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1-Alkyl-4-dialkylaminopyridinium Halides as Phase-Transfer Catalysts in Dichlorocarbene Reactions

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Summary. A series of 1-alkyl-4-dialkylaminopyridinium halides derived from 4-dimethylamino- and 4-morpholinopyridines were synthesized and tested as phase-transfer catalysts in three typical reactions of dichlorocarbene: dehydration of benzamide, N-formylation of diphenylamine, and dichlorocyclopropanation of styrene. The catalytic performance of the above compounds was found comparable or higher than that of conventional quaternary ammonium catalysts. The influence of catalyst structure on the reactivity was evaluated.

Keywords. Carbenes; 1-Alkyl-4-dialkylaminopyridinium halides; 4-Dimethylaminopyridine; Phase-transfer catalysis; Quaternary pyridinium salts.

Introduction

Makosza has established a simple and convenient two-phase catalytic method of dihalocarbene generation from haloform and aqueous alkali in 1969 [1]. A further development, solid-liquid phase-transfer catalysis (PTC) system with powdered KOH or NaOH has been introduced as a very effective dihalocarbene precursor which allows exclusion of the undesirable action of coextracted water [2, 3]. In 1982, *Regen* and *Singh* have applied simultaneous ultrasonication and mechanical stirring of the solid–liquid two-phase system to afford excellent yields of dichlorocarbene adducts [4]. Finally, the principles of PTC and ultrasonication have been combined by *Xu et al*. for selective insertion of dihalocarbenes into strained carbon–hydrogen bonds [5].

Despite the progress in methodology, the choice of catalyst was, for a long time, limited to simple quaternary ammonium salts, mainly due to the widely accepted view regarding benzyltriethylammonium chloride (*TEBA*) as the optimal catalyst [6, 7]. Although some authors have pointed out that more lipophilic quaternary salts show a better performance in the presence of concentrated aqueous alkali [8, 9], there are only a few examples reporting the use of other types of quaternary ammonium catalysts in dihalocarbene reactions [10, 11]. Crown ethers

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as an alternative are of limited value because of their high price and toxicity [12, 13]. Meanwhile, the search for new stable, active, selective, and non-toxic catalysts became urgent.

Quaternary pyridinium salts possess numerous significant advantages in comparison with quaternary ammonium catalysts including enhanced thermal stability and simple recycling from the reaction mixture. Therefore they have found use in PTC reactions of nucleophilic aromatic substitution and dehydrohalogenation where high temperatures are normally employed [10, 12–15]. Thus, branched 1-alkyl-4-dialkylaminopyridinium salts proved to be effective catalysts for the preparation of aromatic *bis*-etherimides [14], whereas *bis*-aminopyridinium salts have found applications for the alkylation of dianionic phenoxides and thiophenoxides [13, 15]. 4-Dialkylaminopyridinium salts containing 1-alkyl- or alkoxysilyl groups are useful as PT catalysts in esterification of alkali metal acrylates and methacrylates [16, 17]. So far, no attempts have been reported of their use in reactions of dihalocarbenes.

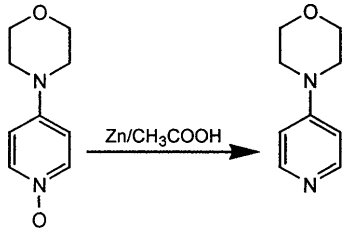
In the search for advanced phase-transfer catalysts we explored a number of quaternary pyridinium salts. The goal of the present work was the synthesis of a series of quaternary 4-dialkylaminopyridinium halides and a detailed study of their performance in different PTC reactions of dichlorocarbene, including the influence of structure on the catalytic activity.

