Preparation of Chloroalkyloxypyridinium Salts by Conjugative Chlorination of Olefins in the Presence of Pyridine *N*-Oxides

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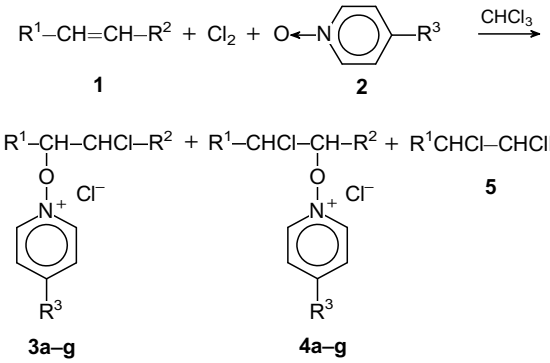
The participation of pyridine oxides in conjugative chlorination reactions of alkenes and in the formation of chloroalkyloxypyridinium salts has been observed.

Conjugative halogenation reactions of unsaturated compounds attract attention because they allow bifunctional derivatives of hydrocarbons to be obtained by simple one-step processes.

We were the first to show the participation of the *N*-oxide of pyridine and its derivatives (*N*-oxides of 4-nitropyridine and 4-methylpyridine) in conjugative chlorination of olefins. From this reaction vicinal dichloroalkanes and chloroalkyloxypyridinium chlorides have been obtained; the latter were isolated as iodine salts in 32–65% yields.



			3:**4** = 1:1
1:**2** = 1:5	**a**	R^1 = Bu, R^2 = R^3 = H	36%
	b	R^1 = C_8H_{17}, R^2 = R^3 = H	46%
	c	R^1 = $C_{14}H_{29}$, R^2 = R^3 = H	44%
	d	R^1 = Ph, R^2 = R^3 = H	48%
	e	R^1 = R^2 = Ph, R^3 = H	65%
1:**2** = 1:2	**f**	R^1 = C_8H_{17}, R^2 = H, R^3 = Me	27%
	g	R^1 = C_8H_{17}, R^2 = H, R^3 = NO_2	10%

Similar kinds of pyridinium salts have not been previously investigated. In the literature only methoxypyridinium salts obtained by alkylation of *N*-oxides of pyridine with methyl iodide[1] or dimethyl sulfate[2] are known.

According to NMR spectroscopy the reaction with terminal alkenes is an unselective process. The product obtained is a mixture of two regioisomers **3** and **4**, ratio *ca*. 1. In the NMR spectrum three pairs of aromatic proton signals in the interval 9.7–8.7 and six (or five with alignment of two signals) methyne and methylene proton signals in the interval 6.0–4.0 are observed (ABX system). Since the alkoxypyridine group is a stronger acceptor than a chlorine atom, the methyne proton connected with the first group displays a signal in a weaker area (5.6–5.7) than the proton connected with the chlorine (4.3–4.4). The methylene protons have similar properties.

Addition to cyclohexene is *trans*-stereospecific (signal width $w_{\frac{1}{2}}$ = 22–24 Hz [3]) and the quaternary salt yield is smaller (25%) than that, for example, for terminal alkenes.

It is found that the yield of alkoxypyridine salt increases with an increase in pyridine oxide content in the reaction mixture. When the decene/pyridine oxide ratio varies from 1:1 to 1:5 the product yield increases from 23% to 46%. An increase in the yield of conjugative products in the presence of styrene and (*E*)-1,2-diphenylethylene (32–65%) is explained by the stabilization of the intermediate due to the electronic density of the aromatic ring and the influence of steric hindrance. An acceptor group (NO_2) in the aromatic ring decreases the nucleophilic properties of the alkoxypyridine derivative which follows, thus decreasing the yield of salts **3** and **4**.

To conclude, a convenient, one-step method of synthesis for a variety of alkoxypyridine salts has been obtained.† The structures of all newly-synthesised compounds have been proved by NMR, IR and elemental analysis data.‡

References

1 E. Klingsberg, *Pyridine and its Derivatives*, Interscience Publishers, New York, 1961, Part 2, p. 117.
2 D. Redmore, *US Patent*, 3786055, 1974.
3 N. S. Zefirov, A. S. Koz'min, V. V. Zhdankin, A. V. Nikulin and N. V. Zyk, *J. Org. Chem.*, 1982, **47**, 3679.

