

Polyhalogeno-aromatic Compounds. Part XXV.¹ Quaternisation of Polyhalogenopyridines and Reactions of the Pyridinium Salts

By E. Ager and H. Suschitzky,* Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, Lancashire

Pentachloropyridine, tetrachloro-2-fluoropyridine, 3,5-dichlorotrifluoropyridine, pentabromopyridine, and pentachloropyridine 1-oxide were methylated with methyl fluorosulphonate to give products which reacted extremely readily with nucleophiles.

WE have briefly reported² the quaternisation of some polyhalogenopyridines by methyl fluorosulphonate. We now give details of this work.

The *N*-methyl polyhalogenopyridinium salts underwent substitution with aqueous solutions of nucleophiles usually at ambient temperature (see Scheme 1). The action of water (Scheme 2), ammonia, and methylamine appears to proceed with HX elimination, which deactivates the molecule to further substitution by an excess of the nucleophile under the mild conditions employed. The use of triethyloxonium fluoroborate as an alkylating agent gave only a low yield (12%) of *N*-ethylpentachloropyridinium fluoroborate.

Alkylation of pentachloropyridine 1-oxide has recently been reported³ to occur with dimethyl sulphate at 100°. However, no salt was isolated and when the reaction mixture was treated with water only a poor yield (6%) of *N*-methoxytetrachloro-2-pyridone was obtained, together with much pentachloropyridine and pentachloropyridine 1-oxide. We repeated this reaction with a large excess of dimethyl sulphate and found the yield of the pyridone was increased to 43%.

¹ Part XXIV, D. J. Berry, J. D. Cook, and B. J. Wakefield, *J.C.S. Perkin I*, 1972, 2190.

² E. Ager and H. Suschitzky, *J. Fluorine Chem.*, 1973, **3**, 230.

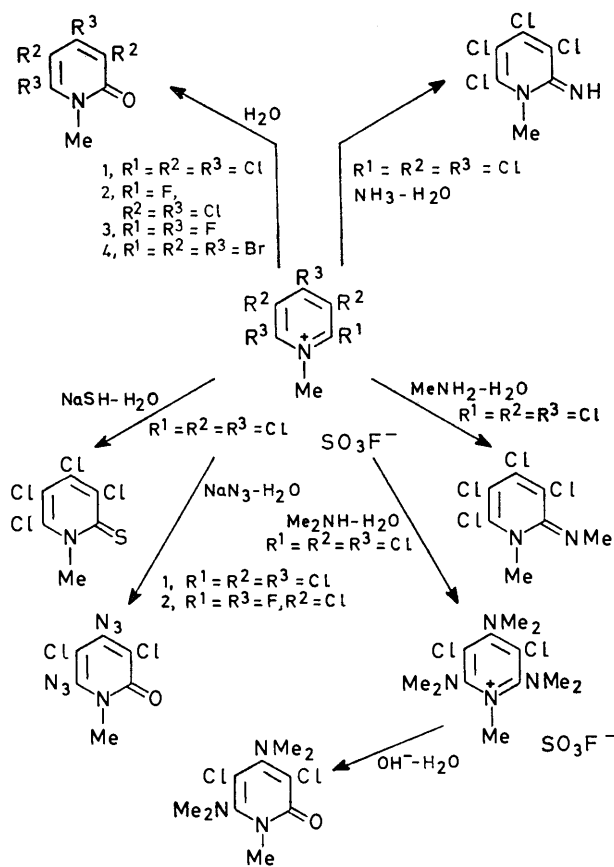
Pentachloropyridine 1-oxide reacted with methyl fluorosulphonate (1 equiv.) in dry methylene chloride at room temperature to give a high yield of *N*-methoxy-pentachloropyridinium fluorosulphonate, which on treatment with cold water gave *N*-methoxy-tetrachloro-2-pyridone. Treatment of the pyridone with excess of aqueous sodium azide gave 2,4,6-triazidodichloropyridine, with loss of the *N*-methoxy-group. This reaction probably proceeds *via* a mechanism involving attack of water on the intermediate *N*-methoxy-triazidodichloropyridinium fluorosulphonate, in agreement with the normal reaction of *N*-methoxyheterocyclic salts with water to give formaldehyde and the heterocycle⁴ (Scheme 3).