Results and Discussion

Synthesis of 1-alkyl-4-dialkylaminopyridinium halides

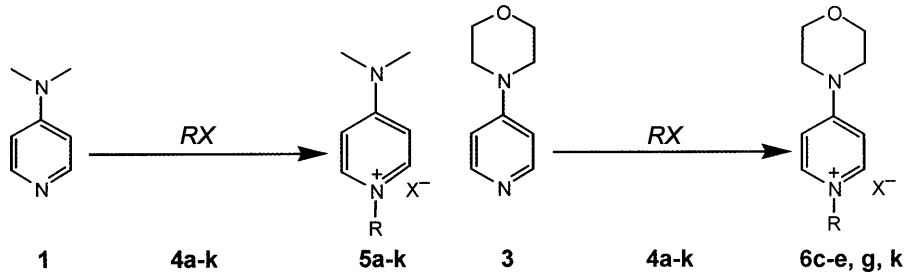
In the present work we synthesized a series of quaternary 4-dialkylaminopyridinium halides with 1-alkyl substituents of different chain length. Commercial 4-dimethylaminopyridine (**1**) was used. 4-Morpholinopyridine (**3**) was prepared from its 1-oxide **2** which, in turn, was synthesized from 4-nitropyridine-1-oxide according to described procedures [18] (Scheme 1).

Quaternization was carried out by refluxing pyridines **1** and **3** in acetone with the corresponding *n*-alkyl bromides (**4a–i**), *n*-heptyl chloride (**4j**), or benzyl chloride (**4k**) (Scheme 2). The reaction products **5a–k**, **6c–e**, **6g**, and **6k** appeared as colourless crystalline or waxy solids, hygroscopic to some extent. Their lipophilic character becomes more pronounced with the growth of the 1-alkyl chain length. They were purified by recrystallization from acetonitrile or acetone. IR spectra of compounds **5a–k**, **6c–e**, **6g**, and **6k** showed an absorption band at 1650–1630 cm^{-1}



2 **3**

Scheme 1



Scheme 2. $R = C_3H_7$ (**4a**, **5a**), C_4H_9 (**4b**, **5b**), C_5H_{11} (**4c**, **5c**, **6c**), C_6H_{13} (**4d**, **5d**, **6d**), C_7H_{15} (**4e**, **4j**, **5e**, **5j**, **6e**), C_8H_{17} (**4f**, **5f**), C_9H_{19} (**4g**, **5g**, **6g**), $C_{10}H_{21}$ (**4h**, **5h**), $C_{12}H_{25}$ (**4i**, **5i**), $CH_2C_6H_5$ (**4k**, **5k**, **6k**); $X = Br$ (**4a–i**, **5a–i**, **6c–e**, **6g**), Cl (**4j–k**, **5j–k**, **6k**)

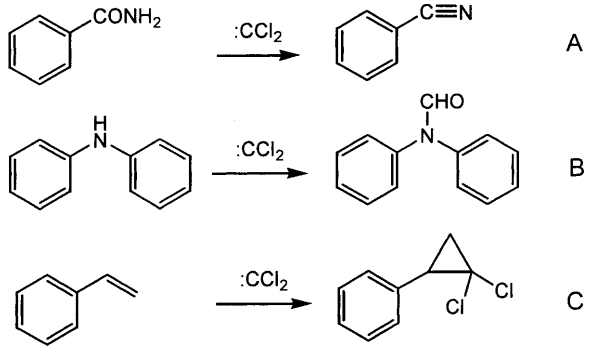
ascribed to the $C{=}N^+$ group and confirming the formation of a quaternary salt. In the ^1H NMR spectra, the signal of the α-methylene protons (CH_2-N^+) appeared at 4.14–4.60 ppm. Reaction times, yields, and physical and spectroscopic data are presented in the Experimental section.

Catalytic properties of 1-alkyl-4-dialkylaminopyridinium halides

The quaternary salts **5a–k**, **6c–e**, **6g**, and **6k** were tested as catalysts in three typical phase-transfer catalysis reactions of dichlorocarbene: dehydration of benzamide (reaction A), N-formylation of diphenylamine (reaction B), and dichlorocyclopropanation of styrene (reaction C) (Scheme 3). Two commercial PT catalysts, *TEBA* and tetrabutylammonium bromide (*TBAB*), as well as 4-dimethylaminopyridine were tested for the comparison.

