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Recoverable Phase-Transfer Catalysts with Fluorinated Anions: Generation and Reactions of Dichlorocarbene and CCl_3 Anion in the Heterogeneous System KOH(s)/$CHCl_3$/$n$$Bu_4NPF_6$

Galina V. Kryshtal,[a] Galina M. Zhdankina,[a] and Sergei G. Zlotin*[a]

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Tetraalkylammonium salts bearing PF_6^- and BF_4^- anions have been recognized as recoverable phase-transfer catalysts for the synthesis of 1,1-dichlorocyclopropane and α-(trichloromethyl)carbinol derivatives from alkenes or aldehydes in the heterogeneous system KOH(s)/$CHCl_3$. The catalysts retained their catalytic activity over several reaction cycles.

Introduction

In the last decade, organic salts with fluorinated anions, particularly integral components of ionic liquids,[1] have attracted attention as green neoteric solvents and catalysts for chemical reactions.[2] They are stable, nonvolatile, nonflammable[3] and capable of dissolving a majority of organic, inorganic and organometallic compounds.[4] Due to their poor solubility in hydrocarbons and, in some cases, in water, they may be readily separated from reagents and products and reused.[5] Many heterogeneous organic reactions proceed with high yields and selectivities in multiphase liquid/liquid or solid/liquid systems bearing ionic phases composed of these salts.[6]

Organic salts with fluorinated anions may act as phase-transfer catalysts (PTCs) in multi-phase organic reactions. The presence of lipophilic organic cations, similar to those present in conventional PTCs,[7] along with weakly solvating fluorinated anions, creates a favorable combination of properties from the green chemistry viewpoint:[8] the ability to transfer anionic reagents from the aqueous phase or polar solid surface to the organic phase, and recoverability. Despite this, the area of phase-transfer catalysis by fluorinated organic salts has so far been nearly unexplored. They were applied in alkylation reactions without focusing on recovery and without comparing catalyst efficacy to that of conventional PTCs containing chloride or bromide anions.[9] In addition, we have recently found that tetraalkylammonium and 1,3-dialkylimidazolium salts with fluorinated anions act as efficient, recoverable PTCs for solid base-promoted cross-aldol condensations and for Michael reactions of nitroalkanes with electron-deficient alkenes.[10]

Herein we report the first application of PTCs bearing BF_4^- and PF_6^- anions to the synthesis of practically important 1,1-dichlorocyclopropane and α-(trichloromethyl)carbinol derivatives. 1,1-Dichlorocyclopropanes possess fungicide, insecticide and acaricide activities,[11] and can be used for the synthesis of insect juvenile hormone analogs.[12] Trichloromethylcarbinol derivatives are valuable intermediates in pyrethroid syntheses.[13]

The most efficient approaches to these compounds are tandem reactions, including the generation of dichlorocarbene or the CCl_3 anion in 50% aqueous[8,14] or solid[8,15] metal hydroxide/$CHCl_3$ heterogeneous systems, followed by their reactions with unsaturated compounds. The syntheses in the liquid/liquid systems are well documented, whereas the solid/liquid systems, which are more important for chemical technology, have not been studied in detail. In both cases, when $BnNEt_3Cl$ (TEBA-Cl) was used as a PTC, it was irreversibly lost during product isolation. It might be expected that the replacement of $BnNEt_3Cl$ by the corresponding salt with a fluorinated anion would allow catalyst recovery and retain the process efficacy.

Results and Discussion

To examine this assumption we first studied the reactions of cinnamaldehyde dimethyl acetal (**1a**) with the KOH/$CHCl_3$ solid/liquid system in the presence of tetraalkylammonium or 1,3-dialkylimidazolium salts bearing Cl^-, Br^-, BF_4^- and PF_6^- anions (Table 1). For convenient processing, the organic phase was diluted with an equal amount of benzene. The reactions were run at 50 °C for 7 h.

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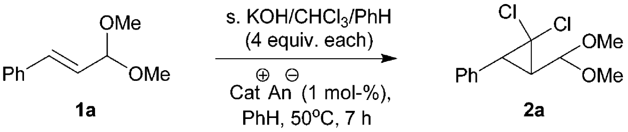
[a] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
Leninsky prospect 47, 119991 Moscow, Russia
Fax: +7-499-1355328
E-mail: zlotin@ioc.ac.ru

In all experiments the **1a**/KOH(s)/$CHCl_3$/PhH ratio was 1:4:4:4; the PTC amount was 1 mol-% with respect to the alkene **1a**. Cyclopropane derivative **2a** was isolated as the major reaction product.

Table 1. Comparison of phase-transfer catalysts in the synthesis of **2a**.



Cation	Anion	Yield of **2a**
$n\mathrm{Bu_4N^+}$	BF_4^-	69
$n\mathrm{Bu_4N^+}$	PF_6^-	72, 72[a], 66[b], 72[c]
$n\mathrm{Bu_4N^+}$	Br^-	64
Et_3NBn^+	BF_4^-	63
Et_3NBn^+	PF_6^-	60
Et_3NBn^+	Cl^-	63
$Bmim^+$	PF_6^-	17
None	none	0

[a] $n\mathrm{Bu_4NPF_6}$ (5 mol-%) was used. [b] $n\mathrm{Bu_4NPF_6}$ (0.25 mol-%) was used. [c] Yield in the system KOH (s)/$CHCl_3$/$PhCH_3$ (4 equiv. each)/$n\mathrm{Bu_4NPF_6}$ (1 mol-%).

