, we obtained 3-pyridiniopropyl (*Z*)-12-hydroxy-9-octadecenoates **XIIa**, **XIIb**, and **XIId** (Scheme 5). Their structure was confirmed by the data of elemental analysis and IR spectroscopy.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples prepared as films between KBr plates. The 13 C and 13 C- $\{^{1}$ H $\}$ NMR spectra were obtained on a Bruker MSL-400 instrument operating at 100.6 MHz in methanol- d_4 at 35°C. The reaction mixtures and products were analyzed by TLC on Silufol plates (Czechia, Kavalier) using MeOH–AcOH (1:3) as eluent; spots were visualized under UV light and with iodine vapor.

Pyridinium salts **VIIa–VIIc** were prepared by heating equimolar amounts of pyridine and the corresponding acid in dry diethyl ether. 2,3-Epoxypropyl (*Z*)-12-hydroxy-9-octadecenoate (**XIII**) was prepared by the procedure reported in [6].

Reaction of 1-chloro-2,3-epoxypropane (VI) with pyridinium 2-hydroxybenzoate (VIIa). A mixture of 1.8 ml (19.5 mmol) of chloromethyloxirane **VI** and 5 g (23 mmol) of salt **VIIa** in 5 ml of pyridine was kept for 2 days at 20°C until it became homogeneous. The solvent was distilled off under reduced pressure to obtain 6.7 g of 1-(3-chloro-2-hydroxypropyl)pyridinium 2-hydroxybenzoate (**VIIIa**) as an oily substance. R_f 0.44. IR spectrum, v, cm⁻¹: 665, 685, 710, 725, 1100, 1130, 1145, 1163, 1193, 1220, 1255, 1300, 1330, 1386, 1460, 1489; 1590, 1612, 1632, 1675, 1720 sh (C=N, C=C, COO⁻); 2730–2800, 2860–2880, 2930, 2970, 3020–3030 sh, 3060–3070,

Atom	Chemical shifts $\delta_{\mathbb{C}}$, ppm	Coupling constants $J_{C,H}$, Hz
C^1	150.86 s (d.d.d)	181.3 (HC ¹), 11.3(HC ⁵ HC ¹), 5.5 (HC ³ CC ¹)
C^2	132.21 s (m) or 126.96 s (br.d.d)	a
C^3	138.46 s (d.d.d)	$165.9 \text{ (HC}^3), 5.5 \text{ (HC}^1\text{CC}^3), 6.3 \text{ (HC}^5\text{CC}^3)$
$ \begin{array}{c} C^1 \\ C^2 \\ C^3 \\ C^4 \\ C^5 \end{array} $	124.41 s (br.d.d)	$166.6 \text{ (HC}^4), 7.8-7.9 \text{ (HC}^5\text{C}^4)$
C^5	151.73 br.s (d.d.d.d)	$179.6 \text{ (HC}^5), 11.0 \text{ (HC}^1\text{HC}^5), 7.3 \text{ (HC}^3\text{CC}^5), 3.6–3.7 \text{ (HC}^4\text{C}^5)$
C^o	146.40 br.s (br.d.m)	190.7–191.2 (HC ^o)
\mathbf{C}^m	128.70 br.s (br.d.m)	175.0 (HC ^m), 7.4 (HC ^m 'CC ^m), 3.2 (HC ^o C ^m)
\mathbf{C}^p	146.66 br.s (br.d.t)	172.2 (HC p), 6.2 (HC o CC p)
C^9	162.34 s (br.d.d)	$7.8-8.0 \text{ (HC}^{13}\text{CC}^9), 7.8-8.0 \text{ (HC}^{13}\text{CC}^9)$
C^{10}	119.57 s (m)	_
C^{11}	131.35 s (d.d)	158.3 (HC ¹¹), 8.7–8.8 (HC ¹³ CC ¹¹)
C^{12}	118.78 s (d.d)	$161.3 \text{ (HC}^{12}), 8.1 \text{ (HC}^{14}\text{CC}^{12})$
C^{13}	133.35 s (d.d)	158.0 (HC ¹³), 9.1–9.2 (HC ¹¹ CC ¹³)
C^{14}	117.05 s (d.d)	159.7 (HC^{14}), 8.1–8.2 ($HC^{12}CC^{14}$)
OCH ₂	67.13 s (br.t)	149.5 (HC)
CHOH	69.16 s (br.d)	146.5 (HC)
CH_2N^+	64.99 s (br.t)	145.3 (HC)
COO-	175.06 s (br.m)	_
COO	165.85 s (br.m)	_