Results of the kinetic study are summarized in Table 1. The quaternary salts **5a–k**, **6c–e**, **6g**, and **6k** effectively catalyze reactions A, B, and C. In some instances, the efficiency of those catalysts is higher than that of *TEBA* and *TBAB*. Some characteristic points of catalytic performance in different reactions should be pointed out.

The influence of the structure of the 1-alkyl substituent is particularly evident in reactions A and B (Fig. 1). Higher yields are achieved with catalysts containing an 1-alkyl chain of 5–9 carbon atoms. In the series of 4-dimethylaminopyridinium



Scheme 3

Table 1. PTC Reactions in the presence of 1-alkyl-4-dialkylaminopyridinium halides

Catalyst	*R*	Reaction A[a]		Reaction B[a]	Reaction C[a]	
		mol% catalyst	Yield %[b]	Yield %[c]	mol% catalyst	Yield %[d]
5a	propyl	5	75	45	2	91
5b	butyl	5	73	45	2	96
5c	pentyl	5	80	47	2	90
5d	hexyl	5	91	43	2	94
5d	hexyl	1	58		1	71
5e	heptyl	5	85	53	2	98
5f	octyl	5	77	41	2	97
5g	nonyl	5	78	56	2	99
5h	decyl	5	67	39	2	87
5i	dodecyl	5	73	39	2	81
5j	heptyl	5	78		2	86
5k	benzyl	5	75	85	2	62
5k	benzyl	1	58		1	47
6c	pentyl	5	95	57	1	27
6d	hexyl	5	87	54	1	24
6e	heptyl	5	83	59	2	33
6g	nonyl	5	95		1	21
6k	benzyl	5	86	65	1	9
–			7.5	0.9		1
TEBA		5	61	58		
TBAB					2	94
DMAP[e]		5	26			

[a] Reaction conditions: see Experimental; [b] after 4 h (GC data); [c] after 5 h (GC data); [d] after 3 h (GC data); [e] 4-dimethylaminopyridine

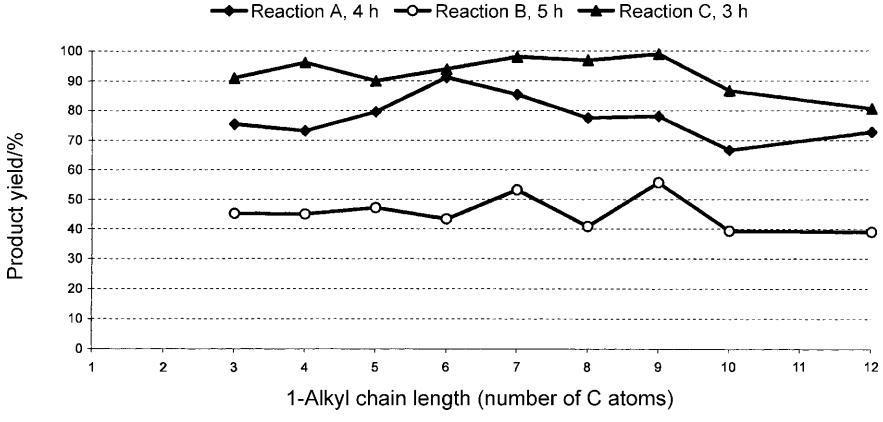


Fig. 1. Influence of alkyl chain length in 1-alkyl-4-dialkylaminopyridinium bromides **5a**–**i** on the catalytic activity

bromides **5a**–**i**, the maximum activity is displayed by **5d** (6 C atoms) in reaction A and **5g** (9 C atoms) in reaction B. A similar characteristic phenomenon has already been observed for quaternary ammonium bromides whose reactivity passes through

a maximum at increasing catalyst size. The catalysts have also been found to reduce the interfacial tension between two phases in such a way that both parameters were in correlation [9, 19]. Obviously, a similar rule should hold for quaternary pyridinium salts as well. Moreover, an alternating reactivity order of catalysts with odd and even numbers of 1-alkyl carbon atoms was observed in the majority of cases, the former generally are displaying a higher reactivity (Fig. 1).

