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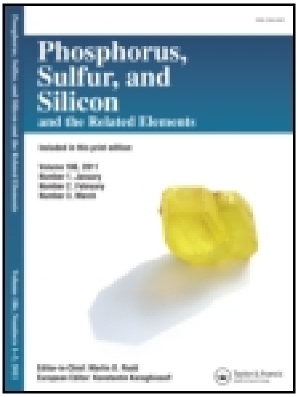

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Synthesis of Phosphonium Salts—Phosphine Structure and Inorganic Salts Effects

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Synthesis of Phosphonium Salts—Phosphine Structure and Inorganic Salts Effects

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Solvent-free reactions of 2- and 3-halopyridines with PPh_3, PBu_3, and PCy_3 were studied under conventional heating, as well as under microwave irradiation. No difference was observed in the reaction course between classical and microwave reactions. 2-Bromopyridine gave quantitative yields of 2-pyridyltriphenylphosphonium bromide within few minutes at 190°C. Equimolar amounts of some inorganic salts ($LiPF_6$, LiOTf, LiBr, $NaPF_6$, KPF_6) were necessary for the reactions of the other 2-halopyridines. 3-Halopyridines did not react with PPh_3 even in the presence of $LiPF_6$. Their reactions with PCy_3 in the presence of $LiPF_6$ resulted in the quantitative formation of dicyclohexylphosphine oxide.

Keywords Phosphonium salts; inorganic salt effects; phosphine structure effects; halopyridines; S_NAr mechanism; microwave irradiation

INTRODUCTION

In our previous work,[1] we examined the reactions of neutral ($PhCH_2Cl$ and $PhCH_2Br$) and ionic ($PhCH_2N^+Me_3Cl^-$) benzylating agents with phosphines. We have found that the effect of microwave irradiation on these reactions depended essentially on the leaving group.

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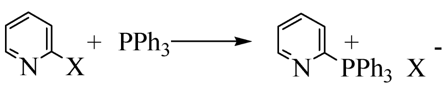
Rather poor acceleration of the reaction was observed with benzyl bromide, more pronounced with benzyl chloride and high with benzyl trialkylammonium salts. The solvent-free reaction of tributylphosphine with $PhCH_2N^+Me_3Cl^-$ occurred only under microwave irradiation. Microwave reaction with PBu_3 (100°C, 10 min) gave $PhCH_2P^+Bu_3Cl^-$ quantitatively.

Solid-liquid phase transfer catalysis coupled with microwave irradiation was shown to be an efficient method for S_NAr reaction of quinoline and pyridine halides with potassium methoxide or phenoxide.[2,3] Microwave acceleration of the reaction was observed for phenoxylation.[4]

These earlier results, as well as the fact that there was just one paper published on the reactions of halopyridines with triphenylphosphine,[5] prompted us to study S_NAr reactions of pyridine halides with several phosphines (PPh_3, PBu_3, and PCy_3) under solvent-free conditions, both under classical heating, as well as under microwave irradiation.

RESULTS AND DISCUSSION

We started our work with the study of reactions of 2-halopyridines with triphenylphosphine (PPh_3) (Scheme 1). Reactions were carried out with equimolar quantities of reactants at the same temperature both under thermal heating, as well as under microwave irradiation. In the case of the classical experiment, a flask containing the reaction mixture was immersed into the pre-heated oil bath. The results are given in Table I.



1 **2**

a X = F

b X = Cl

c X = Br

d X = I

SCHEME 1 Reactions of 2-halopyridines **1a–d** with triphenylphosphine.

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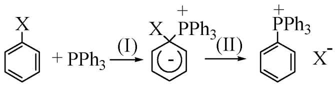
TABLE I Reactions of 2-Halopyridines with Triphenylphosphine Under Classical Heating (CH) or Microwave Irradiation (MWI)

				Yield %	
X	Temperature °C	Time min	Product	CH	MWI
F	120	120	—	0[a]	0[a]
Cl	160	120	**2b**	7	10
Br	160	30	**2c**	52	53
Br	190	10	**2c**	35	38
Br	190	15	**2c**	88	93
Br	190	20	**2c**	97	95
Br	190	30	**2c**	95	95
I	190	120	**2d**	68	73

[a]Only starting materials were detected in the reaction mixture.