The yields of **2a** in reactions catalyzed by tetraalkylammonium salts bearing BF_4^- and PF_6^- anions were comparable to or higher than those attained in the reactions catalyzed by conventional PTCs. Alternatively, 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6] showed modest efficacy in the studied reaction, presumably because of the decomposition of the imidazolium cation under the basic reaction conditions.[16] No reactions occurred in the absence of PTC. The highest yield of **2a** (72%) was attained in the presence of tetrabutylammonium hexafluorophosphate ($n\mathrm{Bu_4NPF_6}$). Increasing the catalyst amount to 5 mol-% did not influence the product yield, whereas its reduction to 0.25 mol-% lowered it slightly. The process efficacy remained high where toluene was used as a cosolvent instead of toxic benzene.

The system KOH(s)/$CHCl_3$/$n\mathrm{Bu_4NPF_6}$ (1 mol-%), which was most efficient in the model reaction, was further studied in reactions with various alkenes, in particular with those bearing isoprenoid moieties. The corresponding cyclopropane derivatives **2b**–**h** were obtained in all cases. The yields of the known compounds **2b**,**c**,**e**–**h** and **3f** were higher than those reported in the literature (Table 2).

Dienes **1d**,**f** afforded different products depending on the **1**/KOH/$CHCl_3$/ratio. Monocyclopropanation products **2d**,**f** were isolated in a 1:2:2 ratio. Aldehyde **2f** formed as a mixture of (*Z*) and (*E*) isomers (2:3) by hydrolysis of the acetal group during chromatography of the product on SiO_2. Compounds **3d**,**f**, bearing two cyclopropane moieties, formed in a 1:8:8 ratio. Yet, linalool (**1c**) afforded monocyclopropanation product **2c** even at the latter diene/KOH/$CHCl_3$ ratio; the double bond located at the β-position with respect to the hydroxy group remained intact.

α,β-Unsaturated ketones bearing no alkyl group at the α-position, in particular isophorone and pseudoionone, remained unchanged under the studied conditions. Yet, (–)-L-carvone (**1i**) afforded a mixture of isomeric dichlorocyclopropanes **2i**,**j**, which were isolated by column chromatography (silica gel) in 26% and 63% yields, respectively.

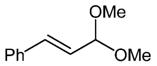
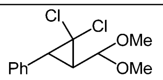
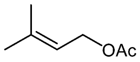
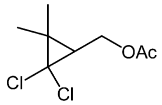
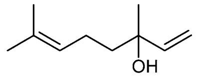
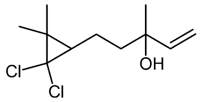
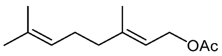
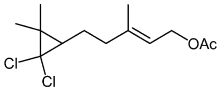
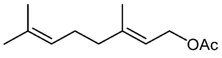
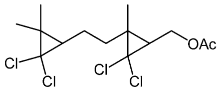
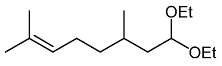
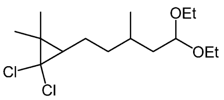
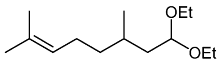
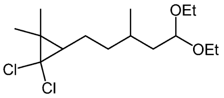
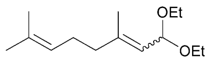
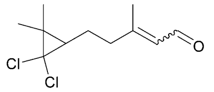
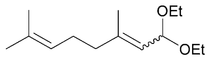
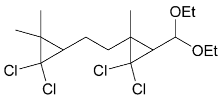
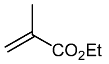
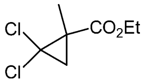
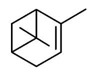
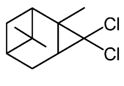
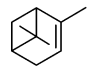
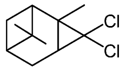
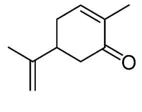
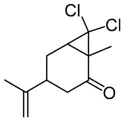
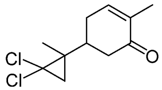
In the presence of acrylic acid derivatives **4a**,**b**, vinyl acetate (**4c**), or aldehydes **5**, the reactions ran in another direction affording addition products **7** and **8** with the CCl_3 group. Under the same conditions, aldehyde acylals **6a**,**b** substituted one of the two acetate groups for the CCl_3 group, yielding β,β,β-trichlorocarbinol acetates **9a**,**b** (Table 3).

It is worth mentioning that methacrylic ester **1g** and acrylic ester **4b** behaved differently under the studied conditions. Compound **4b**, being a strong electrophile, yielded trichloromethyl derivative **7b** (Table 3), whereas compound **1g**, possessing nucleophilic properties, gave dichlorocyclopropane **2g** (Table 2).

Fluorinated PTCs appeared recoverable and reusable in the studied reactions (see Tables 2 and 3; compounds **2e**,**h** and **9a**). The regeneration procedure consisted of extracting the product with an organic solvent followed by washing the remaining $n\mathrm{Bu_4NPF_6}$/KOH/KCl mixture with water to remove inorganic compounds. The protocol is suitable for recovery of various PTCs with fluorinated anions that are poorly soluble in water, in particular $n\mathrm{Bu_4NBF_4}$, $BnNEt_3BF_4$ and $BnNEt_3PF_6$. The consistency of $n\mathrm{Bu_4NPF_6}$ under the studied conditions was confirmed by the identity of ^1H, ^{19}F NMR and microanalysis data of the recovered and freshly prepared catalyst samples (see Exp. Sect.). Using the $n\mathrm{Bu_4NPF_6}$/KOH/KCl mixture instead of pure PTC resulted in gradual yield lowering (Table 2; compound **2h**, cycles 2–4), probably due to the deactivation of the catalyst by the adsorbed inorganic compounds. PTC activity was restored after treatment of the mixture with water (Table 2; compound **2h**, cycle 5).

