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PYRIDYL SULFOBETAINES AS PHASE-TRANSFER CATALYSTS FOR REACTIONS INVOLVING DICHLOROCARBENE

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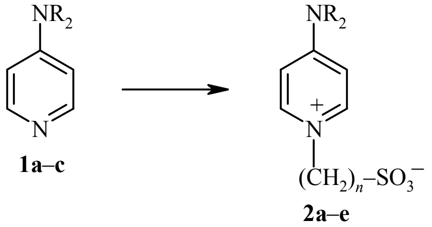
Not much information is available about the use of sulfobetaines in phase-transfer catalysis. It has been established [1,2] that the presence of the zwitterionic salt $C_{12}H_{25}N^+(CH_3)_2CH_2CH_2SO_3^-$ in the reaction of chloromethylation of acenaphthene increases the yield of 5-chloromethylacenaphthene up to 79%, i.e., by more than a factor of two. According to the patent [3], carboxybetaines or sulfobetaines are used in the synthesis of glycidyl ethers. These data inspired us to synthesize some pyridyl sulfobetaines in order to study the feasibility of using them as phase transfer catalysts.

We synthesized the pyridyl sulfobetaines **2a-e** by quaternization of 4-amino-, 4-dimethylamino-, and 4-morpholinopyridines **1a-c** with an equimolar amount of sodium bromoethanesulfonate or 1,3-propanesultone in DMF, and we showed (^{1}H NMR spectra) that quaternization proceeds only at the pyridinium nitrogen:



1a, 2a,c R = H; **1b, 2b,d** CH_3; **1c, 2e** NR_2 = 4-morpholyl;
2a,b *n* = 2; **2c-e** *n* = 3

We tested the pyridyl sulfobetaines **2a-e** as phase-transfer catalysts in reactions involving dichlorocarbene, generated by the Makosza method [4,5]: dehydration of benzamide and N-formylation of diphenylamine (reactions (1) and (2), respectively):

$$PhCONH_2 \rightarrow PhC{\equiv}N \tag{1}$$

$$PhNH \rightarrow Ph_2N\text{–}CHO \tag{2}$$

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Reaction (1): benzamide (0.05 mol), $CHCl_3$ (35 ml), 40% NaOH (0.2 mol, 12 ml), catalyst (5 mol %), 50°C, 3 h; reaction (2): diphenylamine (0.05 mol), $CHCl_3$ (44 ml), 45% NaOH (0.2 mol, 10 ml), catalyst (5 mol %), 55°C, 5-6 h.

Dehydration of benzamide to benzonitrile at 50°C in the absence of catalyst occurs with 7% yield; in the presence of catalysts **2a-e**, the yield of benzonitrile in 3 h is respectively 15%, 38%, 16%, 44%, and 38% (monitored by GC-MS). The use of catalyst **2d** accelerates the course of reaction (1) by a factor of 6; at 30°C in the presence of **2d**, the yield of benzonitrile in 6 h was 36% (without the catalyst, only traces). In reaction (2), including an additional step of dehydration of the N-dichloromethyl derivative formed, these compounds exhibit an insignificant catalytic effect. The yield of diphenylformamide when using **2b**, **2d**, and **2e** is respectively 4%, 7%, and 5% (without a catalyst, about 1%).

We also tested the catalysts we synthesized, along with other quaternary compounds in the pyridine series, in other phase transfer catalysis reactions.

2-(4-Amino-1-pyridinium)-1-ethanesulfonate (2a). Yield 62%; mp > 331°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 1050, 1190 (SO_2); 1660 ($C=N^+$). ^1H NMR spectrum (80 MHz, D_2O), δ, ppm: 3.42 (2H, t, $–CH_2SO_3$); 4.55 (2H, t, $–CH_2N$); 6.85 (2H, d, 3-PyH): 8.04 (2H, d, 2-PyH). Found, %: C 48.95; H 6.76; N 11.32. $C_7H_{12}N_2O_3S$. Calculated, %: C 49.16; H 6.60; N 11.46.

2-(4-Dimethylamino-1-pyridinium)-1-ethanesulfonate (2b). Yield 72%; mp > 335°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 1050, 1201 (SO_2); 1653 ($C=N^+$). ^1H NMR spectrum (D_2O), δ, ppm: 3.14 (6H, s, $(CH_3)_2N$); 3.36 (2H, t, $–CH_2SO_3$); 4.47 (2H, t, $–CH_2N$); 6.82 (2H, d, 3-PyH); 7.98 (2H, d, 2-PyH). Found, %: C 46.71; H 6.25; N 12.23. $C_9H_{14}N_2O_3S$. Calculated, %: C 46.94; H 6.13; N 12.16.

3-(4-Amino-1-pyridinium)-1-propanesulfonate (2c). Yield 94%; mp 284-286°C. IR spectrum (KBr), ν, cm^{-1}: 1032, 1188 (SO_2); 1669 ($C=N^+$). ^1H NMR spectrum (D_2O), δ, ppm: 2.22 (2H, m, $–CH_2–$); 2.87 (2H, t, $–CH_2SO_3$); 4.22 (2H, t, $–CH_2N$); 6.79 (2H, d, 3-PyH); 7.95 (2H, d, 2-PyH). Found, %: C 44.21; H 5.71; N 12.83. $C_8H_{12}N_2O_3S$. Calculated, %: C 44.43; H 5.59; N 12.95.

3-(4-Dimethylamino-1-pyridinium)-1-propanesulfonate (2d). Yield 92%; mp 226-228°C. IR spectrum (KBr), ν, cm^{-1}: 1034, 1209 (SO_2); 1655 ($C=N^+$). ^1H NMR spectrum (D_2O), δ, ppm: 2.19 (2H, dd, $–CH_2–$); 2.83 (2H, t, $–CH_2SO_3$); 3.11 (6H, s, $(CH_3)_2N$); 4.19 (2H, t, $–CH_2N^+$); 6.80 (2H, d, 3-PyH); 7.93 (2H, d, 2-PyH). Found, %: C 48.95; H 6.76; N 11.32. $C_{10}H_{16}N_2O_3S$. Calculated, %: C 49.16; H 6.60; N 11.46.

3-(4-Morpholino-1-pyridinium)-1-propanesulfonate (2e). Yield 84%; mp > 305°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 1045, 1193 (SO_2); 1652 ($C=N^+$). ^1H NMR spectrum (D_2O), δ, ppm; 2.23 (2H, dd, $–CH_2–$); 2.86 (2H, t, $–CH_2SO_3$); 3.67 (4H, t, CH_2NCH_2); 3.76 (4H, t, CH_2OCH_2); 4.25 (2H, t, $–CH_2N$); 7.00 (2H, d, 3-PyH); 8.04 (2H, d, 2-PyH). Found, %: C 50.22; H 6.45; N 9.70. $C_{12}H_{18}N_2O_4S$. Calculated, %; C 50.33; H 6.33; N 9.78.

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