Quantitative yields of **2c** were obtained from the reaction with 2-bromopyridine **1c** after 20 min at 190°C. 2-Iodopyridine **1d** gave 73% and 68% of **2d** by CH or MWI under similar conditions (2 h at 190°C), respectively. On the other hand, 2-chloropyridine **1b** gave only a small amount (7–10%) of the product **2c**. 2-Fluoropyridine **1a** did not react under these conditions and only the starting materials were recovered.

The sequence of reactivity according to halide nature is not the classical one (Br > I ≫ Cl, F). It is not the one we could expect from normal S_NAr mechanism, where the first step (I) is usually rate-determining[6] (Scheme 2).



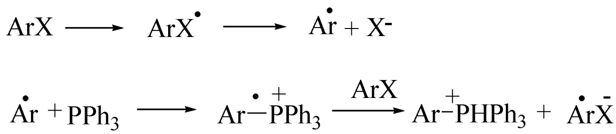
(I) Nucleophilic attack of phosphine on *ipso* carbon atom; halide effect: F > Cl > Br > I

(II) Cleavage of C–X bond; halide effect: I > Br > Cl > F

SCHEME 2 The two-step S_NAr mechanism (addition-elimination).

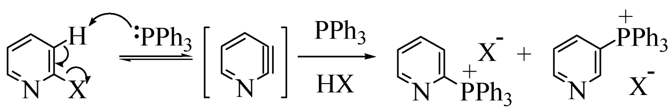
Other mechanisms have been proposed: a radical mechanism $S_{RN}1$[7] (Scheme 3) and an aryne (here dehydropyridine) mechanism (Scheme 4). The aryne mechanism involves HX *β*-elimination and subsequent phosphine / HX addition, leading to the formation of two regioisomers.[6]

The aryne mechanism was excluded because no Diels-Alder cycloadduct was observed when anthracene was added to the reaction mixture in the case of the experiment with 2-bromopyridine.



Halide effect: I > Br > Cl > F

SCHEME 3 The $S_{RN}1$ radical mechanism (elimination-addition).



β-Elimination: C–X bond cleavage in the order: I > Br > Cl > F

SCHEME 4 The aryne mechanism.

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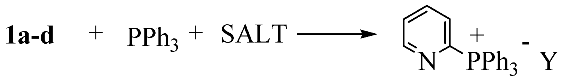
It was described that addition of inorganic salts can substantially affect the course of different reactions.[8] For that reason, we next studied the consequence of addition of various inorganic salts to the reaction mixture. We hoped that addition of salts can enhance the reaction rate and that could gave us a hint on the reaction mechanism. Essentially, alkaline salts were added and their effects could be important and indicative of the mechanism concerned: either negative if step (I) or positive if step (II) is the rate-determining step (Scheme 2).[8] Therefore, equivalent amounts of Li, Na, or K salts containing either halide anions (which also facilitate the halide exchange with halopyridine) or non-nucleophilic anions such as PF_6^- or OTf^- were added to the reaction mixture (Scheme 5). The results are given in Table II.

Reaction of 2-fluoropyridine **1a** with PPh_3 now proceeded efficiently with the assistance of LiBr (62–67%), $LiPF_6$ (72–76%) or $NaPF_6$ (74–78%). No reaction was induced by LiCl. 2-Chloropyridine **1b** gave the corresponding phosphonium salts in moderate to very good yields in the presence of lithium salts (LiBr, LiI, $LiPF_6$, LiOTf) and with the assistance of $NaPF_6$ and KPF_6. Addition of LiCl to the reaction mixture of chloropyridine **1b** and PPh_3 did not affect the reaction course and only very low yields of **2b** (6 and 10%, respectively) were isolated after classical as well as microwave reaction. Addition of $LiPF_6$ to the reaction mixture of 2-bromopyridine **1c** and PPh_3 resulted in the formation of 2-pyridyltriphenylphosphonium hexafluorophosphate **2e** in high yields (70–84%). It becomes evident that Li and Na salts have important effects that allow high yields of the products. These effects appeared to