Table 2. ¹³C–{ ¹H} and ¹³C NMR spectra of 1-(2-hydroxy-3-nicotinoyloxypropyl)pyridinium 2-hydroxybenzoate (**Xa**)

3080, 3080–3090, 3140 (=C-H); 3160–3230 (OH). Found, %: C 57.75; H 4.98; N 4.05. $C_{15}H_{16}CINO_4$. Calculated, %: C 58.15; H 5.4; N 4.52.

Salts **VIIIb–VIIId** were synthesized in a similar way. The products were oily substances.

1-(3-Chloro-2-hydroxypropyl)pyridinium perfluoropentanoate (VIIIb) was synthesized from 2.69 g (29.1 mmol) of chloromethyloxirane **VI** and 10 g (29.2 mmol) of salt **VIIb**. Yield 11.36 g. $R_{\rm f}$ 0.37. IR spectrum, ν , cm⁻¹: 690, 715, 745, 775, 809, 870, 885, 912, 1025 (C₅H₅N), 1060, 1135 (C-OH), 1160, 1190– 1210 (C₅H₅N, CF), 1215 (CF), 1240–1245, 1300, 1345 (C-OH), 1389, 1435, 1450, 1495 (C₅H₅N), 1590, 1660 (C=N, C=C), 1680–1695 (COO⁻), 3050–3100 (=C-H), 3230 (OH).

1-(3-Chloro-2-hydroxypropyl)pyridinium α-hydroxyphenylacetate (VIIIc) was synthesized from 7 ml (75.7 mmol) of chloromethyloxirane VI and 20 g (86.5 mmol) of salt VIIc. Yield 20.6 g. IR spectrum, ν, cm⁻¹: 685, 705, 740, 765, 1030, 1065, 1095–1100, 1120, 1175–1190, 1210–1225, 1265, 1310, 1340–1360, 1455, 1495; 1580, 1610–1620, 1632 sh (C=N, C=C), 1741 (COO⁻), 2700–2750, 2850–2950, 2970, 3035, 3065, 3090–3100 (=C−H); 3150–3250 (OH). Found, %: C 58.64; H 4.99; N 4.14. $C_{16}H_{18}CINO_4$. Calculated, %: C 58.94; H 5.01; N 4.17.

1-(3-Chloro-2-hydroxypropyl)pyridinium 6-chloro-2-oxo-4-phenyl-2*H*-1,2 λ^5 -benzoxaphosphinin-2-olate (VIIId) was synthesized from 0.6 ml (6.49 mmol) of chloromethyloxirane VI and 2.5 g (6.72 mmol) of salt VIId. Yield 3.1 g. R_f 0.67. IR spectrum, ν , cm⁻¹: 536, 570, 615, 650, 675, 688, 705, 725, 750, 765, 810, 825, 870, 950; 1035, 1075, 1120, 1155, 1195 sh, 1210–1240, 1230, 1270 sh (POC, C–OH, P=O); 1340 (C–OH); 1380, 1400, 1450, 1490 (δC–H); 1550, 1590, 1640 (C=N, C=C, COO), 2670–2700, 2720–2760, 3040–3200 (=C–H), 3300–3350 (OH). Found, %: N 2.84; P 6.17. C₂₂H₂₀Cl₂NO₄P. Calculated, %: N 3.01; P 6.68.

