Polyhalogeno-aromatic Compounds. Part XXVII.[1] Reactions of Polyhalogenopyridines and their *N*-Oxides with Benzenethiols, with Nitrite, and with Trialkyl Phosphites, and of Pentachloropyridine *N*-Oxide with Magnesium

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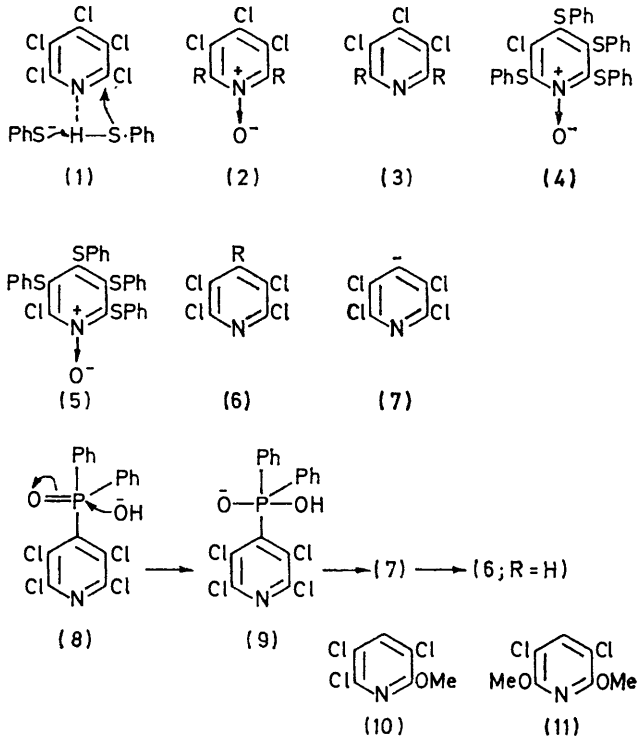
Nucleophilic substitution of pentachloro- and of polychlorofluoro-pyridines with benzenethiols leads to 2- and 4-monosubstituted, 2,4-disubstituted, and 2,4,6-trisubstituted pyridines in various proportions according to the reaction conditions. In pentachloropyridine 1-oxide four chlorine atoms are replaced by sodium benzenethiolate at room temperature and all halogens are replaced at 60°. Treatment of these halogenopyridines with sodium nitrite in dimethylformamide provides a simple route to 4-hydroxypolyhalogenopyridines, and similar reactions with trialkyl phosphites furnish the expected dialkyl phosphonates (by a Michaelis–Arbusov reaction) together with dehalogenated pyridines. Attempts to prepare a Grignard reagent from pentachloropyridine 1-oxide failed. Mechanisms are discussed.

THE presence of a phenylthio-[2] or alkylthio-[3] substituent in a polyhalogeno-aromatic ring activates *para*- and *ortho*-halogen atoms towards nucleophilic attack.[4] This effect, which has been demonstrated for polychloro-[3] as well as polyfluoro-compounds[2,4] was ascribed to the stabilisation of the negative charge in the S_N2 aromatic transition complex by involvement of the vacant *d* orbitals of the sulphur atom.[5]

We set out to establish whether this activation would affect the 3-halogen atom in perhalogenopyridines and thereby open up a route to the relatively inaccessible[6] 3-substituted polyhalogenopyridines. So far only a 4-cyano-group, as for instance in tetrachloropyridine-4-carbonitrile, appears to induce nucleophilicity in the 3-halogen atom.[7] Treatment of pentachloropyridine with 1 equiv. of benzenethiolate in ethanol[8] or benzenethiol[9] is reported to give only tetrachloro-4-phenylthiopyridine. We found, however, that 1 mol. equiv. of potassium benzenethiolate in an excess of benzenethiol yielded a mixture of the 4- and the 2-phenylthiotetrachloropyridines in the ratio 40 : 60. By contrast, in propan-2-ol as solvent 4-substitution occurred almost exclusively. It is surprising that propan-2-ol and benzenethiol, both protic solvents, cause different substitution patterns with the same nucleophile. We believe that H-bonding of propan-2-ol or any other protic solvent[8] with the ring nitrogen atom prevents approach of the large nucleophile to the 2-position in pyridine, and thus favours 4-substitution. In the case of benzenethiol, H-bonding of the solvent could generate the nucleophile near the 2-position if an exchange reaction occurred between the benzenethiolate ion and the H-bonded benzenethiol as indicated in formula (1). The dependence of the substitution pattern on the solvent has been noticed before.[10,11] Use of an excess of potassium benzenethiolate[9] in benzenethiol at 140° gave the *sym*-trisubstituted derivative (see Scheme 1) and no further substitution occurred even under forcing conditions. The structure of this product followed from its formation from 3,5-dichlorotrifluoropyridine and 3 mol. equiv. of