2b-f

b	X, Y = Cl
c	X, Y = Br
d	X, Y = I
e	Y = PF_6
f	Y = OTf

SCHEME 5 Reactions of 2-halopyridines **1a–d** with triphenylphosphine in the presence of various inorganic salts.

be consistent with the intervention of Li^+ or Na^+ions to promote electrophilic assistance to C—X bond breaking in the second step of the S_NAr mechanism (Figure 1). When adding LiBr or LiI, one can also expect a halide exchange to produce 2-bromo (or -iodo) pyridine, which would be more reactive under these conditions. On the contrary, the halide exchange induced by addition of LiCl in the case of fluoropyridine **1a** would result in the formation of a less reactive chloro compound **1c**.

We next examined reactions of the 3-halopyridines **3b,c**, which are usually much less reactive than their 2-regioisomers, under conventional heating and under microwave irradiation. No similar reaction was described in the literature. Unfortunately, no reaction occurred regardless of the conditions applied and only the starting materials were recovered. Even addition of $LiPF_6$ resulted only in 7−9% yields of **4** for the reactions of 3-chloro- as well as 3-bromopyridine (Scheme 6).

These results suggest that the mechanism operating here is the S_NAr mechanism, where the rate-determining step involves the elimination of the leaving group under electrophilic assistance by the alkaline

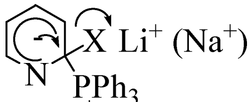


FIGURE 1 Electrophilic assistance by Li^+ in the second step of S_N Ar mechanism.

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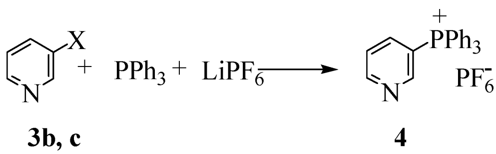

SCHEME 6 Reactions of 3-halopyridines **3b**, **c** with triphenylphosphine in the presence of $LiPF_6$.

cation. Control experiments carried out in the presence of hydroquinone as radical scavenger, which did not induce any change in the yields, thus precluding a radical mechanism. We performed also experiments in the presence of anthracene (reactant for trapping possible "aryne" intermediate in Diels-Alder reaction), but no cycloaddition product was observed, which excluded the elimination-addition mechanism. Such mechanism can be excluded also by the fact that just one regioisomer of the product was isolated in each case.

TABLE II Reactions of 2-Halopyridines 1a–d with Triphenylphosphine in the Presence of Inorganic Salts Under CH or MWI

X	Salt	Y	Temperature °C	Time h	Product	Yield % CH	Yield % MWI
F	—	—	120	2	—	0[a]	0[a]
F	LiBr	Br	120	2	**2c**	62	67
F	$LiPF_6$	PF_6	120	2	**2e**	76	72
F	$NaPF_6$	PF_6	120	2	**2e**	**78**	**74**
F	LiCl	Cl	120	2	—	0[a]	0[a]
Cl	—	—	160	2	**2b**	7	10
Cl	LiCl	Cl	160	2	**2b**	6	10
Cl	LiBr	Br	160	2	**2c**	67	71
Cl	LiI	I	160	2	**2d**	64	60
Cl	$LiPF_6$	PF_6	160	5 min	**2e**	**82**	**88**
Cl	LiOTf	OTf	160	2	**2f**	40	37
Cl	$NaPF_6$	PF_6	160	2	**2e**	**82**	**82**
Cl	KPF_6	PF_6	160	2	**2e**	29	31
Br	—	—	160	0.5	**2c**	52	53
Br	$LiPF_6$	PF_6	180	0.25	**2e**	70	70
Br	$LiPF_6$	PF_6	180	0.5	**2e**	**86**	**84**

[a]Only starting materials were recovered from the reaction mixture.