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† *General chlorination procedure*: A mixture of alkene (0.02 mol), pyridine *N*-oxide (0.1 mol) and 10 ml of $CHCl_3$ was stirred at 25–30 °C with passage of chlorine (0.02 mol, 0.45 l). The precipitate obtained after passing an excess of dry hydrogen chloride was filtered off and the filtrate was concentrated *in vacuo*. The mixture was extracted with hexane, the residue obtained after removal of hexane was dissolved in 30 ml of chloroform and 30 ml of a 10% solution of KI was added to the chloroformic solution. The separated organic layer was dried ($MgSO_4$) and evaporated *in vacuo*. The crude product was recrystallized from acetone–hexane (1:1). 1,2-Dichloroalkane was isolated from the hexane extract.

‡ Selected physical data for compounds **3** and **4**:

3a m.p. 103–104 °C; ^{1}H NMR ($CDCl_3$, δ): 9.57 (d, 2H, *o*-H_{Ar}), 8.82 (m, 1H, *p*-H_{Ar}), 8.45 (m, 2H, *m*-H_{Ar}), 5.62 (m, 1H, CH–OPy), 4.37 (m, 1H, H_a–CHCl), 3.90 (m, 1H, H_b–CHCl); IR (KBr, ν/cm^{-1}): 3100, 2900 (Ar), 1490 (C=N), 1290, 980, 860.

4a m.p. 91–92 °C; ^{1}H NMR ($CDCl_3$, δ): 9.73 (d, 2H, *o*-H_{Ar}), 8.82 (m, 1H, *p*-H_{Ar}), 8.45 (m, 2H, *m*-H_{Ar}), 5.40 (*m*, 1H, H_a–CHOPy), 4.96 (m, 1H, H_b–CHOPy), 4.37 (m, 1H, CHCl); IR (KBr, ν/cm^{-1}): 3100, 2900 (Ar), 1480(C=N), 1270, 1140, 990, 850.

3b m.p. 109–110 °C; ^{1}H NMR ($CDCl_3$, δ): 9.55 (d, 2H, *o*-H_{Ar}), 8.81 (m, 1H, *p*-H_{Ar}), 8.44 (m, 2H, *m*-H_{Ar}), 5.61 (m, 1H, CHOPy), 4.38 (m, 1H, H_a–CHCl), 3.90 (m, 1H, H_b–CHCl); IR (KBr, ν/cm^{-1}): 3100, 2900 (Ar), 1490 (C=N), 1290, 980.

4b m.p. 101–102 °C; ^{1}H NMR ($CDCl_3$, δ): 9.71 (d, 2H, *o*-H_{Ar}), 8.83 (m, 1H, *p*-H_{Ar}), 8.46 (m, 2H, *m*-H_{Ar}), 5.36 (m, 1H, H_a–CHOPy), 4.97 (m, 1H, H_b–CHOPy), 4.38 (m, 1H, CHCl); IR (KBr, ν/cm^{-1}): 3100, 2900 (Ar), 1480 (C=N), 1270, 1140, 960.

3f ^{1}H NMR ($CDCl_3$, δ): 9.36 (d, 2H, *o*-H_{Ar}), 8.18 (d, 2H, *m*-H_{Ar}), 5.51 (m, 1H, CHOPy), 4.38 (m, 1H) and 3.9 (m, 1H, CH_2Cl); IR (KBr, ν/cm^{-1}): 3100–2900 (Ar), 1620 (Ar), 1470 (C=N), 1290, 760.

4f ^{1}H NMR ($CDCl_3$, δ): 9.53 (d, 2H, *o*-H_{Ar}), 8.18 (d, 2H, *m*-H_{Ar}), 5.25 (m, 1H) and 4.83 (m, 1H) CH_2OPy, 4.32 (m, 1H, CHCl); IR (KBr, ν/cm^{-1}): 3100–2900 (Ar), 1620 (Ar), 1470 (C=N), 1290, 760.