EXPERIMENTAL

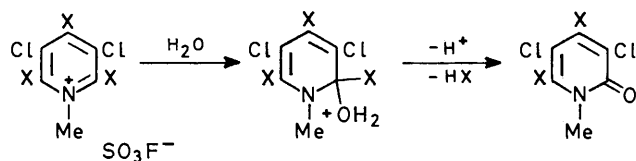
N-Methyl Pentahalogenopyridinium Fluorosulphonates.—In a typical example, a mixture of pentachloropyridine (3.4 g, 13.6 mmol) and methyl fluorosulphonate (5.0 g, 44 mmol) was heated under reflux for 0.5 h. The mixture was cooled to 25°, dry methylene chloride (20 ml) was added, and *N*-methylpentachloropyridinium fluorosulphonate (4.1 g, 83%), m.p. 224–226°, was filtered off, washed with methylene chloride, and stored over phosphorus

³ D. E. Bublitz, *J. Heterocyclic Chem.*, 1972, **9**, 471.

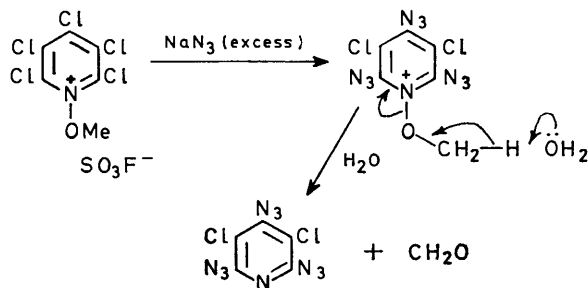
⁴ M. Henze, *Ber.*, 1937, **70**, 1270.



SCHEME 1



SCHEME 2



SCHEME 3

pentoxide. Tetrachloro-2-fluoropyridine, 3,5-dichlorotrifluoropyridine, and pentabromopyridine were *N*-methylated similarly (see Table). The high reactivity of these salts precluded a good elemental analysis and their structures followed from spectroscopic data and their reactions.

R^1	R^2	R^3	Time (h)	M.p. ($^{\circ}\text{C}$)	Yield (%)
Cl	Cl	Cl	0.5	224—226	83
Cl	Cl	F	1.0	146—149	80
Cl	F	F	2.0	136—138	67
Br	Br	Br	24	150 (decomp.)	80

Reactions of N-methylpentachloropyridinium Fluorosulphonate with Nucleophiles.—(a) *Water.* A mixture of *N*-methylpentachloropyridinium fluorosulphonate (1.0 g, 2.7 mmol) and water was stirred at room temperature for 24 h to give a precipitate of *N*-methyltetrachloro-2-pyridone (0.6 g, 89%), m.p. 149.5—150.5 $^{\circ}$ (from methanol) (lit.,⁵ 148.5—149.5). (b) *Aqueous ammonia.* A mixture of the pyridinium salt (1.0 g, 2.7 mmol) and aqueous ammonia (10 ml; s.g. 0.88) was stirred for 0.5 h at room temperature to give a precipitate of *N*(1)-methyltetrachloropyridin-2-imine (0.6 g, 89%), m.p. 173—175 $^{\circ}$ (decomp.) (from methanol), $\tau(\text{CCl}_4\text{-C}_2\text{D}_6\text{CO})$ 6.25 and 2.8 (exch.), ν_{max} 3350 (NH) and 1610 cm^{-1} (C=N) (Found: C, 29.2; H, 1.7; N, 11.0. $\text{C}_6\text{H}_4\text{Cl}_4\text{N}_2$ requires C, 29.3; H, 1.6; N, 11.4%). (c) *Aqueous methylamine.* A mixture of the pyridinium salt (1.0 g, 2.7 mmol) and excess of aqueous methylamine was stirred for 5 min at 0 $^{\circ}$. *NN'*-Dimethyltetrachloropyridin-2-imine (0.6 g, 85%) was filtered off and recrystallised from ethanol-water (2 : 1); m.p. 86—88 $^{\circ}$, $\tau(\text{CDCl}_3)$ 6.46 and 6.48, ν_{max} 1640 cm^{-1} (C=N) (Found: C, 32.8; H, 2.4; N, 10.8. $\text{C}_7\text{H}_6\text{Cl}_4\text{N}_2$ requires C, 32.3; H, 2.3; N, 10.8%). (d) *Aqueous dimethylamine.* The product, obtained as in (c), *N*-methyl-2,4,6-tris(dimethylamino)dichloropyridinium fluorosulphonate (0.68 g, 63%) was filtered off and recrystallised from water keeping the temperature below 30 $^{\circ}$; m.p. 158—160 $^{\circ}$, τ 6.22, 6.75, and 6.96 (1 : 2 : 4) (Found: C, 37.1; H, 5.4; N, 14.4. $\text{C}_{12}\text{H}_{21}\text{Cl}_2\text{FN}_4\text{O}_3\text{S}$ requires C, 36.9; H, 5.4; N, 14.4%). (e) *Aqueous sodium hydrogen sulphide.* *N*-Methyltetrachloropyridine-2-thione (0.3 g, 42%) was recrystallised from chloroform-methanol (70 : 30); m.p. 221—222 $^{\circ}$, $\tau(\text{CDCl}_3)$ 5.63 (Found: C, 27.5; H, 1.2; N, 5.3. $\text{C}_6\text{H}_3\text{Cl}_4\text{NS}$ requires C, 27.4; H, 1.1; N, 5.3%). (f) *Aqueous sodium azide.* The product, obtained by reaction at 50 $^{\circ}$, *N*-methyl-4,6-diazidodichloro-2-pyridone (6.1 g, 86%), was filtered off and recrystallised from ethanol; m.p. 115 $^{\circ}$ (decomp.), $\tau(\text{CCl}_4)$ 6.45, ν_{max} 1655 (C=O), 2110, and 2120 cm^{-1} (N_3) (Found: C, 27.3; H, 1.3; N, 37.6. $\text{C}_6\text{H}_3\text{Cl}_2\text{N}_7$ requires C, 27.7; H, 1.2; N, 37.7%).