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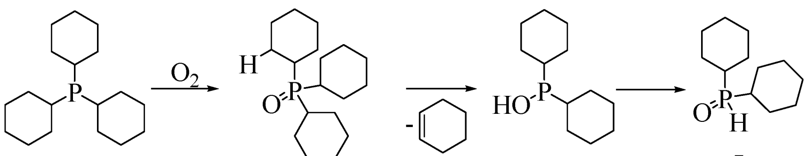
Next the reaction of tricyclohexylphosphine (PCy_3) with 2-halopyridines was studied. Even with 2-bromopyridine no reaction was observed. Instead decomposition of PCy_3 or side-products takes place and only black tarry materials were isolated from the reactions at high temperature (190°C). Performing the reaction of 2-halopyridines with PCy_3 in the presence of $LiPF_6$ at lower temperatures (100 and 120°C, respectively) gave dicyclohexylphosphine oxide **5** as the only product in high yields (89–96%).

Presumably **5** is formed by a competing reaction of tricyclohexylphosphine with oxygen. To investigate this hypothesis the following experiments were performed: Heating of PCy_3 with $LiPF_6$ in air (2 h at 120°C) without any halopyridines gave quantitative amounts of dicyclohexylphosphine oxide **5**. No oxidation was observed, when we heated PCy_3 (2 h at 120°C) without $LiPF_6$ and only unreacted starting material was detected (^{1}H NMR) in the product mixture. Performing the reaction of 2-bromopyridine with PCy_3 in the presence of $LiPF_6$ at 120 °C under a nitrogen atmosphere gave only traces of dicyclohexylphosphine oxide **5** as the only product. These experiments confirmed our hypothesis and a plausible reaction path is shown in Scheme 7. We observed no difference between the course of classically heated reactions and microwave reactions.

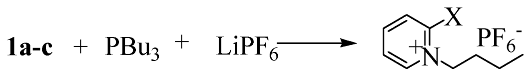


5

SCHEME 7 Proposed reaction path for the formation of dicyclohexylphosphine oxide **5**.

Finally, we checked the reactivity of 2- and 3-halopyridines with tributylphosphine (PBu_3) under conventional heating as well as under microwave irradiation (Schemes 8 and 9). 2-Halopyridines showed no reaction with PBu_3. Only the starting materials and some unidentified products resulting from the thermal decomposition of PBu_3 were detected by TLC in the reaction mixtures. Addition of $LiPF_6$ to the reaction mixture resulted in isolation of 2-chloro-*N*-butylpyridinium hexafluorophosphate (24–28%) and 2-bromo-*N*-butylpyridinium hexafluorophosphate (10%). 2-Fluoropyridine did not react even in the presence of $LiPF_6$.

In contrast to the reaction with PPh_3, 2-chloropyridine **1b** did not react with PBu_3 in the presence of LiBr, $NaPF_6$ or LiOTf. Starting materials and some products of decomposition were detected (TLC) in the

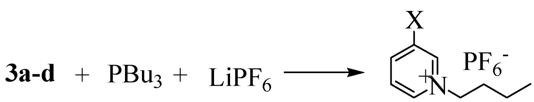


6b,c

b `X = Cl

c X = Br

SCHEME 8 Reactions of 2-halopyridines **1a–c** with tributylphosphine in the presence of $LiPF_6$.



7b-d

b X = Cl

c X = Br

d X = I

SCHEME 9 Reactions of 3-halopyridines **3a–d** with tributylphosphine in the presence of $LiPF_6$.

reaction mixture under both conventional and microwave conditions. Only unreacted starting material was detected (^{1}H NMR) after heating of 2-bromopyridine **1c** with PBu_3 in the presence of $LiPF_6$ at 150°C (4 h) under inert atmosphere.

The isolation of a pyridine alkylation product in the presence of $LiPF_6$ can be explained by the higher thermodynamic stability of *N*-butylpyridinium PF_6 salt compared to its bromide salt. On the other hand the bromide anion has reasonable nucleophilicity and can dealkylate an *N*-butylpyridinium salt (1-bromobutane can be formed). 3-Chloro-, 3-bromo-, and 3-iodopyridines reacted with PBu_3 in the presence of $LiPF_6$ to give 3-halo-*N*-butylpyridinium hexafluorophosphate in low (9−11%) yields. No reaction of PBu_3 with 3-fluoropyridine was observed (Scheme 9). The low yields of *N*-alkylation products observed in the reaction with 3-chloro, 3-bromo- and 3-iodopyridines can be explained by the lower nucleophilicity of the nitrogen atom owing to

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the –I effect of the halogen atom located at position 3 of the pyridine ring.