Reaction of potassium 3-pyridinecarboxylate (IX) with pyridinium salt (VIIIa). A mixture of 1 g (6.2 mmol) of potassium salt IX, 1.92 g (6.2 mmol) of pyridinium salt VIIIa, and 20 ml of DMF was heated for 5 h at 70°C. The solvent was distilled off under reduced pressure (12 mm), the residue was dissolved in methanol heated to 50°C, the precipitate of potassium chloride was filtered off, and the filtrate was evaporated under reduced pressure to isolate 1.91 g of 1-(2-hydroxy-3-nicotinoyloxypropyl)pyridinium 2-hydroxybenzoate (Xa) as an oily substance. R_f 0.28. IR spectrum, v, cm⁻¹: 745, 765, 1035, 1260, 1285–1290, 1330, 1460, 1490; 1592, 1617, 1631, 1670 (C=N, C=C, COO⁻), 1730 (C=O); 2830–2840,

^a Superposition with a component of the C^{11} signal; J = 6.6 ($HC^{12}CC^{10}$), 6.6 Hz ($HC^{14}CC^{10}$).

Table 3. ¹³ C–{ ¹ H} and ¹³ C NMR spectra of 1-(2-hydroxy-3-nicotinoyloxypropyl)pyridinium 6-chloro-2-oxo-4-phenyl-
$2H-1,2\lambda^5$ -benzoxaphosphinine-2-olate (Xc)

Atom	Chemical shifts $\delta_{\rm C}$, ppm	Coupling constants J, Hz
C ¹	150.94 br.s (d.d.d)	182.0 (HC ¹), 11.0–11.5 (HC ⁵ HC ¹), 5.5 (HC ³ CC ¹)
C^2	127.59 br.s (br.m)	_
C^3	138.32 br.s (br.d.d.d)	$166.6 \text{ (HC}^3), 5.9-6.0 \text{ (HC}^1\text{CC}^3), 5.9-6.0 \text{ (HC}^5\text{CC}^3)$
$ \begin{array}{c} C^2 \\ C^3 \\ C^4 \\ C^5 \end{array} $	124.83 s (br.d.d)	$166.5 \text{ (HC}^4), 7.8 \text{ (HC}^5\text{C}^4)$
	151.16 br.s (br.d.d.d)	$179.9 \text{ (HC}^5), 12.0 \text{ (HC}^1\text{HC}^5), 7.3 \text{ (HC}^3\text{CC}^5)$
C^o	146.54 br.s (br.d.m)	190.1 (HC ^o)
C^m	128.73 s (br.d.d.d)	175.0 (HC ^m), 7.0–8.0 (HC ^m 'CC ^m), 3.5 (HC ^o C ^m)
\mathbf{C}^p	146.54 br.s (br.d.m)	172.0 (HC p), 5.9 (HC o CC p)
$ C^6 $ $ C^7 $	122.50 br.d (br.d.d)	165.9 (PC), 158.6 (HC)
C^7	149.02 br.s (br.m)	_
C_8	126.09 br.d (br.d.d.d)	15.8 (PCCC ⁸), 8.3 (HC ⁶ CC ⁸), 5.4 (HC ¹⁰ CC ⁸)
C^9	152.86 br.d (br.m)	6.6 (POC^9)
C^{10}	121.76 br.d (d.d)	165.0 (HC ¹⁰), 6.4 (POCC ¹⁰)
C^{11}	130.24 s (d.d)	167.7 (HC ¹¹), 6.3 (HC ¹³ CC ¹¹)
C^{12}	127.67 s (d.d.d)	11.8 ($HC^{10}CC^{12}$), 3.5 ($HC^{11}C^{12}$), 3.5 ($HC^{13}C^{12}$)
C^{13}	128.58 s (d.d)	$164.3 \text{ (HC}^{13}), 5.5 \text{ (HC}^{11}\text{CC}^{13})$
C^{14}	140.44 br.d (br.d.d.t)	$16.7 \text{ (POCC}^{14}), 7.5 \text{ (HC}^{16}\text{CC}^{14}), 6.0 \text{ (HC}^{6}\text{CC}^{14})$
C^{15}	129.27 s (br.d.d.d)	159.7 (HC ¹⁵), $6.8-6.9$ (HC ¹⁵ CC ¹⁵), $6.8-6.9$ (HC ¹⁷ CC ¹⁵)
C^{16}	129.49 s (d.d.d)	161.6 (HC ¹⁶), 7.5 (HC ¹⁶ CC ¹⁶), 1.8 (HCC)
C^{17}	129.31 s (d.t)	$161.2 \text{ (HC}^{17}), 7.7 \text{ (HC}^{15}\text{CC}^{17})$
OCH_2	65.34 br.s (br.t)	146.4–147.0 (HC)
CHOH	71.66 s (br.d)	144.7 (HC)
CH_2N^+	64.0 s (br.t)	143.2–144.0 (HC)
COO	166.27 br.s (br.m)	_
	<u> </u>	