Addition reactions in the studied solid/liquid system are assumed to start with CH-acid deprotonation on the solid base surface followed by carbanion interception by a PTC and its transfer from the solid/liquid interfacial region (a so-called “omega phase”[15b,29]) into the organic phase (Scheme 1). A further reaction pathway depends on the reagent structure. Electrophiles **4**–**6** add the CCl_3 anion, yielding compounds **7**–**9** and $n\mathrm{Bu_4NOH}$, which may further act as a catalyst for the trichloromethylation reaction itself (Cycle A). This assumption is in compliance with observation that freshly prepared $n\mathrm{Bu_4NOH}$, used in amounts as high as 1 equiv., catalyzed the homogeneous reaction between aldehyde **5b** and $CHCl_3$ in benzene in the absence of KOH. However, conversion of **5b** was only 47% after 6 h, possibly due to gradual decomposition of the organic base under the reaction conditions.[7] In the absence of an electrophile, the CCl_3 anion decomposes to Cl^- and dichlorocarbene, which reacts with alkenes **1** yielding 1,1-dichlorocyclopropane derivatives **2** and **3** (Cycle B).[30] Presumably, fluorinated PTC returns to the process by a metathesis reaction (Cycle C). The feasibility of ion exchange between $n\mathrm{Bu_4NCl}$ and KPF_6

Table 2. Synthesis of 1,1-dichlorocyclopropanes **2** and **3** from alkenes **1** in the system KOH (s)/$CHCl_3$/PhH/nBu_4NPF_6 (1 mol-%).

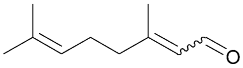
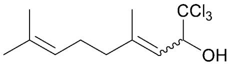
	1	**1**/KOH/ $CHCl_3$/PhH molar ratio	*T* [°C]	*t* [h]		**2**, **3**	Yield [%] (cycle)[a]
1a		1:4:4:4	50	7	**2a**		72 (45[17])[b]
1b		1:2:2:2	15	6	**2b**		88 (70[18])
1c		1:2:2:2	20	7	**2c**		99 (89[19])
1d		1:2:2:2	15	6	**2d**		97 (61[20])[c]
1d		1:8:8:8	15	6	**3d**		95
1e		1:4:4:4	45	7	**2e**		97 (1), 98 (2[d]), 97 (3[d]), 98(4[d]), 97 (5[d]), 97 (6[d]) (84[12a])
1e		1:4:4:4[e]	45	7	**2e**		85 (1) 86 (2[d])
1f		1:2:2:2	45	6	**2f**		68 (53[21])
1f		1:8:8:8	45	6	**3f**		81 (77[21])
1g		1:4:4:4	15	4	**2g**		86 (85[22])
1h		1:2:2:2	45	6	**2h**		83 (1) 81 (2[f]) 79 (3[f]) 57 (4[f]) 83 (5[d]) (62[15c])[g]
1h		1:2:2:2[e]	45	6	**2h**		84 (1) 83 (2[d])
1i		1:4:4:4	45	30	**2i**		26 (7[23])[h]
					2j		63 (50[23])[h]

[a] Reported data were obtained in the system NaOH (aq.)/$CHCl_3$/$BnNEt_3Cl$ unless noted otherwise. [b] Yield of corresponding diethyl acetal. [c] Prepared by the electrolysis of CCl_4 in the **1d**/$CHCl_3$ mixture. [d] nBu_4NPF_6 recovered from previous cycle and washed with H_2O and Et_2O was used. [e] $PhCH_3$ was used instead of PhH. [f] A mixture of nBu_4NPF_6, KOH and KCl recovered from previous cycle was used. [g] Yield in the system NaOH (s)/$CHCl_3$/$BnNEt_3Cl$. [h] Yield in the system NaOH (aq.)/$CHCl_3$/$CtNMe_3Br$.

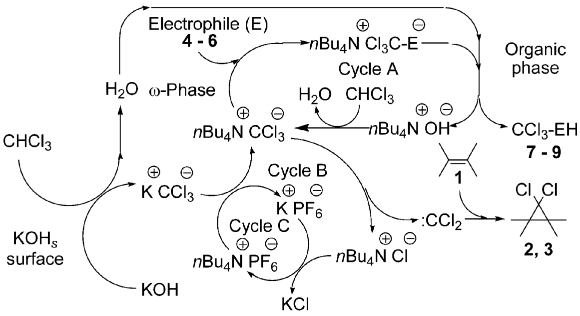
was indirectly confirmed by the synthesis of $BnNEt_3BF_4$ from $BnNEt_3Cl$ and KBF_4 under the reaction conditions (see Exp. Sect.).

The catalytic Cycle C makes the studied reaction different from similar reactions catalyzed by conventional PTCs containing chloride or bromide anions.[15b,29,30] An

Table 3. Synthesis of trichloromethyl derivatives **7**–**9** from compounds **4**–**6** in the catalytic system KOH (s)/$CHCl_3$/PhH/$n$$Bu_4NPF_6$ (1 mol-%).

	4–6	T [°C]	t [h]		**7–9**	Yield[a] [%] (cycle)[b]
4a	CH_2=CHCN	5	5	**7a**	$Cl_3CCH_2CH_2CN$	76 (72[22])
4b	CH_2=$CHCO_2Et$	5	5	**7b**	$Cl_3CCH_2CH_2CO_2Et$	45 (55[24])[c]
4c	CH_2=CHOAc	5	4	**7c**	$CH_3CH(CCl_3)OAc$	81 (75[22])
5a	PhCHO	20	5	**8a**	$PhCH(CCl_3)OH$	85 (80[25a])
5b	PhCH=CHCHO	20	4	**8b**	$PhCH$=$CHCH(CCl_3)OH$	76 (44[26])
5c		5	5	**8c**		55 (44[27])
6a	$PhCH(OAc)_2$	20	6	**9a**	$PhCH(CCl_3)OAc$	84 (1) 82 (2[d]) 86 (3[d])
6a	$PhCH(OAc)_2$	20	6	**9a**	$PhCH(CCl_3)OAc$	89[e] (1) 88[e] (2[d]) 88[e] (3[d])
6b	$MeCH$=$CHCH(OAc)_2$	15	6	**9b**	$MeCH$=$CHCH(CCl_3)OAc$	70 (57[28])