Catalysts with shorter alkyl chains (3–4 C atoms) obviously are not lipophilic enough to ensure effective extraction of dichlorocarbene into the organic phase. On the other hand, quaternary salts with longer alkyl chains (10–12 C atoms) are probably less stable at the reaction conditions and are undergoing degradation in the organic phase. As a proof of this statement, corresponding alkyl chlorides (by-products of the degradation) were detected in the organic phase (GC analysis), their concentration growing with time (up to 2.26% with **5h** and 4.26% with **5i**).

Another phenomenon observed in reaction B was that **5k** and **6k** (both with an 1-benzyl residue) are the best catalysts; this was not the case in reactions A and C. Such a behaviour is possibly related to the fact that formylation of secondary amines under PTC conditions proceeds through a three-step process [20]. Most probably, the above catalysts better promote one of the steps following the addition of dichlorocarbene, *i.e.* the rearrangement to the N-dichloromethyl derivative or hydrolysis to the final formyl derivative [21].

Characteristic influence of a 1-alkyl chain was less evident in reaction C since the best catalysts (**5g**–**j**) at a concentration of 2 mol% give nearly a quantitative yield of 1,1-dichloro-2-phenylcyclopropane. However, a major difference is that, surprisingly, quaternary salts of 4-morpholinopyridine (**6c**–**e**, **6g**, and **6k**) display much lower activity in comparison with 4-dimethylaminopyridinium halides (**5a**–**k**), although in the reactions A and B the former are as efficient as the latter. To explain that fact, more experimental data are necessary.

A comparison of the catalysts **5e** (bromide) and **5j** (chloride) allows to evaluate an influence of the anion on the reactivity. In reactions A and C, **5j** displays slightly lower catalytic activity (Table 1). This can be explained by a lower stability of

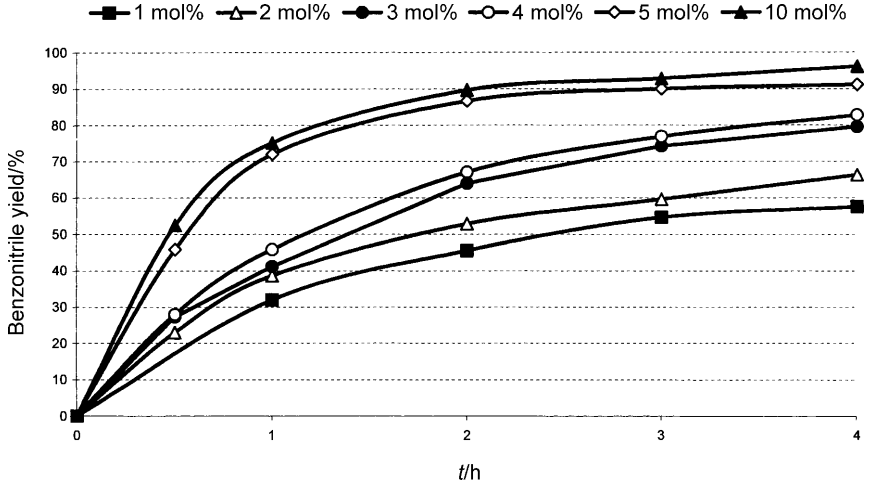


Fig. 2. Influence of catalyst **5d** concentration on benzonitrile yield

$R_4N^+Cl^-$ in the organic phase which in the presence of concentrated alkali undergoes slow degradation *via* extraction of hydroxide anion (as $R_4N^+OH^-$) as stated by *Landini et al*. [8].

A more detailed kinetic study was carried out by varying the catalyst concentration in reaction A (at 50°C). The results showed that the best catalysts are effective at lower concentrations (2–3 mol%) as well. As known, *TEBA* is usually employed for dehydration of amides at a concentration of 5 mol%. Marked differences of the reaction rate are observed within the first two hours of the reaction. A further increase of the reaction time as well as of the catalyst concentration gives only a slight improvement (Fig. 2). At 30°C, the yield of benzonitrile in the presence of 5 mol% of **5d** was 48% (at 6 h).

