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Tetrahedron Letters 48 (2007) 7778–7781
Tetrahedron Letters

N-Arylated pyridinium salts having reactive groups

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Received 2 August 2007; revised 31 August 2007; accepted 4 September 2007
Available online 6 September 2007

Abstract—The pyridinium salts having reactive amine and/or pyridyl groups were obtained by the reaction using Zincke salts. Optical properties and anion exchange behavior of the obtained pyridinium salts were investigated.

Pyridinium salts are an important class of compounds that are used as initiators of cationic polymerization,[1] cationic surfactants,[2] non-linear optical materials,[3] and phase transfer catalysts.[4] Among the several synthetic approaches to obtain pyridinium salts, Zincke's reaction is a versatile method. The reaction of Zincke salts, a highly electrophilic species formed by reaction between a pyridine derivative and 1-chloro-2,4-dinitrobenzene, with primary amines has been employed for the synthesis of various pyridinium salts.[5] Synthesis of *N*-arylpyridinium salts from the Zincke salt was for the first time reported by Marvell and Ise.[5f–h] Recently, pyridinium salts containing a chiral alkyl group[5a] and electron donor and acceptor groups for nonlinear optical materials[3b] have been synthesized. For the Zincke's reaction, use of Zincke salts with a functional group on the pyridine ring and diamine instead of amine will yield pyridinium salts having functional and reactive NH_2 groups. The reactive pyridinium salts could be used as a starting species for functional materials such as dyes, nonlinear optical polymers, and polymer catalysts. However, reports on such reactive pyridinium salts are limited.[5a]

Organic reactions in aqueous media have received considerable attention because of their potential advantages with regard to costs, safety, and environmental concerns.[6] In contrast to many reports on the organic reactions in the mixtures of water and organic solvents, organic syntheses in water, except for simple hydrolysis reactions, are limited due to the poor solubility of organic reactants in water. The Zincke salts and certain amines used as starting materials in this work are soluble in water. These situations urged us to carry out the reaction of Zincke salts with amines in water.

Herein, we report the synthesis of Zincke salts having a phenyl, pyridyl, 9-anthryl, or 9-anthrylvinylene group on the pyridine ring and their reactions with amines or diamines (**2**) in EtOH and water to afford pyridinium salts (**3**). Optical properties and anion exchange of the obtained pyridinium salts are also reported. To our best knowledge, there has been no report on investigation of anion exchange behavior of pyridinium salt by electric conductivity measurement so far.

The Zincke salts, *N*-(2,4-dinitrophenyl)-4-arylpyridinium chlorides (aryl (Ar) = phenyl; **1a**, 4-pyridyl; **1b**, 9-anthryl; **1c**,[7] and 9-anthrylvinylene; **1d**[8]), were obtained by reaction of 1-chloro-2,4-dinitrobenzene with the corresponding pyridine derivatives in 70, 85, 63, and 91% yields, respectively (Scheme 1).[9]

The pyridinium salts (**3**) were obtained by the reaction of **1** with **2** in refluxing EtOH, as shown in Scheme 2.[10] The reaction of water-soluble pyridinium salts **1a** and **1b** with the water-soluble amines **2a** and **2b** in refluxing water also yielded the pyridinium salts (**3**).

The results of these reactions are summarized in Table 1. The reactions in both EtOH and water gave the pyridinium salts in moderate to high yields. The yields are independent of the amine substituent(s). On the other hand, the reactions of **1a** with 4-nitroaniline and with

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Keywords: Pyridinium salts; Pyridines; Reactive group; Zincke's reaction.

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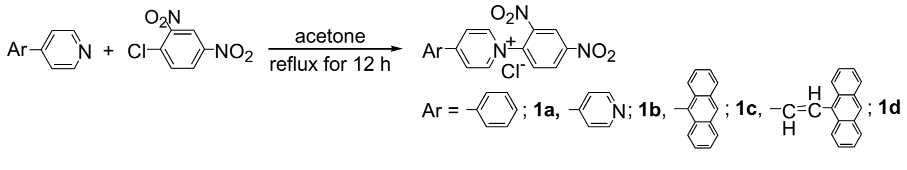
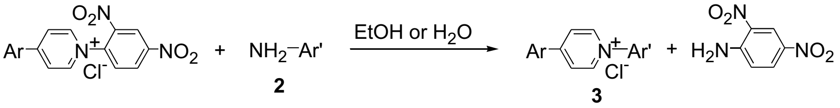
doi:10.1016/j.tetlet.2007.09.009

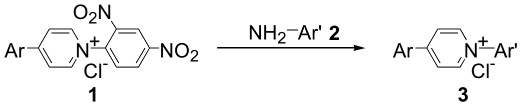


Scheme 1. Synthesis of *N*-(2,4-dinitrophenyl)-4-arylpyridinium chlorides (**1**).



Scheme 2. Synthesis of pyridinium salts (**3**) using Zincke's reaction.