[a] Reaction conditions: **4**–**6** (10 mmol), KOH (s) (20 mmol), $CHCl_3$ (20 mmol), PhH (20 mmol). [b] Reported data were obtained in the system NaOH (aq.)/$CHCl_3$/$BnNEt_3Cl$ unless noted otherwise. [c] Yield of corresponding *i*Pr ester. [d] $n$$Bu_4NPF_6$ recovered from the previous cycle and washed with H_2O and Et_2O was used. [e] $PhCH_3$ (20 mmol) was used as cosolvent instead of PhH.



Scheme 1. Plausible mechanism for the synthesis of compounds **2**, **3** and **7**–**9** in the heterogeneous system KOH (s)/$CHCl_3$/PhH/$n$$Bu_4NPF_6$.

equilibrium between organic salts with lipophilic (CCl_3^- and Cl^-) and weakly solvating fluorinated (PF_6^- or BF_4^-) anions strongly shifts to salts with PF_6^- or BF_4^- anions which are poorly soluble in the organic phase,[10a] enabling recovery of ≥85% of fluorinated PTC.

Conclusions

Tetraalkylammonium salts bearing PF_6^- or BF_4^- anions have been applied for the first time as efficient phase-transfer catalysts for dichlorocyclopropanation and trichloromethylation reactions, including the generation of dichlorocarbene or CCl_3 anion in solid base/$CHCl_3$ systems. Unlike conventional PTCs, they can be easily separated from the reaction products and used repeatedly.

Experimental Section

General Remarks: NMR spectra were recorded with Bruker WM-250 [250.13 MHz (^1H)], AM-300 [300.13 MHz (^1H)], and DRX-500 [500.13 MHz (^1H), 125.76 MHz (^{13}C), 470.4 MHz (^{19}F)] instruments in $CDCl_3$ unless noted otherwise. ^1H, ^{13}C and ^{19}F chemical shifts are relative to Me_4Si, [D_6]acetone and $CClF_3$, respectively. The reactions were monitored by TLC [silufol plates; eluent: ethyl acetate/PhH (1:19) or hexane, visualization by I_2 or UV] and GLC (LKhM-80 chromatograph with a flame ionization detector, N_2, 1.4×0.003 m glass column with 5% SE-30 on Chromaton N-AW-DMCS). $n$$Bu_4NBr$, $BnNEt_3Cl$, KPF_6, benzaldehyde, cinnamaldehyde, citral, acrylonitrile, ethyl acrylate, vinyl acetate, α-pinene, linalool, prenyl acetate and geranyl acetate were purchased from Acros and used without further purification. PTCs $n$$Bu_4NPF_6$,[10a] $n$$Bu_4NBF_4$,[10a] $BnNEt_3PF_6$,[10a] [bmim]PF6[31] and compounds **1a**,**e**,**f**[32] and **6a**,**b**[33] were synthesized according to the reported methods.

Synthesis of $BnNEt_3BF_4$: A mixture of $BnNEt_3Cl$ (4.55 g, 20 mmol), KBF_4 (2.52 g, 20 mmol), $CHCl_3$ (15 mL) and benzene (15 mL) was vigorously stirred at 20 °C for 30–35 h. The precipitate was filtered off and washed with $CHCl_3$ (3 × 10 mL). The combined organic solutions were concentrated under reduced pressure (15 Torr). Water (20 mL) was added to the residue, and the solid was filtered and washed successively with water (3 × 5 mL), Et_2O (3 × 5 mL) and dried at 40 °C (20 Torr) yielding $BnNEt_3BF_4$ (4.20 g, 75%) as a colorless solid; m.p. 114–115 °C (ref.[34] 114 °C). ^1H NMR ([D_6]DMSO): δ = 1.30 (t, J = 7.5 Hz, 9 H, 3 × CH_3), 3.15 (q, J = 7.5 Hz, 6 H, 3 × CH_2), 4.47 (s, 2 H, CH_2), 7.5 (br. s, 5 H, Ph) ppm. ^{19}F NMR ([D_6]DMSO): δ = –147.5 ppm.

Synthesis of Compounds 2,3,7–9. General Procedure: A solution of compound **1** or **4**–**6** (10 mmol) in $CHCl_3$ was added to a suspension of finely powdered KOH and PTC (0.1 mmol) in PhH or toluene (the ratio of starting compounds and reaction conditions are given in Tables 2 and 3). The mixture was stirred until the reaction was complete (TLC and GLC monitoring). The organic phase was decanted, and the residue extracted with Et_2O (3 × 5 mL). The combined organic solutions were washed with water (3 × 20 mL) and dried with anhydrous $MgSO_4$. The solvents were evaporated under reduced pressure (15 Torr). The residue was purified by column chromatography [silica gel, 0.060–0.200 µm; eluents *n*-hexane and *n*-hexane/PhH (95:5, 90:10, 80:20, 50:50)] yielding compounds **2**, **3**, and **7**–**9** (the yields are given in Tables 2 and 3).

2a: Oil; n_D^{20} = 1.5215 (ref.[17] 1.5220, data for corresponding diethyl acetal). ^{1}H NMR: δ = 2.32 (dd, *J* = 6.0, 8.5 Hz, 1 H, CH_{cPr}), 2.88 (d, *J* = 8.5 Hz, 1 H, CH_{cPr}), 3.42 and 3.51 (2 s, 3 H, OMe), 4.52 [d, *J* = 6.0 Hz, 1 H, C*H*(OMe)$_2$], 7.25–7.45 (m, 5 H, Ph) ppm.