Under our experimental conditions (open systems exposed to air) the formation of trialkylphosphine oxides was feasible. Triphenylphosphine is less nucleophilic than trialkylphosphines and therefore less susceptible to attack by oxygen. Probably tributylphosphine oxide acts as an alkylating agent enabling *N*-alkylation of pyridine to occur. In the case of tricyclohexylphosphine, owing to steric constraints alkylation appears less probable, allowing a competitive elimination process to occur to give cyclohexene and dicyclohexylphosphine oxide **5**.

CONCLUSION

Nucleophilic substitutions of 2-halopyridines with triphenylphosphine proceeded straightforward in the case of 2-bromo- and 2-iodopyridine and comparable results were achieved in experiments with and without MW irradiation. No effect of microwave irradiation was observed. Reactivity of 2-fluoro- and 2-chloropyridines was strongly enhanced by addition of lithium salts and especially with LiBr or $LiPF_6$ a specific Li effect was observed. 2-Halopyridines behaved very differently in the reactions with tributylphosphine and tricyclohexylphosphine. These phosphines can undergo reaction with atmospheric oxygen to form corresponding trialkylphosphine oxides. Tributylphosphine oxide in turn could act as an alkylating agent forming *N*-butylpyridinium salts, especially when $LiPF_6$ was present. Tricyclohexylphosphine oxide is rather bulky and therefore no alkylation of pyridine was observed. Instead it underwent cyclohexene elimination and dicyclohexylphosphine oxide was isolated in quantitative yield.

EXPERIMENTAL

NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 300 MHz (^{1}H), 75 MHz (^{13}C) and 121.5 MHz (^{31}P). Tetramethylsilane was used as an internal standard (^{1}H, ^{13}C) and H_3PO_4 (85%) was used as an external standard (^{31}P). Melting points were determined on a Kofler apparatus. The elemental analyses were recorded on a Carlo-Erba instrument. Halopyridines, phosphines and inorganic salts were purchased in reagent grade (Aldrich, Acros Organics, Fluka, Merck, Janssen Chimica, Avocado) and used without further purification. All microwave experiments were carried out in a monomode reactor Synthewave® 402 from Prolabo (France).[9] The temperature was measured by IR detection, which indicates the surface temperature after previous calibration of emissivity in each case using an optical fiber inside the reaction mixture. The reactions were conducted using a cylinder tube in Pyrex under mechanical stirring to allow homogeneity in the temperature.

General Microwave Procedure

A homogeneous mixture of the halopyridine (10 mmol), the phosphine (10 mmol) and the inorganic salt (10 mmol) was irradiated in the Synthewave® 402 MW reactor for the times and temperatures indicated in Tables I and II. After cooling down to room temperature, the solid material was dissolved in a mixture of dichloromethane (50 mL) and water (50 mL). The organic phase was separated, extracted twice with water (50 mL) to remove inorganic salts and then dried over anhydrous magnesium sulfate. Dichloromethane was evaporated under reduced pressure and the solid residue was washed with diethyl ether (100 mL) to remove unreacted starting materials. The products thus obtained were analytically pure. When the reactions were performed without an inorganic salt, the solid material after irradiation was washed directly with diethyl ether and the products were analyzed by ^{1}H, ^{13}C, and ^{31}P spectroscopy.

General Procedure under Conventional Heating

The experiments were carried out in a thermostated oil bath at the same temperature, in identical reaction vessels, for the same time and with similar profiles of raising the temperature as for the microwave experiments (Tables I and II). The treatment of the reaction mixture and the analysis of the products were identical to those described in the microwave procedure.

