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NEW COMPLEXING SURFACTANTS. SYNTHESES OF 4-ALKOXYPYRIDINES AND BIPYRIDINES

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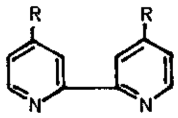
Abstract - Some of the long chain 4-alkoxypyridines 2, 4-alkoxy- 3 and 4,4'-dialkoxy-2,2'-bipyridines 1 were synthesized as the new complexing surfactants.

Recently much attention has been paid to the surfactant complexes of ruthenium with 1 where R was the ester group e.g. $-COOC_{18}H_{37}$ as the possible catalyst of water photolysis for the energy storage system[1,2].



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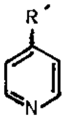

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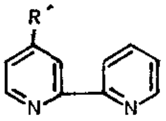

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where: $R = OC_4H_9$ 1a ; $OC_{12}H_{25}$ 1b ; $OC_{18}H_{37}$ 1c
$R' = OC_{12}H_{25}$ 2a or 3a ; $O-(CH_2-CH_2O)_4-C_4H_9$ 2b or 3b

It was found, however, that the hydrolysis of the ester group occured during the photolysis. Gains et al.[2] suggested that the alkyl derivatives of 1 should be more stable. In our opinion the alkoxy derivatives of 1 should be also suitable for such purpose as well. On the other hand, our interest in the oxidative deetherification of hydroquinone ethers to the biologically important quinones with argentic oxide in the presence of pyridine derivatives[3] led us to find the suitable surfactant ligands. With both purposes in mind, we synthesized unknown 4-alkoxypyridines (2) and 2,2'-bipyridines (1 and 3).

4-Alkoxypyridines 2 and 4,4'-dialkoxy-2,2'-bipyridines 1 were prepared from the corresponding N-oxides and 4,4'-dialkoxy-2,2'-bipyridine 1,1'-dioxydes were obtained in the reaction of sodium alkoxides in the DMSO-THF mixture from 4-nitropyridine 1-oxide and 4,4'-dinitro-2,2'-bipyridine 1,1'-dioxide[4], respectively.

2,2'-Bipyridine 1-oxide was obtained from the partial oxidation of 2,2'-bipyridine with hydrogen peroxide in acetic acic monitored by TLC analogously as reported in literature[5]. After evaporation of acetic acid and peroxides followed by neutralization with ammonium carbonate the excess of 2,2'-bipyridine was washed out with benzene. 2,2'-Bipyridine 1-oxide was extracted with chloroform from the remaining solution, then nitrated to give 4-nitro-2,2'-bipyridine 1-oxide as the sole product in 67% yield. This procedure gave an essential yield improvement compared to 22% yield reported by Jones et al.[6].

4-Nitro-2,2'-bipyridine 1-oxide was refluxed with phosphorus trichloride in chloroform for 2.5 h. 4-Nitro-2,2'-bipyridine reacted with sodium alkoxides gave the desired alkoxyderivatives 3.

All obtained 2,2'-bipyridine derivatives gave the characteristic complexes with Fe(II) salts. The formed complexes in the cases of 1a-c and 3b were soluble in benzene and chloroform and could be extracted from water with these solvents. Except partially soluble oxyethylene derivatives, the ligands were insoluble in water.

The experimental results and properties of the products obtained are listed below. All the new compounds gave satisfactory elemental analyses.

1a was recrystallized from methanol, 81% yield, m.p. 95°C, ir(KBr) 1243, 1030 (C-O-C) cm^{-1}, NMR ($CDCl_3$) δ (ppm) 1.32 (t, J=7 Hz, $-CH_3$) ; 1.60 - 2.27 (m, $-CH_2CH_2-$) ; 4.42 (t, J=7 Hz, $-OCH_2-$) ; 7.07 (dd, J=6 and 2 Hz, 5-H, and 5'-H); 8.22 (d, J=2 Hz, 3-H and 3'-H) ; 8.71 (d, J=6 Hz, 6-H and 6'-H).

1a dioxide, recrystallized from acetone, 23% yield, m.p. 152°C, ir (KBr) 1240, 1032 (C-O-C) and 1200 (N-O) cm^{-1}, NMR ($CDCl_3$) δ (ppm) 1.31 (t, J=7 Hz, $-CH_3$); 1.67 - 2.27 (m, $-CH_2CH_2-$) ; 4.40 (t, J=7 Hz, $-OCH_2-$) ; 7.30 (dd, J=4 and 7.5 Hz, 5-H and 5'-H) ; 7.72 (d, J=4 Hz, 3-H, and 3'-H) ; 8.60 (d, J=7.5 Hz, 6-H and 6'-H).

1b, recrystallized from hexane, 50% yield, m.p. 96-97°C, ir(KBr) 1243, 1022 (C-O-C) cm^{-1}, NMR ($CDCl_3$) δ (ppm) 1.14 (t, J=6 Hz, $-CH_3$); 1.69 (m, $18xCH_2$) ; 2.19 (m, $-OCH_2\underline{CH_2}-$) ; 4.47 (t, J=6 Hz, $-OCH_2-$) ; 7.12 (dd, J=5 and 2.5 Hz, 5-H and 5'-H); 8.25 (d, J=2.5 Hz, 3-H and 3'-H) ; 8.75 (d , J=5 Hz, 6-H, and 6'-H).