2b: Oil; n_D^{20} = 1.4675 (ref.[18] 1.4660). ^{1}H NMR: δ = 1.24, 1.38, 2.09 (3 s, 3 H, CH_3), 1.55 (t, *J* = 7.0 Hz, 1 H, CH_{cPr}), 4.18 (d, *J* = 7.0 Hz, 2 H, CH_2) ppm.

2c: Oil; n_D^{20} = 1.4860. ^{1}H NMR: δ = 1.12, 1.27, 1.31 (3 s, 3 H, CH_3), 1.40–1.76 (m, 6 H, 2 × CH_2, CH_{cPr} and OH), 5.05 (d, *J* = 10.3 Hz, 1 H, CH=), 5.20 (d, *J* = 17.4 Hz, 1 H, CH=), 5.90 (dd, *J* = 10.3, 17.4 Hz, 1 H, CH=) ppm. $C_{11}H_{18}Cl_2O$ (237.17): calcd. C 55.71, H 7.65, Cl 29.90; found C 55.90, H 7.52, Cl 29.64.

2d: Oil; n_D^{25} = 1.4770 (ref.[20] n_D^{17} = 1.4833). ^{1}H NMR: δ = 1.13, 1.32, 1.70, 2.05 (4 s, 3 H, CH_3), 1.45–1.78 (m, 3 H, CH_2, CH_{cPr}), 2.10–2.20 (m, 2 H, CH_2C=), 4.57 (d, *J* = 7.0 Hz, 2 H, CH_2O), 5.36 (t, *J* = 7.0 Hz, 1 H, CH=) ppm.

3d: Oil; n_D^{20} = 1.4950. ^{1}H NMR: δ = 1.15, 1.23, 1.32, 2.08 (4 s, 3 H, CH_3), 1.55–1.82 (m, 6 H, 2 × CH_2, 2 × CH_{cPr}), 4.12 (ddd, *J* = 1.8, 7.3, 11.8 Hz, 1 H, C*H*HO), 4.26 (dd, *J* = 7.3, *J* = 11.8 Hz, 1 H, CH*H*O) ppm. ^{13}C NMR: δ = 17.1, 20.8, 22.5, 23.9, 24.8, 28.4, 32.5, 35.7, 37.0, 37.9, 38.1, 38.2, 61.0 (*C*H$_2$OAc), 69.6 (CCl_2), 71.5 (CCl_2), 170.6 (C=O) ppm. $C_{14}H_{20}Cl_4O_2$ (362.12): calcd. C 46.43, H 5.57, Cl 39.16; found C 46.71, H 5.69, Cl 38.92.

2e: Oil; n_D^{20} = 1.4575. ^{1}H NMR: δ = 0.90 (d, *J* = 6.0 Hz, 3 H, CH_3), 1.06 (t, *J* = 6.0 Hz, 1 H); 1.12, 1.30 (2 s, 1 H); 1.16 (t, *J* = 7.0 Hz, 6 H, 2 × CH_3), 1.35–1.50 (m, 5 H, 2 × CH_2, CH); 1.60–1.70 (m, 2 H, CH_2); 3.43–3.55, 3.57–3.70 (2 m, 2 H, OCH_2), 4.59 [t, *J* = 5.8 Hz, 1 H, C*H*(OEt)$_2$] ppm. $C_{15}H_{28}Cl_2O_2$ (311.29): calcd. C 57.88, H 9.07, Cl 22.78; found C 58.09, H 8.98, Cl 22.57.

2f: Oil; n_D^{20} = 1.5040 (ref.[21] 1.5060). ^{1}H NMR: δ = 1.03–1.20 (m, 1 H, CH_{cPr}), 1.12, 1.30 (2 s, 3 H, CH_3), 1.6–1.75 (m, 2 H, CH_2), 1.98 [s, 1.2 H, CH_3C=, (*Z*) isomer], 2.17 [s, 1.8 H, CH_3C=, (*E*) isomer], 2.25–2.40 [m, 0.8 H, CH_2C=, (*Z*) isomer], 2.70 [t, *J* = 7.5 Hz, 1.2 H, CH_2C=, (*E*) isomer], 5.87 [d, *J* = 8.2 Hz, 0.6 H, CH=C, (*E*) isomer], 5.91 [d, *J* = 8.2 Hz, 0.4 H, CH=C, (*Z*) isomer], 9.95 [d, *J* = 8.2 Hz, 0.4 H, CH=O, (*Z*) isomer], 9.97 [d, *J* = 8.2 Hz, 0.6 H, CH=O, (*E*) isomer] ppm.

3f: Oil; n_D^{20} = 1.4850 (ref.[21] 1.4885). ^{1}H NMR: δ = 1.12–1.40 (m, 15 H, 5 × CH_3), 1.5–1.85 (m, 6 H, 2 × CH_2, CH_{cPr}), 3.45–3.70 (m, 4 H, 2 × CH_2O), 4.37 [d, *J* = 7.8 Hz, 0.6 H, C*H*(OEt)$_2$], 4.47, 4.50 [2 d, *J* = 7.8 Hz, 0.2 H, C*H*(OEt)$_2$] ppm.

2g: Oil; n_D^{25} = 1.4490 (ref.[24] n_D^{20} = 1.4519 for *i*Pr ester). ^{1}H NMR: δ = 1.26 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.40 (dd, *J* = 7.5, 1.5 Hz, 1 H, C*H*H), 1.57 (s, 3 H, CH_3), 2.25 (dd, *J* = 7.5, 1.5 Hz, 1 H, CH*H*), 4.20 (q, *J* = 7.0 Hz, 2 H, CH_2O) ppm.