2-Pyridyltriphenylphosphonium Chloride (2b)

Colorless solid, m.p. 250–253°C, lit.[5] 254–256°C; ^{1}H NMR ($CDCl_3$): δ 7.68–7.91 (m, 16H, Ar—H), 8.02–8.06 (m, 1H, pyridine—H), 8.40–8.42 (m, 1H, pyridine—H), 9.00–9.02 (m, 1H, pyridine—H); ^{13}C NMR ($CDCl_3$): δ 117.3 (d, $J = 88.4$ Hz, C-*i*), 129.0 (d, $J = 3.7$ Hz, C5-pyridine), 130.9 (d, $J = 13.0$ Hz, C-*m*), 132.6 (d, $J = 24.7$ Hz, C3-pyridine), 134.9 (d, $J = 10.2$ Hz, C-o), 136.0 (d, $J = 3.1$ Hz, C-*p*), 139.6 (d, $J = 10.5$ Hz, C4-pyridine), 144,3 (d, $J = 119.6$ Hz, C2-pyridine), 152.7 (d, $J = 19.5$ Hz, C6-pyridine); ^{31}P NMR ($CDCl_3$): δ 15.6.

2-Pyridyltriphenylphosphonium Bromide (2c)

Colorless solid, m.p. 271–274°C, lit.[5] 272–274°C; ^{1}H NMR ($CDCl_3$): δ 7.67–7.93 (m, 16H, Ar—H), 8.06–8.10 (m, 1H, pyridine—H), 8.38–8.47

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(m, 1H, pyridine—H), 9.00−9.01 (m, 1H, pyridine—H); ^{13}C NMR ($CDCl_3$): δ 117.3 (d, $J = 88.4$ Hz, C-*i*), 129.0 (d, $J = 3.8$ Hz, C5-pyridine), 130.9 (d, $J = 12.6$ Hz, C-*m*), 132.6 (d, $J = 24.7$ Hz, C3-pyridine), 134.9 (d, $J = 9.8$ Hz, C-o), 136.0 (d, $J = 2.8$ Hz, C—*p*), 139.5 (d, $J = 10.5$ Hz, C4-pyridine), 144,5 (d, $J = 119.9$ Hz, C2-pyridine), 152.7 (d, $J = 19.5$ Hz, C6-pyridine); ^{31}P NMR ($CDCl_3$): δ 15.6.

2-Pyridyltriphenylphosphonium Iodide (2d)

Colorless solid, m.p. 289−292°C; ^{1}H NMR ($CDCl_3$): δ 7.69−7.93 (m, 16H, Ar−H), 8.09−8.14 (m, 1H, pyridine−H), 8.32−8.47 (m, 1H, pyridine—H), 8.99−9.00 (m, 1H, pyridine—H); ^{13}C NMR ($CDCl_3$): δ 117.2 (d, $J = 88.4$ Hz, C—*i*), 128.8 (d, $J = 3.4$ Hz, C5-pyridine), 130.9 (d, $J = 13.0$ Hz, C-*m*), 132.7 (d, $J = 24.7$ Hz, C3-pyridine), 134.9 (d, $J = 10.0$ Hz, C-*o*), 135.9 (d, $J = 2.8$ Hz, C-*p*), 139.5 (d, $J = 10.5$ Hz, C4-pyridine), 144,5 (d, $J = 119.6$ Hz, C2-pyridine), 152.7 (d, $J = 19.4$ Hz, C6-pyridine); ^{31}P NMR ($CDCl_3$): δ 15.6.

2-Pyridyltriphenylphosphonium Hexafluorophosphate (2e)

Colorless solid, m.p. 314–317°C; ^{1}H NMR (DMSO): δ 7.74–7.99 (m, 17 H, Ar—H), 8.16–8.22 (m, 1H, pyridine—H), 9.08–9.09 (m, 1H, pyridine-H); ^{13}C NMR (DMSO): δ 117.2 (d, $J = 88.2$ Hz, C-*i*), 128.4 (d, $J = 3.4$ Hz, C5-pyridine), 130.3 (d, $J = 12.8$ Hz, C-*m*), 132.1 (d, $J = 24.4$ Hz, C3-pyridine), 134.7 (d, $J = 10.5$ Hz, C-*o*), 135.3 (d, $J = 2.9$ Hz, C—*p*), 138.4 (d, $J = 10.5$ Hz, C4-pyridine), 144,2 (d, $J = 119.7$ Hz, C2-pyridine), 152.3 (d, $J = 19.3$ Hz, C6-pyridine); ^{31}P NMR (DMSO): δ -143.0 (PF_6^-), 16.5.