benzenethiolate. The *ortho-para* activating effect of the phenylthio-group apparently is not sufficient to cause 3-substitution, which would require the negative charge of the transition complex not to be on the ring nitrogen atom. Interaction of 2 mol. equiv. of benzenethiolate with pentachloropyridine led to an intractable mixture and not to the 2,4-disubstituted derivative as reported.[9]

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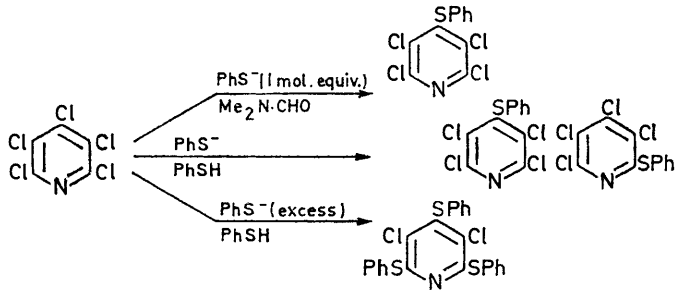
It has been shown that a fluorine [12] or a chlorine [13] atom in the 3-position of pyridine 1-oxide is susceptible to nucleophilic replacement. Reaction of pentachloropyridine 1-oxide with 1 equiv. of benzenethiolate in



SCHEME 1

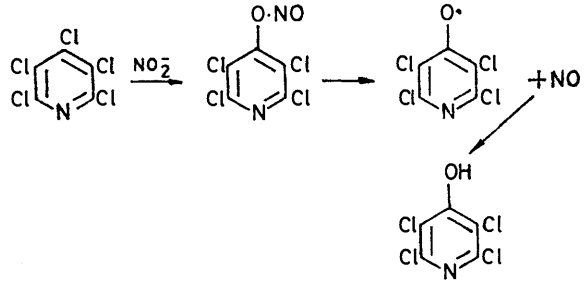
propan-2-ol gave an intractable mixture, but with 2 equiv. of benzenethiolate at room temperature the 2,6-disubstituted product (2; R = SPh) was obtained. This was deoxygenated with phosphorus trichloride to the corresponding pyridine (3; R = SPh), treatment of which with peroxyacetic acid gave the bisphenylsulphonyl compound (3; R = SO_2Ph). Use of 3 mol. equiv. of benzenethiolate with pentachloropyridine 1-oxide again gave an inseparable mixture, and not the *sym*-trisubstituted compound as would be expected. The enhanced reactivity of the 3-chlorine atom must be responsible for the multiplicity of products. Use of 4 mol. equiv. of benzenethiolate at room temperature in propan-2-ol gave the tetrakisphenylthiopyridine 1-oxide (4), which was easily deoxygenated to the pyridine. The structure of (4) was established by its production from 4-bromotetrachloropyridine 1-oxide and benzenethiolate. The alternative structure (5) is excluded on the grounds that the 2- and 6-positions in the *N*-oxide are very readily substituted (see before). Use of an excess of benzenethiolate at 50° yielded a mixture of the tetra- and the penta-substituted products, which appeared as one spot on t.l.c. but was analysed by mass spectrometry.

Trichloro-2,6-difluoropyridine and 2 mol. equiv. of benzenethiolate in propan-2-ol gave the 2,4-bisphenylthio-compound; this substitution pattern is unexpected in view of the usual halogen lability, but it has previously been observed.[14] It may be due to a levelling effect [15] on halogen lability by the phenylthio-group, which reduces the nucleophilicity of the 2(6)-fluorine atom.

3,5-Dichlorotrifluoropyridine gave the 4-phenylthio-derivative with 1 mol. equiv. of benzenethiolate and the 2,4-bisphenylthio-compound with 2 mol. equiv. of the reagent. 3-Chlorotetrafluoropyridine and 1 mol. equiv. of benzenethiolate again gave the 4-substituted product, like pentafluoropyridine.[16] The preference for 4-substitution by nucleophiles in the polyfluoropyridines is well documented.[17] Oxidation of some of these derivatives gave the corresponding sulphonylpyridines.