2940–2950, 3030–3040 sh, 3070, 3090–3100, 3140 (C–H); 3300–3350 (OH). Found, %: C 63.26; H 4.98; N 6.27. $C_{21}H_{20}N_2O_6$. Calculated, %: C 63.63; H 5.05; N 7.07.

Following the above procedure, the reaction of 1.47 g (9.13 mmol) of potassium salt **IX** with 4.23 g (9.13 mmol) of pyridinium salt **VIIId** gave 5.03 g of 1-(2-hydroxy-3-nicotinoyloxypropyl)pyridinium 6-chloro-2-oxo-4-phenyl-2H-1,2 λ ⁵-benzoxaphosphinin-2-olate (**Xc**) as an oily substance. R_f 0.21. IR spectrum, v, cm⁻¹: 540, 570, 675, 690, 705, 725, 745, 755, 810, 830, 880, 950, 1030, 1080–1090, 1120, 1140–1152, 1220–1245, 1282 (P=O), 1336, 1386, 1425, 1444, 1473, 1495, 1505 sh, 1551, 1592, 1610 sh, 1628, 1660–1673, 1730, 2750–2780, 2870, 2930, 2960, 2980, 3015, 3030–3040, 3060–3070, 3090, 3200, 3350 sh. Found, %: C 57.38; H 4.89; N 5.69; Cl 6.98. $C_{24}H_{24}ClN_2O_6P$. Calculated, %: C 57.31; H 4.77; N 5.57; Cl 7.06.

Likewise, from 6 g (37.27 mmol) of potassium salt **IX** and 16.23 g (37.27 mmol) of pyridinium salt **VIIIb** in 140 ml of DMF we obtained 18.5 g of

1-(2-hydroxy-3-nicotinoyloxypropyl)pyridinium pentafluoropentanoate (**Xb**) as an oily substance. $R_{\rm f}$ 0.29. IR spectrum, v, cm $^{-1}$: 505, 534, 565, 660, 686, 705–710, 740, 765, 800, 884, 1030, 1133, 1195–1205, 1210, 1230–1240, 1280, 1340, 1380, 1420, 1490, 1586, 1600–1610, 1631, 1669–1683, 1720, 1860–2870, 2925–2980, 3040, 3060–3070, 3080–3090, 3220–3260 (OH). Found, %: C 43.89; H 3.11. $\rm C_{19}H_{15}F_{9}N_{2}O_{5}$. Calculated, %: C 43.67; H 2.87.

Reaction of compound VIIIa with sodium (*Z*)-12-hydroxy-9-octadecenoate (*XI*). A mixture of 0.87 g (2.97 mmol) of compound *VIIIa* and 1 g (2.97 mmol) of salt *XI* in 10 ml of DMF was heated for 3 h at 70°C. It was then poured into water, and the product was extracted into 1-butanol. The extract was evaporated under reduced pressure (12 mm) to obtain 1.87 g of 1-[2-hydroxy-3-[(*Z*)-12-hydroxy-9-octadecenoyloxy]propyl]pyridinium 2-hydroxybenzoate (*XIIa*) as an oily substance. R_f 0.31. IR spectrum, v, cm⁻¹: 670, 680, 705–710, 760, 855, 865, 1040, 1090, 1145, 1164, 1190 (C-OH, aliph.), 1220, 1250–1260 (C-OH, arom.), 1295–1310, 1330–1345,

1385, 1410 sh, 1420 sh, 1465, 1485, 1565–1580 sh, 1590, 1615, 1630, 1680 (C=C, COO⁻), 1710, 1725–1740 (C=O), 3020–3140 (=C-H), 2600–2800, 3200–3300 (OH). Found, %: C 69.03; H 8.43. $C_{33}H_{49}NO_7$. Calculated, %: C 69.33; H 8.63.