2h: Colorless crystals; m.p. 63–64 °C (ref.[15c] 64–65 °C). ^{1}H NMR: δ = 1.0, 1.32, 1.38 (3 s, 3 H, CH_3), 1.51 (d, *J* = 9.6 Hz, 1 H), 1.67–1.72 (m, 1 H), 1.98 (d, *J* = 11.7 Hz, 1 H), 2.00 (dtd, *J* = 13.1, 5.7, 2.3 Hz, 1 H), 2.12 (t, *J* = 5.7 Hz, 1 H), 2.23 (dddd, *J* = 13.1, 9.6, 3.5, 2.3 Hz, 1 H), 2.38 (d, *J* = 11.7 Hz, 1 H) ppm.

2i: Oil; n_D^{20} = 1.5170. ^{1}H NMR: δ = 1.45 (s, 3 H, CH_3), 1.75 (s, 3 H, CH_3), 2.05–2.25 (m, 1 H, CH), 2.30–2.45 (m, 4 H, 2 × CH_2), 2.65 (m, 1 H, CH), 4.58 (s, 1 H, CH=), 4.85 (s, 1 H, CH=) ppm. $C_{11}H_{14}Cl_2O$ (233.13): calcd. C 56.67, H 6.05, Cl 30.41; found C 56.89, H 6.22, Cl 30.24.

2j: Oil; n_D^{20} = 1.5210. ^{1}H NMR: δ = 1.25 (s, 2 H, CH_2C=), 1.27 (s, 3 H, CH_3), 1.75 (s, 3 H, CH_3C=), 2.10–2.65 (m, 5 H, 2 × CH_2, CH), 6.73 (br. s, 1 H, CH=) ppm. $C_{11}H_{14}Cl_2O$ (233.13): calcd. C 56.67, H 6.05, Cl 30.41; found C 56.81, H 5.98, Cl 30.30.

7a: Colorless crystals; m.p. 39–40 °C (ref.[22] 41 °C). ^{1}H NMR: δ = 2.82, 3.07 (2 t, *J* = 7.8 Hz, 2 H, CH_2) ppm.

7b: Oil; n_D^{20} = 1.4660 (ref.[35] n_D^{25} = 1.4648 for Me ester). ^{1}H NMR: δ = 1.28 (t, *J* = 7.8 Hz, 3 H, CH_3), 2.80, 3.05 (2 t, *J* = 8.0 Hz, 2 H, CH_2), 4.18 (q, *J* = 7.8 Hz, 2 H, OCH_2) ppm. $C_6H_9Cl_3O_2$ (219.49): calcd. C 32.83, H 4.13, Cl 48.46; found C 33.01, H 3.98, Cl 48.29.

7c: Oil; n_D^{20} = 1.4540 (ref.[28] 1.4574). ^{1}H NMR: δ = 1.62 (d, *J* = 6.6 Hz, 3 H, CH_3), 2.30 [s, 3 H, C(O)CH_3], 5.50 (q, *J* = 6.6 Hz, 1 H, CH) ppm.

8a: Oil; n_D^{20} = 1.5670 (ref.[25b] 1.5650). ^{1}H NMR: δ = 3.70 (br. s, 1 H, OH), 5.23 (s, 1 H, CH), 7.42 (m, 3 H, Ph), 7.66 (d, *J* = 8.5 Hz, 2 H, Ph) ppm.

8b: Colorless crystals; m.p. 62–63 °C (ref.[36] 65–66 °C). ^{1}H NMR: δ = 2.98 (d, *J* = 5.9 Hz, 1 H, OH), 4.80 (t, *J* = 5.9 Hz, 1 H, C*H*OH), 6.4 (dd, *J* = 5.9, 17.4 Hz, CH=), 6.92 (d, *J* = 17.4 Hz, 1 H, PhCH=), 7.25–7.50 (m, 5 H, Ph) ppm.

8c: Oil; n_D^{20} = 1.5100 (ref.[27] 1.5095). ^{1}H NMR: δ = 1.60 1.68, 1.80 (3 s, 3 H, CH_3), 2.15 (br. s, 4 H, 2 × CH_2), 2.78 (br. s, 1 H, OH), 4.80 (br. s, 1 H, C*H*OH), 5.09 (br. s, 1 H, CH=), 5.38 (d, *J* = 8.4 Hz, 1 H,=CH) ppm.

9a: Colorless crystals; m.p. 88–89 °C (ref.[37] 87.5 °C). ^{1}H NMR: δ = 2.25 (s, 3 H, CH_3), 6.40 (s, 1 H, CH), 7.40 (m, 3 H, Ph), 7.63 (br. s, 2 H, Ph).

9b: Oil; n_D^{20} = 1.4690 (ref.[28] 1.4705). ^{1}H NMR: δ = 1.78 (d, *J* = 7.5 Hz, 3 H, CH_3), 2.15 [s, 3 H, C(O)CH_3], 5.60 (dd, *J* = 7.5, 15.8 Hz, 1 H, CH=), 5.77 (d, *J* = 7.5 Hz, 1 H, C*H*OAc), 6.03 (dq, *J* = 7.5, 15.8 Hz, 1 H, CH=) ppm.