We have shown [18] that polychloronitropyridines are obtained by oxidation of the corresponding amino- or alkylamino-pyridines. An obvious one-step preparation of these nitro-compounds would involve nucleophilic substitution of a halogen atom by a nitrite group. Although this route is well established for aliphatic nitro-compounds,[19] reports on the reaction of activated aromatic halides with nitrite appear to be confined to chloroanthraquinones.[20] Thus, treatment of 1,5-dichloroanthraquinone with sodium nitrite for 8 h in dimethylformamide at 140° gave the 1-hydroxy-5-nitro-compound.

When sodium nitrite was added to a solution of pentachloropyridine in dimethylformamide at room temperature, brown fumes were evolved rapidly and tetrachloropyridin-4-ol was the only substitution product (73%). The nitrite ion thus attacks with its oxygen atom (in contrast to its behaviour towards alkyl halides) to form an unstable nitrito-intermediate, which decomposes to give the 4-hydroxy-derivative (Scheme 2). The nitrite



SCHEME 2

ion is presumably prevented by the bulk of the *ortho*-halogen atoms from acting as an ambident nucleophile. Analogous results were obtained with 3,5-dichlorotrifluoro- and pentafluoro-pyridine, which at room temperature gave exclusively the 4-hydroxy-derivatives. Pentachloropyridine 1-oxide reacted to give tetrachloro-2-hydroxypyridine 1-oxide. The presence of one hydroxy-group deactivated the *N*-oxide with respect to further nucleophilic substitution, even with an excess of nitrite at 100°. Treatment of tetrachloro-4-phenylsulphonylpyridine gave the 4-hydroxy-compound (6; R = OH), and the 2-isomer yielded trichloro-2-phenylsulphonylpyridin-4-ol. No reaction occurred with hexachlorobenzene even at high temperature.

Although these reactions did not give the desired nitro-

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compounds they represent an excellent method of preparing certain hydroxy-compounds from reactive halides under mild conditions. Reaction in a protic solvent (EtOH), in which the more electronegative atom tends to be solvated,[19] thus favouring attack by the less negative atom, also produced only hydroxy-pyridines, albeit in much lower yield than in dimethylformamide. The interaction between the nitrite and polyhalogenopyridines thus resembles that of α-branched alkyl halides which gives predominantly nitrite esters.

Our results concerning chlorine replacement in pentachloropyridine by trialkyl phosphites were partly anticipated by Russian workers,[21] who reported that reactions with triethyl, tri-n-propyl, and tri-n-butyl phosphites gave the corresponding dialkyl tetrachloro-4-pyridylphosphonates. With triethyl phosphite we observed not only the diethyl phosphonate [6; R = $OP(OEt)_2$], the expected product of a Michaelis–Arbusov reaction, but also the tetrachloropyridine (6; R = H). The latter results from attack by the phosphite on the 4-chlorine atom with generation of the pyridinide ion (7), which is then protonated. Nucleophilic abstraction of aromatic halogen by phosphorus reagents has been observed previously.[22] Reaction of the dimethyl phosphonate [6; R = $OP(OMe)_2$] with aqueous sodium hydroxide gave the 4-hydroxypyridine (6; R = OH), presumably by a nucleophilic displacement. In contrast, the diphenylphosphine oxide [6; R = $(O)PPh_2$], when heated with sodium hydroxide, gave diphenylphosphinic acid [$Ph_2P(O)OH$] and the tetrachloropyridine (6; R = H). Horner reports an analogous reaction for triphenylphosphine oxide,[23] which presumably involves nucleophilic attack on phosphorus of the type illustrated [(8) ⟶ (9) ⟶ (7) ⟶ (6)]. With 1 mol. equiv. of sodium methoxide in methanol the dimethyl phosphonate [6; R = $OP(OMe)_2$] gave the tetrachloropyridine (6; R = H) and the methoxy-compound (10), and with an excess of the reagent the dimethoxypyridine (11) was obtained as well. The protiodehalogenation probably proceeds by a mechanism similar to that operative for the hydroxide [(8) ⟶ (9) ⟶ (7) ⟶ (6)], and the formation of the two methoxides [(10) and (11)] arises from the usual anionic substitution of the resulting polychloropyridine (6; R = H) by sodium methoxide. The diethyl phosphonate [6; R = $OP(OEt)_2$] and the diphenylphosphine oxide [6; R = $(O)PPh_2$] also give the methoxy-compound (10) when treated with 1 mol. equiv. of sodium methoxide. Pentafluorophenyldiphenylphosphine oxide similarly loses the phosphine group on treatment with sodium methoxide[24] to give pentafluorobenzene.