Reaction of 2,3-epoxypropyl (Z)-12-hydroxy-9-octadecenoate (XIII) with salt VIIa. A mixture of 1 g (2.79 mmol) of ester XIII and 0.47 g (2.79 mmol) of salt VIIa in 10 ml of pyridine was kept for 2 days at 20°C (until the reaction was complete according to the TLC data). The solvent was distilled off under reduced pressure (12 mm) to obtain 1.45 g of oily pyridinium salt XIIa.

1-[2-Hydroxy-3-[(Z)-12-hydroxy-9-octadecenoyloxy]propyl]pyridinium perfluoropentanoate (XIIb) was obtained in a similar way from 2 g (5.83 mmol) of salt **VIIb** and 2.09 g (5.83 mmol) of ester **XIII**. Yield 3.97 g. Oily substance, $R_{\rm f}$ 0.18. IR spectrum, v, cm⁻¹: 690, 720, 730, 750, 760, 780, 812, 870, 887, 1030, 1060, 1135 (C-OH), 1160–1170, 1190–1210 (C-F), 1215, 1235–1245 (C-F), 1300, 1345 (C-OH), 1382, 1480, 1493, 1585, 1640, 1680 sh, 1690 (C=C, COO), 1730–1740 (C=O); 3010–3020, 3070, 3095, 3140 (=C-H); 3350 (OH). Found, %: C 52.05; H 6.17. $C_{30}H_{44}F_{9}NO_{6}$. Calculated, %: C 52.55; H 6.47.

1-[2-Hydroxy-3-[(Z)-12-hydroxy-9-octadecenoyloxy]propyl]pyridinium 6-chloro-2-oxo-4-phenyl-2H-1,2 λ^5 -benzoxaphosphinin-2-olate (XIId) was synthesized in a similar way from 2 g (5.36 mmol) of salt **VIId** and 1.92 g (5.36 mmol) of ester **XIII**. Yield 3.43 g. Oily substance, R_f 0.67. IR spectrum, ν , cm⁻¹:

1082 (C-OH, POC); 1120, 1166, 1170–1190, 1230–1240, 1250 sh, 1280 (POC, POO), 1340, 1400, 1460, 1472, 1495; 1555, 1580, 1595, 1607, 1640 (C=C), 1740 (C=O); 3015–3040, 3075, 3090–3100, 3130–3140 (=C-H), 3230–3240 (OH). Found, %: C 63.98; H 7.17. $C_{40}H_{53}CINO_7P$. Calculated, %: C 64.18; N 7.78.

REFERENCES

- 1. Hayes, F.N., King, L.C., and Peterson, D.E., *J. Am. Chem. Soc.*, 1956, vol. 78, no. 6, pp. 2527–2528.
- Breitmaier, E. and Voelter, W., Carbon-13 NMR Spectroscopy. High-Resolution Methods and Applications in Organic Chemistry and Biochemistry, Weinheim: VCH, 1987.
- 3. Denisov, A.Yu., Mamatyuk, V.I., and Shkurko, O.P., *Khim. Geterotsikl. Soedin.*, 1984, no. 9, pp. 1223–1230.
- Denisov, A.Yu. and Mamatyuk, V.I., Spin-spinovoe vzaimodeistvie ¹³C-¹³C i ¹³C-¹H v spektrakh YaMR organicheskikh soedinenii (¹³C-¹³C and ¹³C-¹H Spin-Spin Coupling in NMR Spectra of Organic Compounds), Novosibirsk: Novosib. Inst. Org. Khim. Sib. Otd. Akad. Nauk SSSR, 1989, pp. 366–389.
- Mironov, V.F., Konovalov, A.I., Litvinov, I.A., Gubaidullin, A.T., Petrov, R.R., Shtyrlina, A.A., Zyablikova, T.A., Musin, R.Z., Azancheev, N.M., and Il'yasov, A.V., *Russ. J. Gen. Chem.*, 1998, vol. 68, no. 9, pp. 1414–1442.
- Macrker, G., Saggese, J., and Fort, W.S., J. Am. Oil Chem. Soc., 1961, vol. 38, pp. 194–198; Chem. Abstr., 1961, vol. 55, p. 13878i.