Reaction of N-Methyltetrachloro-2-fluoropyridinium Fluorosulphonate with Water.—A mixture of the pyridinium salt (0.5 g, 1.4 mmol) and water (20 ml) was stirred for 1 h at room temperature. The product, *N*-methyltetrachloro-2-pyridone (0.28 g, 80%), was filtered off and recrystallised from methanol (m.p. 149—150 $^{\circ}$) and was identical with an authentic sample.⁵

Reactions of N-Methyl-3,5-dichlorotrifluoropyridinium Fluorosulphonate with Nucleophiles.—(a) *Water.* A mixture of the pyridinium salt (1.0 g, 3.1 mmol) and water (10 ml) was stirred at room temperature for 10 min. The product, *N*-methyl-3,5-dichlorodifluoro-2-pyridone (0.53 g, 80%) was filtered off and recrystallised from aqueous ethanol (1 : 3) (m.p. 81—82 $^{\circ}$) and was identical with an authentic sample.⁶ (b) *Aqueous sodium azide.* Reaction at 50 $^{\circ}$ for 0.5 h gave *N*-methyl-4,6-diazidodichloro-2-pyridone (0.32 g, 80%), identical with the product formed from *N*-methylpentachloropyridinium fluorosulphonate and sodium azide.

Reaction of N-Methylpentabromopyridinium Fluorosulphonate with Water.—A mixture of the pyridinium salt (1.0 g, 1.7 mmol) and water (5.0 ml) was stirred at 100 $^{\circ}$ for 24 h to give a precipitate of *N*-methyltetrabromo-2-pyridone (0.58 g, 80%), m.p. 183—184.5 $^{\circ}$ (from ethanol),

⁵ A. Roedig and G. Märkl, *Annalen*, 1960, 636, 1.

⁶ B. Iddon, H. Suschitzky, and A. W. Thompson, unpublished results.

$\tau(\text{CDCl}_3)$ 6.08, ν_{max} 1660 cm^{-1} (C=O) (Found: C, 17.5; H, 0.9; N, 3.2. $\text{C}_6\text{H}_3\text{Br}_4\text{NO}$ requires C, 17.0; H, 0.7; N, 3.3%).

Reaction of Pentachloropyridine with Triethyloxonium Fluoroborate.—A mixture of pentachloropyridine (1.0 g, 4.0 mmol) and triethyloxonium fluoroborate (2.0 g) was heated at 100° for 0.5 h. The mixture was cooled and dry methylene chloride (10 ml) was added to give a precipitate of *N*-ethylpentachloropyridinium fluoroborate (0.17 g, 12%). Its analysis was unsatisfactory because of its instability in air.