The 4-nitroso-compound (6; R = NO) reacts readily with triethyl phosphite in ether at 0° to give largely the 4-amino-derivative (6; R = NH_2), presumably by way of a nitrene intermediate.

Pentachloropyridine and other polyhalogeno-aromatic compounds[25] form Grignard reagents readily. However, attempts to bring about the reaction of pentachloropyridine 1-oxide with magnesium were abortive; those reactions which proceeded at all gave intractable tars. This could be due to pyridyne formation, particularly favoured by very labile halogen atoms. Trapping experiments were, however, unsuccessful. Although 2,6-dichloropyridine[26] reacts with magnesium we found that its *N*-oxide was unresponsive.

EXPERIMENTAL

Reactions of Pentachloropyridine with Benzenethiolate.—(a) *With* 1 *mol. equiv. of benzenethiolate.* Pentachloropyridine (20 g), anhydrous potassium carbonate (5·6 g), and benzenethiol (75 ml) were heated at 120° under nitrogen for 24 h. Aqueous sodium hydroxide (30%) was added and the mixture was stirred for 12 h. Water (150 ml) was added and the mixture was extracted with chloroform. Evaporation of the extract followed by chromatography on silica with petroleum (b.p. 60—80°) gave *tetrachloro-2-phenylthiopyridine* (7·3 g, 28%), m.p. 117° (Found: C, 40·85; H, 1·3; N, 3·9. $C_{11}H_5Cl_4NS$ requires C, 40·6; H, 1·5; N, 4·3%), and the 4-isomer[9] (5·3 g, 21%) identical with samples obtained by replacing the nitro-group by a phenylthio-group in the corresponding tetrachloropyridines.[27]

(b) *With* 1 *mol. equiv. of benzenethiolate in propan-2-ol.* Pentachloropyridine (3·0 g), sodium benzenethiolate (1·6 g), and propan-2-ol (50 ml) were kept under reflux for 4 h. Work-up as in (a) gave pentachloropyridine (0·7 g) and tetrachloro-4-phenylthiopyridine (2·6 g, 63%).

(c) *With* 3 *mol. equiv. of benzenethiolate.* Pentachloropyridine (15·0 g), anhydrous potassium carbonate (10·8 g), and benzenethiol (100 ml) were kept at 140° for 18 h and then stirred with an excess of aqueous 30% sodium hydroxide for 12 h. Treatment as in (a) gave 3,5-dichloro-2,4,6-trisphenylthiopyridine (23·0 g, 85%), m.p. 118—119° (lit.,[9] 120—122°).

Reactions of 3,5-Dichloro-2,4,6-trifluoropyridine with Benzenethiolate.—(a) *With* 1 *mol. equiv. of benzenethiolate.* The trifluoropyridine (2·0 g) and sodium benzenethiolate (1·3 g) were stirred in propan-2-ol (25 ml) at room temperature for 24 h. Evaporation gave *3,5-dichloro-2,6-difluoro-4-phenylthiopyridine* (2·2 g, 77%), m.p. 66° (Found: C, 45·4; H, 1·6; N, 4·6. $C_{11}H_5Cl_2F_2NS$ requires C, 45·2; H, 1·7; N, 4·8%), δ_F −9·2 p.p.m.(s) ($CF_3{\cdot}CO_2H$ internal standard).

(b) *With* 2 *mol. equiv. of benzenethiolate.* To a solution of the trifluoropyridine (2·0 g) in pyridine (5 ml) at −20° was added sodium benzenethiolate (2·6 g) in pyridine (20 ml) during 20 min while the mixture was maintained at −10°. It was then allowed to warm to room temperature and an excess of hydrochloric acid was added. Extraction of the product with chloroform followed by evaporation and chromatography of the residue with petroleum on a silica column gave *3,5-dichloro-2-fluoro-4,6-bisphenylthiopyridine* (2·2 g, 55%), m.p. 81° (Found: C, 53·8; H, 2·8;

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N, 3·6. $C_{17}H_{10}Cl_2FNS_2$ requires C, 53·4; H, 2·6; N, 3·7%), δ_F −10·5 p.p.m.(s) ($CF_3{\cdot}CO_2H$ internal standard).