Experimental

All melting points are uncorrected. IR spectra (KBr) were recorded on a FT-IR spectrometer Hartmann & Braun, Canada. ^{1}H NMR spectra were recorded on a Tesla BS-567A NMR spectrometer at 80 MHz with *TMS* as internal standard. GC analysis was performed on a Hewlett Packard instrument HP 5890 equipped with flame-ionization detector and silica capillary column, CP-Sil 8CB (50 m × 0.32 mm i.d., film thickness 0.25 μm). Elemental analyses (C, H, N) are in satisfactory agreement with calculated values.

4-Morpholinopyridine (**3**; $C_9H_{12}N_2O$)

A mixture of 18.02 g **2** (0.1 mol), 19.6 g Zn (0.3 mol), and 50 cm^3 glacial acetic acid was heated on a boiling water bath for 3 h. Concentrated aqueous NaOH was added to $pH = 8$, the mixture was filtered, the filtrate extracted with 3 × 50 cm^3 $CHCl_3$, dried (K_2CO_3), filtered, and evaporated. The residue was crystallized from acetone to afford 10.35 g (63%) of **3** as yellowish crystals.

M.p.: 104–105°C (Ref. [18]: m.p.: 101–104°C); IR (KBr): $\nu = 3901$, 2959, 2835, 1599, 1508 cm^{-1}; ^{1}H NMR (CD_3OD, δ, ppm): 7.94 (2H, d, Py-2H), 6.90 (2H, d, Py-3H), 3.69 (4H, t, O-CH_2), 3.22 (4H, t, N-CH_2).

General procedure for the synthesis of 1-alkyl-4-dimethylaminopyridinium halides (**5a–k**)

To a solution of **1** (0.02 mol) in 40 cm^3 of acetone, an equimolar amount of alkyl halide was added dropwise. The reaction mixture was refluxed until completion of the reaction (see below), and the solid product (partially hygroscopic) was filtered off, washed with cold acetone, dried *in vacuo* (P_2O_5), and recrystallized from the specified solvent.

1-Propyl-4-dimethylaminopyridinium bromide (**5a**; $C_{10}H_{17}BrN_2$)

From **1** and **4a** (5 h); yield: 93%; m.p.: 140–142°C (acetone); IR (KBr): $\nu = 2888$, 1631, 1551 cm^{-1}; ^{1}H NMR (CD_3CN, δ, ppm): 8.10 (2H, d, Py-2H), 6.94 (2H, d, Py-3H), 4.14 (2H, t, N^+-CH_2), 3.22 (6H, s, N-CH_3), 1.89 (2H, m, CH_2), 0.93 (3H, t, CH_3).

1-Butyl-4-dimethylaminopyridinium bromide (**5b**; $C_{11}H_{19}BrN_2$)

From **1** and **4b** (6 h); yield: 91%; m.p.: 205–208°C (acetone); IR (KBr): $\nu = 2876$, 1647, 1572 cm^{-1}; ^{1}H NMR (CD_3CN, δ, ppm): 8.04 (2H, d, Py-2H), 6.91 (2H, d, Py-3H), 4.14 (2H, t, N^+-CH_2), 3.21 (6H, s, N-CH_3), 1.27 (4H, m, CH_2), 0.97 (3H, t, CH_3).

1-Pentyl-4-dimethylaminopyridinium bromide (**5c**; $C_{12}H_{21}BrN_2$)

From **1** and **4c** (6 h); yield: 88%; m.p.: 210–212°C (acetonitrile); IR (KBr): $\nu = 2878$, 1640, 1564 cm^{-1}; ^1H NMR (CD_3CN, δ, ppm): 8.06 (2H, d, Py-2H), 6.92 (2H, d, Py-3H), 4.14 (2H, t, N^+-CH_2), 3.23 (6H, s, N-CH_3), 1.34 (6H, m, CH_2), 0.95 (3H, t, CH_3).