2-Pyridyltriphenylphosphonium Triflate (2f)

Colorless solid, m.p. 256−259°C; ^{1}H NMR ($CDCl_3$): δ 7.66−7.91 (m, 16H, Ar—H), 7.94−7.98 (m, 1H, pyridine—H), 8.18−8.27 (m, 1H, pyridine—H), 8.98−8.99 (m, 1H, pyridine—H); ^{13}C NMR ($CDCl_3$): δ 117.4 (d, $J = 88.3$ Hz, C-*i*), 128.8 (d, $J = 3.8$ Hz, C5-pyridine), 130.8 (d, $J = 13.0$ Hz, C-*m*), 132.6 (d, $J = 24.5$ Hz, C3-pyridine), 134.9 (d, $J = 10.2$ Hz, C-*o*), 135.9 (d, $J = 3.1$ Hz, C—*p*), 139.2 (d, $J = 10.5$ Hz, C4-pyridine), 144,8 (d, $J = 119.9$ Hz, C2-pyridine), 152.6 (d, $J = 19.4$ Hz, C6-pyridine); ^{31}P NMR ($CDCl_3$): δ 15.7.

3-Pyridyltriphenylphosphonium Hexafluorophosphate (4)

Colorless solid, m.p. 316−319°C; ^{1}H NMR (DMSO): δ 7.55−8.01 (m, 16H, Ar—H), 8.18−8.28 (m, 1H, pyridine—H), 8.86−8.89 (m, 1H, pyridine−H), 9.06−9.12 (m, 1H, pyridine—H); ^{13}C NMR (DMSO): δ 114.9 (d, $J = 84.2$ Hz, C3-pyridine), 116.9 (d, $J = 89.3$ Hz, C-*i*), 125.0

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(d, $J = 9.4$ Hz, C5-pyridine), 130.5 (d, $J = 12.8$ Hz, C-*m*), 134.7 (d, $J = 10.8$ Hz, C-*o*), 135.6 (d, $J = 2.8$ Hz, C—*p*), 142.6 (d, $J = 8.8$ Hz, C4-pyridine), 153,8 (d, $J = 11.9$ Hz, C2-pyridine), 155.3 (d, $J = 2.2$ Hz, C6-pyridine); ^{31}P NMR (DMSO): δ -143.0 (PF_6^-), 21.5.

Dicyclohexylphosphine Oxide (5)

Colorless solid, m.p. 233−236°C; ^{1}H NMR ($CDCl_3$): δ 1.28−1.83 (m, 12H, CH_2), 1.92−2.01 (m, 8H, CH_2), 2.40−2.58 (m, 2H, PCH), 5.62 (ddd, $J = 467.7$ Hz, 7.4 Hz, 3.8 Hz, 1H, PH); ^{13}C NMR ($CDCl_3$): δ 25.3 (d, $J =$ 1.0 Hz, C-4), 26.4 (d, $J = 12.7$ Hz, C-2), 28.1 (d, $J = 3.5$ Hz, C-3), 28.4 (d, $J = 36.8$ Hz, C-1); ^{31}P NMR ($CDCl_3$): δ 29.1.

2-Chloro-N-butylpyridinium Hexafluorophosphate (6b)

Colorless solid, m.p. 59−62°C; ^{1}H NMR (DMSO): δ 0.94 (t, $J = 7.4$ Hz, 3H, CH_3), 1.35−1.42 (m, 2H, CH_2), 1.82−1.90 (m, 2H, CH_2), 4.70 (t, $J = 8.0$ Hz, 2H, NCH_2), 8.10−8.16 (m, 1H, pyridine—H), 8.39 (dd, $J = 8.3$ Hz, 1.2 Hz, 1H, pyridine—H), 8.58−8.64 (m, 1H, pyridine—H), 9.19 (dd, $J = 6.2$ Hz, 1.5 Hz, 1H, pyridine—H); ^{13}C NMR (DMSO): δ 13.3 18.8, 30.8, 59.5, 126.5, 130.3, 147.2, 147.2, 147.6; ^{31}P NMR (DMSO): δ –144.2 (septet, $J = 713$ Hz).