Reaction of N-Ethylpentachloropyridinium Fluoroborate with Water.—A mixture of the pyridinium salt (0.1 g, 0.27 mmol) and water (3 ml) was stirred for 18 h to give a precipitate of *N*-ethyltetrachloro-2-pyridone (0.06 g, 80%), m.p. 80–81° (from methanol), ν_{max} 1665 cm^{-1} (C=O) (Found: C, 32.0; H, 2.0; N, 5.4. $\text{C}_7\text{H}_5\text{Cl}_4\text{NO}$ requires C, 32.2; H, 1.9; N, 5.4%).

Reaction of N-Methyl-2,4,6-tris(dimethylamino)dichloropyridinium Fluorosulphonate with Aqueous Sodium Hydroxide.—A mixture of the pyridinium salt (1.0 g, 2.6 mmol), sodium hydroxide (0.32 g, 8.0 mmol), and water (10 ml) was stirred for 1 h. The mixture was extracted with ether; the ethereal solution was dried and evaporated to give *N*-methyl-4,6-bis(dimethylamino)dichloro-2-pyridone (0.4 g, 60%), m.p. 114° (from diethyl ether–light petroleum, 30:70), $\tau(\text{CDCl}_3)$ 6.47, 7.00, and 7.12 (1:2:2) (Found: C, 45.9; H, 5.7; N, 16.4. $\text{C}_{10}\text{H}_{15}\text{Cl}_2\text{N}_3\text{O}$ requires C, 45.5; H, 5.7; N, 15.9%).

N-Methoxypentachloropyridinium Fluorosulphonate.—A solution of pentachloropyridine 1-oxide (10.0 g, 37.7 mmol) and methyl fluorosulphonate (4.6 g, 40.0 mmol) in methylene

chloride (200 ml) was stirred for 48 h at room temperature to give a precipitate of *N*-methoxypentachloropyridinium fluorosulphonate (12.8 g, 90%), m.p. 205° (decomp.).

Reaction of N-Methoxypentachloropyridinium Fluorosulphonate with Nucleophiles.—(a) *Water.* A mixture of the pyridinium salt (1.0 g, 2.6 mmol) and water (10 ml) was stirred at room temperature for 1 h to give a precipitate of *N*-methoxytetrachloro-2-pyridone (0.6 g, 88%), m.p. 134–134.3° (from methanol) $\tau(\text{CCl}_4)$ 5.87, ν_{max} 1670 cm^{-1} (C=O) (lit.,³ m.p. 144–145°) (Found: C, 27.6; H, 1.2; N, 5.3. Calc. for $\text{C}_6\text{H}_3\text{Cl}_4\text{NO}_2$: C, 27.4; H, 1.1; N, 5.3%). (b) *Aqueous sodium azide.* Stirring for 10 min in an aqueous solution of sodium azide gave 2,4,6-triazidodichloropyridine (82%), m.p. 80–81° (decomp.) (Found: C, 22.4; H, 0.3; N, 50.5%; M^+ , 269.9685. $\text{C}_5\text{Cl}_2\text{N}_3$ requires C, 22.1; H, 0; N, 51.7%; M , 269.9683.)

Reaction of Pentachloropyridine 1-Oxide with Dimethyl Sulphate.—A mixture of the 1-oxide (2.0 g, 7.4 mmol) and dimethyl sulphate (5.0 g, 40.0 mmol) was stirred at 90° for 18 h. The mixture was cooled to 20°, chloroform (30 ml) was added (no precipitate was observed), followed by water (30 ml), and the mixture was stirred for 4 h. The organic layer was separated, dried (MgSO_4), and evaporated off and the solid was recrystallised from methanol to give *N*-methoxytetrachloro-2-pyridone (0.85 g, 43%). The mother liquors contained a mixture of pentachloropyridine 1-oxide (mainly) and *N*-methoxytetrachloro-2-pyridone.

We thank the S.R.C. for a Fellowship (to E. A.) and Dr. M. B. Green, I.C.I., Mond Division, for gifts of chemicals.

[2/2858 Received, 20th December, 1972]