1-Hexyl-4-dimethylaminopyridinium bromide (**5d**; $C_{13}H_{23}BrN_2$)

From **1** and **4d** (6 h); yield: 92%; m.p.: 180–182°C (acetonitrile); IR (KBr): $\nu = 2890$, 1650, 1566 cm^{-1}; ^1H NMR (CD_3CN, δ, ppm): 8.07 (2H, d, Py-2H), 6.92 (2H, d, Py-3H), 4.16 (2H, t, N^+-CH_2), 3.23 (6H, s, N-CH_3), 1.34 (8H, m, CH_2), 0.93 (3H, t, CH_3).

1-Heptyl-4-dimethylaminopyridinium bromide (**5e**; $C_{14}H_{25}BrN_2$)

From **1** and **4e** (6 h); yield: 74%; m.p.: 145–147°C (acetone); IR (KBr): $\nu = 2872$, 1650, 1567 cm^{-1}; ^1H NMR ($(CD_3)_2CO$, δ, ppm): 8.89 (2H, d, Py-2H), 7.37 (2H, d, Py-3H), 4.60 (2H, t, N^+-CH_2), 3.46 (6H, s, N-CH_3), 1.41 (10H, m, CH_2), 0.93 (3H, t, CH_3).

1-Octyl-4-dimethylaminopyridinium bromide (**5f**; $C_{15}H_{27}BrN_2$)

From **1** and **4f** (9 h); yield: 50%; m.p.: 112–113°C (acetone); IR (KBr): $\nu = 2864$, 1641, 1551 cm^{-1}; ^1H NMR ($(CD_3)_2CO$, δ, ppm): 8.84 (2H, d, Py-2H), 7.30 (2H, d, Py-3H), 4.61 (2H, t, N^+-CH_2), 3.47 (6H, s, N-CH_3), 1.43 (12H, m, CH_2), 1.00 (3H, t, CH_3).

1-Nonyl-4-dimethylaminopyridinium bromide (**5g**; $C_{16}H_{29}BrN_2$)

From **1** and **4g** (6 h); yield: 93%; m.p.: 108–109°C (acetone); IR (KBr): $\nu = 2862$, 1639, 1564 cm^{-1}; ^1H NMR ($(CD_3)_2CO$, δ, ppm): 8.78 (2H, d, Py-2H), 7.27 (2H, d, Py-3H), 4.57 (2H, t, N^+-CH_2), 3.45 (6H, s, N-CH_3), 1.39 (14H, m, CH_2), 0.97 (3H, t, CH_3).

1-Decyl-4-dimethylaminopyridinium bromide (**5h**; $C_{17}H_{31}BrN_2$)

From **1** and **4h** (10 h); yield: 95%; m.p.: 92–95°C (acetone); IR (KBr): $\nu = 2869$, 1644, 1564 cm^{-1}; ^1H NMR ($(CD_3)_2CO$, δ, ppm): 8.76 (2H, d, Py-2H), 7.28 (2H, d, Py-3H), 4.58 (2H, t, N^+-CH_2), 3.46 (6H, s, N-CH_3), 1.40 (16H, m, CH_2), 0.98 (3H, t, CH_3).

1-Dodecyl-4-dimethylaminopyridinium bromide (**5i**; $C_{19}H_{35}BrN_2$)

From **1** and **4i** (12 h); yield: 91%; m.p.: 63–64°C (acetone); IR (KBr): $\nu = 2851$, 1653, 1570 cm^{-1}; ^1H NMR ($(CD_3)_2CO$, δ, ppm): 8.84 (2H, d, Py-2H), 7.38 (2H, d, Py-3H), 4.60 (2H, t, N^+-CH_2), 3.47 (6H, s, N-CH_3), 1.37 (20H, m, CH_2), 0.96 (3H, t, CH_3).