2-Bromo-N-butylpyridinium Hexafluorophosphate (6c)

Colorless solid, m.p. 76−78°C; ^{1}H NMR (DMSO): δ 0.95 (t, $J = 7.2$ Hz, 3H, CH_3), 1.35−1.43 (m, 2H, CH_2), 1.82−1.90 (m, 2H, CH_2), 4.72 (t, $J = 7.8$ Hz, 2H, NCH_2), 8.12−8.17 (m, 1H, pyridine—H), 8.42−8.54 (m, 2H, pyridine—H), 9.23 (dd, J= 6.2 Hz, 1.5 Hz, 1H, pyridine−H); ^{13}C NMR (DMSO): δ 13.3, 18.8, 31.0, 62.0, 127.0, 134.3, 138.2, 146.2, 148.0; ^{31}P NMR (DMSO): δ –144.2 (septet, $J = 713$ Hz).

3-Chloro-N-butylpyridinium Hexafluorophosphate (7b)

Colorless solid, m.p. 116−119 °C; ^{1}H NMR (DMSO): δ 0.92 (t, $J =$ 7.5 Hz, 3H, CH_3), 1.27−1.35 (m, 2H, CH_2), 1.89−1.94 (m, 2H, CH_2), 4.60 (t, $J = 7.4$ Hz, 2H, CH_2), 8.17−8.22 (m, 1H, pyridine—H), 8.78 (d, $J = 8.4$ Hz, 1H, pyridine—H), 9.08 (d, $J = 6.0$ Hz, 1H, pyridine−H), 9.47 (s, 1H, pyridine—H); ^{13}C NMR (DMSO): δ 13.3, 18.8, 32.4, 61.1, 128.7, 134.1, 143.6, 144.2, 145.1; ^{31}P NMR (DMSO): δ –144.2 (septet, $J = 712$ Hz).

3-Bromo-N-butylpyridinium Hexafluorophosphate (7c)

Colorless solid, m.p. 94−95°C; ^{1}H NMR (DMSO): δ 0.92 (t, $J = 7.4$ Hz, 3H, CH_3), 1.27−1.34 (m, 2H, CH_2), 1.86−1.94 (m, 2H, CH_2), 4.56 (t, $J = 7.5$ Hz, 2H, CH_2), 8.11 (t, $J = 7.4$ Hz, 1H, pyridine—H), 8.88 (d, $J = 8.4$ Hz, 1H, pyridine—H), 9.11 (d, $J = 6.0$ Hz, 1H, pyridine—H),

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9.51 (s, 1H, pyridine—H); ^{13}C NMR (DMSO): δ 13.3, 18.8, 32.5, 61.0, 122.1, 128.8, 143.8, 146.0, 147.8; ^{31}P NMR (DMSO): δ –144.2 (septet, $J = 712$ Hz).

3-Iodo-N-butylpyridinium Hexafluorophosphate (7d)

Colorless solid, m.p. 101–103°C; ^{1}H NMR (DMSO): δ 0.92 (t, $J = 7.4$ Hz, 3H, CH_3), 1.26–1.33 (m, 2H, CH_2), 1.87–1.91 (m, 2H, CH_2), 4.52 (t, $J = 7.1$ Hz, 2H, CH_2), 7.93 (t, $J = 6.9$ Hz, 1H, pyridine—H), 8.96 (d, $J = 7.8$ Hz, 1H, pyridine—H), 9.09 (d, $J = 5.4$ Hz, 1H, pyridine—H), 9.48 (s, 1H, pyridine—H); ^{13}C NMR (DMSO): δ 13.3, 18.8, 32.6, 60.6, 95.5, 128.6, 143.7, 150.0, 153.0; ^{31}P NMR (DMSO): δ – 144.2 (septet, $J = 712$ Hz).

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