Table 1. Synthesis of pyridinium salts by reaction of **1** with **2**



Entry	1	Ar	2	Ar′	Solvent	3, Yield (%)
1	**1a**	C_6H_5	**2a**	*p*-MeO–C_6H_4	EtOH	**3a**, 96
2					H_2O	98
3			**2b**	*p*-F–C_6H_4	EtOH	**3b**, 96
4					H_2O	94
5			**2d**	*p*-Br–C_6H_4	EtOH	**3c**, 64
6			**2f**	4-NH_2-2,5-Me–C_6H_2	EtOH	**3d**, 86
7	**1b**	C_5H_4N	**2a**	*p*-MeO–C_6H_4	EtOH	**3e**, 77
8					H_2O	94
9			**2b**	*p*-F–C_6H_4	EtOH	**3f**, 91
10					H_2O	94
11			**2c**	*p*-Cl–C_6H_4	EtOH	**3g**, 89
12			**2d**	*p*-Br–C_6H_4	EtOH	**3h**, 97
13			**2e**	*p*-I–C_6H_4	EtOH	**3i**, 69
14			**2f**	4-NH_2-2,5-Me–C_6H_2	EtOH	**3j**, 94
15	**1c**	9-Anthryl	**2a**	*p*-MeO–C_6H_4	EtOH	**3k**, 94
16			**2b**	*p*-F–C_6H_4	EtOH	**3l**, 63
17	**1d**	9-Anthrylvinylene	**2a**	*p*-MeO–C_6H_4	EtOH	**3m**, 89
18			**2d**	*p*-Br–C_6H_4	EtOH	**3n**, 90
19			**2f**	4-NH_2-2,5-Me–C_6H_2	EtOH	**3o**, 98
20			**2g**	*p*-NH_2–C_6H_4	EtOH	**3p**, 80
21			**2h**	2,5-Me–C_6H_3	EtOH	**3q**, 72

4-aminoacetophenone gave no pyridinium salts. A possible reason for this is that low basicity of the amines prevents nucleophilic addition to the pyridinium ring of **1a**. The pyridinium salts **3** were soluble in water and in organic solvents such as methanol, *N*,*N*-dimethylformamide, and dimethyl sulfoxide. Their structures were determined by ^1H and ^{13}C NMR spectroscopy and elemental analysis.

It has been reported that anions in aqueous solutions of pyridinium salts influence their optical properties.[11] To investigate the behavior of anion exchange in aqueous solutions of **3**, electric conductivity measurements of aqueous solutions of **3a** were carried out when limited amounts of $AgClO_4$ were added to the solutions. During the measurements, AgCl precipitated from the solutions. As depicted in Figure 1, the conductivities of these solutions decrease until the addition of an equimolar amount of $AgClO_4$ and then increase in proportion to the amounts of $AgClO_4$ after the equivalence point. These results suggest that the Cl^- of **3a** is exchanged with ClO_4^- until the addition of an equimolar amount of the silver salt. The decrease of the conductivities seems to be ascribed to a smaller mobility of the pyridinium perchlorate having a larger molecular size than the pyridinium chloride.

The absorption positions of **3** are influenced by the structures of the substituents, as summarized in Table 2. Pyridinium salts **3k–q** give rise to characteristic absorptions due to π–π^* and n–π^* transitions of the anthryl and anthrylvinylene groups at approximately 255 nm and in the range of 283–475 nm, respectively. Among the pyridinium salts having a phenyl or pyridyl group, **3a**,**d**,**e**, and **3j** with electron-donating substituent(s) show peaks at longer wavelengths as compared to the other pyridinium salts with an electron-accepting substituent. These observations seem to be ascribed to the occurrence

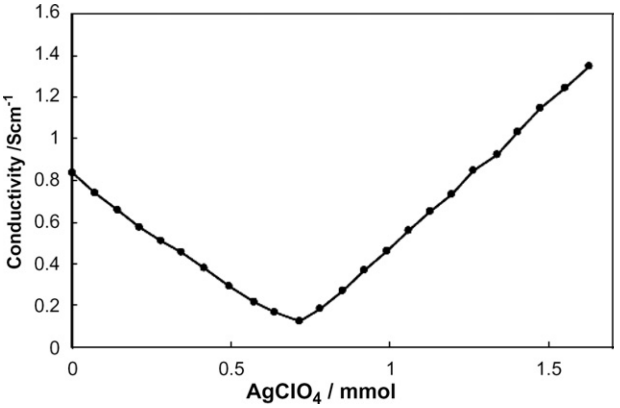


Figure 1. Conductivity changes of aqueous solutions of **3a** (0.01 mM, 70 mL) by addition of $AgClO_4$ in amounts of every 0.07 mmol.