1-Heptyl-4-dimethylaminopyridinium chloride (**5j**; $C_{14}H_{25}ClN_2$)

From **1** and **4j** (15 h); yield: 32%; m.p.: 100–102°C (acetone); IR (KBr): $\nu = 2854$, 1651, 1568 cm^{-1}; ^1H NMR (CD_3CN, δ, ppm): 8.10 (2H, d, Py-2H), 6.94 (2H, d, Py-3H), 4.14 (2H, t, N^+-CH_2), 3.22 (6H, s, N-CH_3), 1.89 (2H, m, CH_2), 0.93 (3H, t, CH_3).

1-Benzyl-4-dimethylaminopyridinium chloride (**5k**; $C_{14}H_{17}ClN_2$)

From **1** and **4k** (3 h); yield: 93%; m.p.: 253–254°C (acetonitrile); IR (KBr): $\nu = 3030$, 2993, 2874, 1641, 1572 cm^{-1}; ^1H NMR (CD_3CN, δ, ppm): 8.20 (2H, d, Py-2H), 7.46 (5H, s, C_6H_5), 6.94 (2H, d, Py-3H), 5.39 (2H, s, N^+-CH_2), 3.21 (6H, s, N-CH_3).

General procedure for the synthesis of 1-alkyl-4-morpholinopyridinium halides (**6c–e**, **6g**, and **6k**)

A mixture of **3** (0.01 mol) and alkyl halide (0.015 mol) in 40 cm^3 of acetone was refluxed for a maximum of 9 h. If necessary, the solvent was evaporated until the precipitation of a solid product started which was filtered off, dried *in vacuo* (P_2O_5), and recrystallized from the specified solvent.

1-Pentyl-4-morpholinopyridinium bromide (**6c**; $C_{14}H_{23}BrN_2O$)

From **3** and **4c** (3 h); yield: 62%; m.p.: 271–272°C (acetonitrile); IR (KBr): $\nu = 2921$, 2853, 1647, 1550 cm^{-1}; ^1H NMR (CD_3CN, δ, ppm): 8.10 (2H, d, Py-2H), 7.07 (2H, d, Py-3H), 4.17 (2H, t, N^+-CH_2), 3.78 (4H, t, O-CH_2), 3.71 (4H, t, N-CH_2), 1.32 (6H, m, CH_2), 0.95 (3H, t, CH_3).

1-Hexyl-4-morpholinopyridinium bromide (**6d**; $C_{15}H_{25}BrN_2O$)

From **3** and **4d** (3 h); yield: 90%; m.p.: 190–192°C (acetonitrile); IR (KBr): $\nu = 2920$, 2856, 1645, 1549 cm^{-1}; ^1H NMR (CD_3CN, δ, ppm): 8.09 (2H, d, Py-2H), 7.07 (2H, d, Py-3H), 4.15 (2H, t, N^+-CH_2), 3.77 (4H, t, O-CH_2), 3.71 (4H, t, N-CH_2), 1.33 (8H, m, CH_2), 0.93 (3H, t, CH_3).

1-Heptyl-4-morpholinopyridinium bromide (**6e**; $C_{16}H_{27}BrN_2O$)

From **3** and **4e** (8 h); yield: 74%; m.p.: 151–152°C (acetonitrile); IR (KBr): $\nu = 2926$, 2858, 1646, 1545 cm^{-1}; ^1H NMR (CD_3CN, δ, ppm): 8.08 (2H, d, Py-2H), 7.05 (2H, d, Py-3H), 4.16 (2H, t, N^+-CH_2), 3.77 (4H, t, O-CH_2), 3.70 (4H, t, N-CH_2), 1.34 (10H, m, CH_2), 0.95 (3H, t, CH_3).