1b dioxide, recrystallized from ethanol, 44% yield, m.p. 143-145°C, ir(KBr) 1240, 1025 (C-O-C) and 1215, 1200 (N-O) cm^{-1}, NMR ($CDCl_3$) δ (ppm) 1.25 (t, J=6 Hz,

$-CH_3$) ; 1.65 (m, 18xCH_2); 2.11 (m, $-OCH_2\underline{CH_2}-$) ; 4.37 (t, J=6 Hz, $-OCH_2-$) ; 7.26 (dd, J=8 and 3 Hz, 5-H and 5´-H) ; 7.75 (d, J=3 Hz, 3-H and 3´-H); 8.55 (d, J=8 Hz, 6-H and 6´-H).

1c, recrystallized from iso-octane, 67% yield, m.p. 100-101°C, ir (KBr) 1245, 1022 (C-O-C) cm^{-1}, NMR ($CDCl_3$) δ (ppm) 0.81 (m, $-CH_3$); 1.27 (m, 30xCH_2); 1.80 (m, $-OCH_2\underline{CH_2}-$); 4.10 (t, J=7 Hz, $-OCH_2-$); 6.74 (dd, J=6 and 2.5 Hz, 5-H and 5´-H); 7.90 (d, J=2.5 Hz, 3-H and 3´-H); 8.37 (d, J=6 Hz, 6-H and 6´-H).

1c dioxide, recrystellized from acetonitrile, 44% yield, m.p. 108-110°C, ir (KBr) 1240, 1032 (C-O-C) and 1215, 1200 (N-O) cm^{-1}, NMR ($CDCl_3$) δ (ppm) 0.88 (m, $-CH_3$); 1.27 (m, 30xCH_2); 1.72 (m, $-OCH_2\underline{CH_2}$); 4.07 (t, J=7 Hz, $-OCH_2-$); 6.85 (dd, J=7 and 3 Hz, 5-H and 5´-H) ; 7.49 (d, J=3 Hz, 3-H and 3´-H) ; 8.13 (d, J=7 Hz, 6-H and 6´-H).

2a, recrystallized from pentane, 81% yield, m.p. 34-35°C, ir (CCl_4) 1286, 1025 (C-O-C) cm^{-1}, NMR (CCl_4) δ (ppm) 1.15 (m, $-CH_3$); 1.56 (m, 9xCH_2); 1.98 (m, $-OCH_2\underline{CH_2}-$) ; 4.18 (t, J=7 Hz, $-OCH_2-$); 6.86 (d, J=5.5 Hz; 3 and 5-H) ; 8.46 (d, J= 5.5 Hz, 2- and 6-H).

2a oxide, recrystallized from iso-octane, 72% yield, m.p. 74-75°C, ir (KBr) 1290, 1030 (C-O-C) and 1220 (N-O) cm^{-1}, NMR ($CDCl_3$) δ (ppm) 1.23 (t, J=6 Hz, $-CH_3$); 1.63 (m, 9xCH_2); 2.12 (m, $-OCH_2\underline{CH_2}-$); 4.36 (t, J=6 Hz, $-OCH_2-$); 7.12 (d, J=7,5 Hz, 3- and 5-H); 8.43 (d, J=7.5 Hz, 2- and 6-H).

2b, oil, chromatographied on basic Al_2O_3 (Fluka) with $CHCl_3$, TLC ($CHCl_3$-MeOH, 20:1 v/v) R_f= 0.62, purity checked by GLPC, ir (film) 1286, 1055 (C-O-C, aromat.) and 1122 (C-O-C oxyethyl group) cm^{-1}, NMR (CCl_4) δ (ppm) 0.89 (m, $-CH_3$); 1.47 (m, $CH_3\underline{CH_2}\underline{CH_2}-$) ; 3.57 (m, $-O\underline{CH_2}CH_2O-$) ; 4.12 (t, J=6 Hz, $ArO\underline{CH_2}-$); 6.77 (d, J=6 Hz, 3- and 5-H); 8.35 (bs, 2- and 6-H).

2b oxide was directly submitted to the preparation of 2b, the overall yield was 49%.

3a, recrystallized from pentane, 77% yield, m.p. 47-48°C, ir (CCl_4) 1305, 1025 (C-O-C) cm^{-1}, NMR (CCl_4) δ (ppm) 1.15 (m, $-CH_3$); 1.56 (m, 9xCH_2); 2.00 (m, $-\underline{CH_2}CH_2O-$); 4.34 (t, J=6.5 Hz, $-O\underline{CH_2}-$) ; 6.95 (dd, J=5 and 2.5 Hz, 5-H); 7.41 (m, 5´-H); 7.92 (t, J=7.5 and 2 Hz, 4´-H); 8.22 (d, J=2.5 Hz, 3-H); 8.62 (m, 6-, 6´-, and 3´-H).

3b, oil, chromatographied on basic Al_2O_3 (Fluka) with $CHCl_3$, TLC ($CHCl_3$ contd. 5% of acetone) R_f= 0.75, 75% yield, ir (film) 1308 , 1060 (C-O-C , aromatic) and 1120 (C-O-C, oxyethyl group) cm^{-1}, NMR (CCl_4) δ (ppm) 1.16 (m, $-CH_3$); 1.60

(m, $CH_3\underline{CH_2}\underline{CH_2}$-); 3.80 (m, -$O\underline{CH_2}\underline{CH_2}$-); 4.05 (t, J=5 Hz, $ArOCH_2\underline{CH_2}$-); 4.50 (t, J=5 Hz, $ArO\underline{CH_2}$-); 7.01 (dd, J=5.5 and 2.5 Hz, 5-H); 7.46 (m, 5′-H); 7.96 (t, J=7.5 and 2 Hz, 4′-H); 8.25 (d, J=2.5 Hz, 3-H); 8.65 (m, 6-, 6′-,and 3′-H).

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