Regeneration of nBu$_4$NPF$_6$: Water (5 mL) was added to the solid left after extractions of compounds **2**, **3**, and **7**–**9** with Et_2O, the precipitate was filtered, washed successively with water (3 × 2 mL) and Et_2O (2 × 2 mL), and then dried in air to afford *n*Bu$_4$NPF$_6$ (33 mg, 85%); m.p. 242–246 °C (ref.[10a] 243–246 °C). ^{1}H NMR ([D$_6$]DMSO): δ = 1.00 (t, *J* = 7.5 Hz, 12 H, 4 × CH_3), 1.35, 1.60 (2 m, 8 H, 4 × CH_2), 3.15 (t, *J* = 7.5 Hz, 8 H, 4 × CH_2) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 13.4 (CH_3), 19.2, 23.0, 57.5 (3 × CH_2) ppm. ^{19}F NMR ([D$_6$]DMSO): δ = –70.7 (d, $J_{P,F}$ = 708 Hz) ppm. $C_{16}H_{36}F_6NP$ (387.43): calcd. C 49.60, H 9.37, F 29.42, N 3.62; found C 49.35, H 9.54, F 29.18, N 3.71.

***n*Bu$_4$NOH-Promoted Reaction between Cinnamaldehyde (5b) and CHCl$_3$:** A solution of aldehyde **5b** (0.66 g, 5.0 mmol) in $CHCl_3$ (0.8 mL) was added to a solution of freshly prepared *n*Bu$_4$NOH (1.30 g, 5.0 mmol) in PhH (8 mL). The reaction mixture was stirred at 20 °C for 6 h, diluted with Et_2O (20 mL) and poured into water (20 mL). The organic phase was separated, washed with water (3 × 10 mL) and dried with anhydrous $MgSO_4$. The solvents were evaporated (40 °C, 40 Torr) to afford a mixture of compounds **5b** and **8b** in a 53:47 ratio (^{1}H NMR).

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[1] a) T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2083; b) P. Wasserscheid, T. Welton (Eds.), *Ionic liquids in Synthesis*, Wiley-VCH, **2003**, pp. 363; c) H. Xue, R. Verma, J. M. Shreeve, *J. Fluorine Chem.* **2006**, *127*, 159–176.

[2] a) D. Zhao, M. Wu, Y. Kou, E. Min, *Catal. Today* **2002**, *74*, 157–189; b) H. Olivier-Bourbigou, L. Magna, *J. Mol. Catal. A* **2002**, *182–183*, 419–437.

[3] a) M. Freemantle, *Science/Technology* **2000**, *78*, 37–50; b) M. J. Earle, K. R. Seddon, *Pure Appl. Chem.* **2000**, *72*, 1391–1398.

[4] a) P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789; b) J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667–3692; c) U. Kragl, M. Eckstein, N. Kaftzic, *Curr. Opin. Biotechnol.* **2002**, *13*, 565–571.

[5] a) R. Hagiwara, Y. Ito, *J. Fluorine Chem.* **2000**, *105*, 221–227; b) S. Cadra-Broch, A. Berthod, D. W. Armstrong, *Anal. Bioanal. Chem.* **2003**, *375*, 191–199; c) P. Bonhôte, A. P. Dias, N. Papageorgiu, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, *35*, 1168–1178.

[6] a) P. J. Dyson, *Chimia* **2005**, *59*, 66–71; b) J. J. M. de Pater, B.-J. Deelman, C. J. Elsevier, J. Cornelis, G. van Koten, *Adv. Synth. Catal.* **2006**, *348*, 1447–1458; c) T. J. Geldbach, D. Zhao, N. C. Castillo, G. Laurenczy, B. Weyershausen, P. J. Dyson, *J. Am. Chem. Soc.* **2006**, *128*, 9773–9780; d) Y. Y. Wang, M. M. Luo, Q. Lin, H. Chen, X. J. Li, *Green Chem.* **2006**, *8*, 545–548; e) T. J. Geldbach, G. Laurenczy, R. Scopelliti, P. J. Dyson, *Organometallics* **2006**, *25*, 733–742; f) P. Rodriguez, A. Caballero, M. M. Diaz-Requejo, M. C. Nicasio, P. J. Perez, *Org. Lett.* **2006**, *8*, 557–560; g) A. S. Kucherenko, M. I. Struchkova, S. G. Zlotin, *Eur. J. Org. Chem.* **2006**, 2000–2004.

[7] E. V. Dehmlow, S. S. Dehmlow, *Phase Transfer Catalysis*, 3rd ed., VCH Verlag, Weinheim, **1993**.

[8] Y. Sasson, G. Rothenberg, in *Handbook of Green Chemistry and Technology* (Eds.: J. Clark, D. Macquarrie), Blackwell Science Ltd., Oxford, **2002**, p. 206–267.

[9] a) T. Tanaka, T. Mukaiama, *Chem. Lett.* **1976**, 1259–1262; b) R. N. M. T. Lourenço, C. A. M. Afonso, *Tetrahedron* **2003**, *59*, 789–794; c) S. Muthusamy, B. Gnanaprakasam, *Tetrahedron Lett.* **2005**, *46*, 635–638; d) H. Sun, J. Li, X. C. Cai, D. Jiang, L. Y. Dai, *Chin. Chem. Lett.* **2007**, *18*, 279–282.

[10] a) G. V. Kryshtal, G. M. Zhdankina, S. G. Zlotin, *Eur. J. Org. Chem.* **2005**, 2822–2827; b) S. G. Zlotin, A. V. Bogolyubov, G. V. Kryshtal, G. M. Zhdankina, M. I. Struchkova, V. A. Tartakovsky, *Synthesis* **2006**, 3849–3854.

[11] a) S. E. Hunter, C. Boyce, B. P. Armitage, P. Ten Haken, W. M. Wagner, Ger. Offen. DE2219710, C07c, A01n, **1972** (*Chem. Abstr.* **1973**, *78*, 29312); b) R. J. G. Searle, R. E. Woodall, Ger. Offen. DE2407024, C07d, A01n, **1974** (*Chem. Abstr.* **1974**, *81*, 169325); c) R. J. G. Searle, R. E. Woodall, E Roger, M. J. Bull, Ger. Offen. DE2422977, C07c, A01n, **1974** (*Chem. Abstr.* **1975**, *82*, 170187); d) I. Okada, Y. Shiga, T. Fukuchi, Jap. Pat. JP172271, C07D285/135, **2001** (*Chem. Abstr.* **2001**, *135*, 61337).