1-Nonyl-4-morpholinopyridinium bromide (**6g**; $C_{18}H_{31}BrN_2O$)

From **3** and **4g** (9 h); yield: 55%; m.p.: 147–149°C (acetone); IR (KBr): $\nu = 2927$, 2860, 1646, 1549 cm^{-1}; ^1H NMR (CD_3CN, δ, ppm): 8.20 (2H, d, Py-2H), 7.13 (2H, d, Py-3H), 4.22 (2H, t, N^+-CH_2), 3.78 (4H, t, O-CH_2), 3.73 (4H, t, N-CH_2), 1.34 (14H, m, CH_2), 0.94 (3H, t, CH_3).

1-Benzyl-4-morpholinopyridinium chloride (**6k**; $C_{16}H_{19}ClN_2O$)

From **3** and **4k** (3 h); yield: 66%; m.p.: 289–290°C (acetonitrile); IR (KBr): $\nu = 3026$, 2997, 2847, 1645, 1554 cm^{-1}; ^1H NMR (CD_3OD, δ, ppm): 8.24 (2H, d, Py-2H), 7.39 (5H, s, C_6H_5), 7.15 (2H, d, Py-3H), 5.36 (2H, s, N^+-CH_2), 3.76 (4H, t, O-CH_2), 3.72 (4H, t, N-CH_2).

General procedures for PTC reactions

Dehydration of benzamide (reaction A): A mixture of benzamide (0.05 mol), $CHCl_3$ (35 cm^3), catalyst (1–10 mol%), and 40% aqu. NaOH (12 cm^3) was stirred at 50°C for 4 h.

N-Formylation of diphenylamine (reaction B): A mixture of diphenylamine (0.05 mol), $CHCl_3$ (45 cm^3), catalyst (5 mol%), and 45% aqu. NaOH (10 cm^3) was stirred at 55°C for 5 h.

Dichlorocyclopropanation of styrene (reaction C): A mixture of styrene (0.05 mol), $CHCl_3$ (35 cm^3), catalyst (1–2 mol%), and 50% aqu. NaOH (8 cm^3) was stirred at 40°C for 3 h.

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References

[1] Makosza M, Wawrzyniewicz M (1969) Tetrahedron Lett 4659
[2] Dehmlow EV (1976) Tetrahedron Lett 91
[3] Julia S, Ginebreda A (1977) Synthesis 682
[4] Regen SL, Singh A (1982) J Org Chem **47**: 1587
[5] Xu L, Smith WB, Brinker UH (1992) J Am Chem Soc **114**: 783
[6] Dehmlow EV, Dehmlow SS (1983) In: Phase Transfer Catalysis. Verlag Chemie, Weinheim, p 45
[7] Makosza M, Fedorynski M (1979) Zh Vses Khim Obshch D I Mendeleeva **24**: 466
[8] Landini D, Maia A, Rampoldi A (1986) J Org Chem **51**: 3187
[9] Mason D, Magdassi S, Sasson Y (1990) J Org Chem **55**: 2714
[10] Freedman HH (1986) Pure Appl Chem **58**: 857
[11] Goldberg Y, Abele E, Bremanis G, Trapenciers P, Gaukhman A, Popelis J, Gomtsyan A, Kalvins I, Shymanska M, Lukevics E (1990) Tetrahedron **46**: 1911
[12] Brunelle DJ, Singleton DA (1984) Tetrahedron Lett **25**: 3383
[13] Brunelle DJ (1987) In: Starks CM (Ed) Phase-Transfer Catalysis. American Chemical Society, Washington, p 38
[14] Brunelle DJ (1984) US Pat 4460778
[15] Brunelle DJ (1986) US Pat 4595760
[16] Bernhardt G, Haas M, Kragl H, Larson GL (1992) Eur Pat 483479
[17] Bernhardt G, Steffen KD, Haas M, Kragl H (1992) Eur Pat 483480
[18] Ochiai E, Itai T, Yoshino K (1944) Proc Imp Acad (Tokyo) **20**: 141; cf. CA **45**: 5151h
[19] Dockx J (1973) Synthesis 441
[20] Saunders M, Murray RW (1960) Tetrahedron **11**: 1
[21] Makosza M, Kacprowicz A (1975) Roczniki Chemii **49**: 1627

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