Table 2. UV–vis data of the pyridinium salts

Entry	3	Absorption,[a] nm ($\log\varepsilon$, M^{-1} cm^{-1})
1	**3a**	280 (3.60),[b] 329 (3.78)
2	**3b**	280 (4.52), 307 (4.50)
3	**3c**	280 (4.49), 316 (4.51)
4	**3d**	300 (4.31), 388 (3.37)
5	**3e**	262 (4.68), 331 (4.48)
6	**3f**	282 (4.40)
7	**3g**	275 (4.90)
8	**3h**	282 (4.41)
9	**3i**	271 (5.02)
10	**3j**	254 (5.00), 365 (3.90)
11	**3k**	251 (5.05), 320 (3.47), 345 (3.94), 382 (3.82), 410 (3.74)
12	**3l**	258 (4.93), 351 (3.63), 368 (3.70), 387 (3.69), 408 (3.56)[b]
13	**3m**	254 (5.57), 286 (4.87), 464 (4.34)
14	**3n**	254 (5.67), 302 (4.88), 475 (4.61)
15	**3o**	253 (5.18), 283 (4.40), 453 (4.16)
16	**3p**	254 (5.26), 274 (4.62), 451 (4.20)
17	**3q**	254 (5.44), 289 (4.60), 462 (4.09)

[a] In EtOH.

[b] Shoulder peak.

of an intramolecular charge transfer (CT) transition between the 4-methoxypheny or 4-amino-2,5-dimethylphenyl and pyridinium groups.

A similar intramolecular CT transition has been reported to give rise to CT absorption peaks in the UV–vis spectrum of the pyridinium salt, 4-MeO–C_6H_4–CH=CH–$C_6H_3N^+(Ph)PF_6^-$.[3b]

The pyridine derivatives 4-(9-anthryl)pyridine and 1-(9-anthryl)-2-(4-pyridyl)ethylene were photoluminescent (PL) in MeOH, and showed a PL peak at 421 and 492 nm, respectively. N-Arylation of those compounds quenched their photoluminescence probably due to intermolecular interactions between the pyridinium salts generated by the N-arylation. It was reported that the N-alkylation of fluorescent pyridine derivatives drastically decreased their fluorescence due to the stronger intermolecular interactions between the N-alkylated molecules.[12]

In conclusion, pyridinium salts having reactive amine and/or pyridyl groups were obtained in moderate to high yields by the Zincke's reaction. The addition of $AgClO_4$ to aqueous solutions of these pyridinium salts caused anion exchange reactions. The UV–vis measurements suggest that intramolecular charge transfer occurred in the pyridinium salts having electron-donating group(s) on *N*-phenyl ring.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.09.009.

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7. The compound **1c** was synthesized by Suzuki cross-coupling of 9-bromoanthracene with 4-pyridineboronic acid. See Supplementary data.
8. The compound **1d** was synthesized by Wittig reaction of anthracene-9-yl-methyltriphenylphosphine chloride with 4-pyridinecarboxaldehyde. See Supplementary data.
9. A representative procedure to obtain the Zincke salt is as follows: After an acetone solution (100 mL) of 1-chloro-2,4-dinitrobenzene (20.3 g, 100 mmol) and 4-phenylpyridine (15.5 g, 100 mmol) was heated at reflux for 11 h, the precipitate from the reaction solution was collected by

filtration, which was washed with *n*-pentane (300 mL) and dried under vacuum to afford **1a** as a light green powder (25.1 g, 70%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.53 (d, $J = 5.2$ Hz, 2H), 9.12 (s, 1H), 8.99 (dd, $J = 2.4$, 8.8 Hz, 1H), 8.89 (d, $J = 7.2$ Hz, 2H), 8.53 (d, $J = 8.8$ Hz, 1H), 8.28 (d, $J = 6.8$ Hz, 2H), 7.68–7.76 (m, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 157.2, 149.0, 145.9, 143.2, 138.5, 133.1, 133.0, 132.2, 130.2, 129.9, 128.7, 124.1, 121.3.

10. A representative procedure to obtain the pyridinium salt is as follows: *N*-(2,4-Dinitrophenyl)-4-phenylpyridinium chloride (**1a)** (0.72 g, 2.0 mmol) and 2,5-dimethyl-1,4-phenylenediamine (**2f)** (0.55 g, 4.0 mmol) were dissolved in 3 mL of dry ethanol under N_2. After the solution was refluxed for 12 h, 2,4-dinitroaniline precipitated from the reaction solution was removed by filtration. The solvent was evaporated under vacuum, and the resulting solid was washed with acetone (300 mL). Compound **3d** was collected by filtration, dried under vacuum, and obtained as a light brown powder (Table 1, entry 6, 0.53 g, 86%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.11 (d, $J = 7.2$ Hz, 2H), 8.58 (d, $J = 7.2$ Hz, 2H), 8.17 (d, $J = 7.2$ Hz, 2H), 7.69–7.66 (m, 3H), 7.21 (s, 1H), 6.64 (s, 1H), 2.09 (s, 3H), 2.04 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 154.6, 149.1, 146.2, 133.4, 132.3, 130.5, 129.7, 129.6, 128.3, 127.1, 124.3, 119.4, 114.9, 16.9, 16.6. Anal. Calcd for $C_{19}H_{19}ClN_2 2.5H_2O$: C, 64.66; H, 6.18; N, 12.57. Found: C, 64.63; H, 5.85; N, 12.30.
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