[12] a) L. Skatteboel, Y. Stenstroem, C. Syvertsen, *J. Agric. Food Chem.* **2004**, *52*, 6944–6949; b) H. R. Hovde, K. Kleveland, N. O. Nilsen, Y. Stenstrom, L. Skattebol, PCT Int. Appl. WO0106853, A01N31/00, **2001** (*Chem. Abstr.* **2001**, *134*, 127290).

[13] D. Arlt, M. Jautelat, R. Lantzsch, *Angew. Chem.* **1981**, *93*, 719–738.

[14] a) M. Makosza, M. Fedorynski, *Adv. Catal.* **1987**, *35*, 375–422; b) M. Makosza, M. Fedorynski, in *Handbook of Phase Transfer Catalysis* (Eds.: Y. Sasson, R. Neumann), Chapman & Hall, London, **1997**, p. 135–167.

[15] a) F. Sirovsky, C. Reichardt, M. Gorokhova, S. Ruban, E. Stoikova, *Tetrahedron* **1999**, *55*, 6363–6374; b) F. Sirovsky, M. Gorokhova, S. Ruban, *J. Mol. Catal. A* **2003**, *197*, 213–222; c) S. Jubia, A. Ginebreda, *Synthesis* **1977**, 682–683.

[16] S. Chowdhurry, R. S. Mohan, J. L. Scott, *Tetrahedron* **2007**, *63*, 2363–2389.

[17] A. Kh. Khusid, G. V. Kryshtal, V. F. Kucherov, L. A. Yanovskaya, *Bull. Acad. Sci. USSR. Div. Chem. Sci.* **1975**, *24*, 2462–2464.

[18] G. V. Kryshtal, L. A. Yanovskaya, Yu. P. Volkov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1987**, *36*, 620–622.

[19] K. Kleveland, L. Scattebol, L. K. Syndes, *Acta Chem. Scand., Ser. B* **1977**, *31*, 463–468.

[20] T. K. Baryshnikova, M. E. Niyazymbetov, V. S. Bogdanov, V. A. Petrosyan, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1988**, *37*, 2093–2095.

[21] G. V. Kryshtal, A. Kh. Khusid, V. F. Kucherov, L. A. Yanovskaya, *Izv. Acad. Nauk SSSR. Ser. Khim.* **1977**, 709–711.

[22] E. V. Dehmlow, *Justus Liebigs Ann. Chem.* **1972**, *758*, 148–154.

[23] M. S. Baird, S. R. Buxton, P. Sadler, *J. Chem. Soc. Perkin Trans. 1* **1984**, 1379–1385.

[24] M. Makosza, J. Gajos, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1972**, *20*, 33–37.

[25] a) A. Merz, R. Tomahogh, *Chem. Ber.* **1977**, *110*, 96–106; b) Yu. P. Volkov, L. A. Yanovskaya, G. V. Kryshtal, V. M. Kalinevich, E. I. Trusova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1986**, *35*, 1242–1246.

[26] G. V. Kryshtal, M. Makosza, M. Fedorynski, L. A. Yanovskaya, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1983**, *32*, 602–606.

[27] G. V. Kryshtal, G. M. Zhdankina, L. A. Yanovskaya, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1986**, *35*, 1081–1083.

[28] G. V. Kryshtal, V. S. Bogdanov, L. A. Yanovskaya, Yu. P. Volkov, E. I. Trusova, *Tetrahedron Lett.* **1982**, *23*, 3607–3610.

[29] a) C. L. Liotta, J. Berkner, J. Wright, B. Fair, in *Phase-Transfer Catalysis: Mechanisms and Synthesis* (Ed.: M. E. Halpern), ACS Symposium Series 659, American Chemical Society, Washington, DC, **1997**, p. 29–40; b) S. S. Yufit, G. V. Kryshtal, I. A. Esikova, in *Phase-Transfer Catalysis: Mechanisms and Synthesis* (Ed.: M. E. Halpern), ACS Symposium Series 659, American Chemical Society, Washington, DC, **1997**, p. 52–67.

[30] a) M. Makosza, *Pure Appl. Chem.* **2000**, *72*, 1399–1403; b) M. Makosza, I. Krylova, *Tetrahedron* **1999**, *55*, 6395–6402.

[31] S. Chun, S. V. Dzyuba, R. A. Bartsch, *Anal. Chem.* **2001**, *73*, 3737–3741.

[32] G. V. Kryshtal, D. Dvořak, Z. Arnold, L. A. Yanovskaya, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1986**, *35*, 838–840.

[33] G. V. Kryshtal, V. S. Bogdanov, L. A. Yanovskaya, Yu. P. Volkov, E. I. Trusova, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 2820–2823.

[34] V. P. Kukhar', V. I. Pasternak, I. V. Shevchenko, M. V. Shevchenko, A. P. Marchenko, Yu. P. Makovetskii, *Zh. Org. Khim. USSR* **1981**, 180–186.

[35] R. E. Foster, A. W. Larchak, R. D. Lipsomb, B. C. McKusick, *J. Am. Chem. Soc.* **1956**, *78*, 5606–5611.

[36] R. Ferraccioli, C. Gallina, C. Giordano, *Synthesis* **1990**, 327–328.

[37] F. D. Chattaway, R. J. K. Muir, *J. Chem. Soc.* **1934**, 701–703.

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