(c) *With 3 mol. equiv. of benzenethiolate.* The pyridine (2·0 g) and sodium benzenethiolate (4·0 g) were refluxed in propan-2-ol (50 ml) for 1 h and the product was worked up as in (a). 3,5-Dichlorotrisphenylthiopyridine (3·4 g, 72%) was obtained, identical with a previous preparation.

Reaction of 3,4,5-Trichloro-2,6-difluoropyridine with Benzenethiolate.—The pyridine (3·0 g) and sodium benzenethiolate (3·6 g, 2 mol. equiv.) were refluxed in propan-2-ol (25 ml) for 4 h to give 3,5-dichloro-2-fluoro-4,6-bisphenylthiopyridine (3·6 g, 69%), identical with that from 2,4,6-trifluoropyridine.

Reaction of 3-Chlorotetrafluoropyridine with Benzenethiolate.—To the 3-chloropyridine (3·0 g) in pyridine (10 ml) at −30° was added sodium benzenethiolate (2·1 g, 1 mol. equiv.) in pyridine (25 ml) during 30 min. The mixture was allowed to warm to room temperature and then poured into an excess of aqueous hydrochloric acid (5%). A chloroform extract gave *3-chloro-2,5,6-trifluoro-4-phenylthiopyridine* (1·3 g, 29%), m.p. 58° (from ethanol) (Found: C, 48·3; H, 2·0; N, 5·0. $C_{11}H_5F_3Cl_2NS$ requires C, 47·9; H, 1·8; N, 5·1%), δ_F −2·63(q), 13·25(q), and 80·25(q) p.p.m.

Preparation of Phenylsulphonylpolyhalogenopyridines.—In a typical example tetrachloro-2-phenylthiopyridine (1·5 g) was oxidised at 100° for 2 h in acetic acid (27 ml) and 30% hydrogen peroxide (9 ml). Addition of water (100 ml) precipitated *tetrachloro-2-phenylsulphonylpyridine* (1·5 g, 91%), m.p. 180° (Found: C, 36·8; H, 1·5; N, 3·9. $C_{11}H_5Cl_4NO_2S$ requires C, 37·0; H, 1·4; N, 3·9%). Similar reactions gave tetrachloro-4-phenylsulphonylpyridine (94%), m.p. 208° (lit.,[9] 207—208°), 3,5-dichloro-2,4,6-trisphenylsulphonylpyridine (60%), m.p. 215° (lit.,[9] 216°), *3,4,5-trichloro-2,6-bisphenylsulphonylpyridine* (70%), m.p. 177° (Found: C, 43·9; H, 2·2; N, 3·3. $C_{17}H_{10}Cl_3NO_4S_2$ requires C, 44·1; H, 2·2; N, 3·0%), the *3,5-dichloro-2,6-difluoro-4-phenylsulphonylpyridine* (64%), m.p. 165° (Found: C, 40·6; H, 1·8; N, 4·2. $C_{11}H_5Cl_2F_2NO_2S$ requires C, 40·8; H, 1·5; N, 4·3%), and tetrafluoro-4-phenylsulphonylpyridine (80%), m.p. 148—149° (lit.,[16] 149°).

Reactions of Polyhalogenopyridine 1-Oxides with Sodium Benzenethiolate.—(a) *Pentachloropyridine 1-oxide.*[28] To a solution of this *N*-oxide (2·0 g) in propan-2-ol (100 ml), a solution of sodium benzenethiolate (2·0 g, 2 mol. equiv.) in propan-2-ol (75 ml) was added dropwise during 30 min. The mixture was stirred for 15 min, evaporated to 50 ml, and poured into water to give *3,4,5-trichloro-2,6-bisphenylthiopyridine 1-oxide* (2·6 g, 84%), m.p. 157° (Found: C, 49·5; H, 2·5; N, 3·2. $C_{17}H_{10}Cl_3NOS_2$ requires C, 49·2; H, 2·4; N, 3·4%). With sodium benzenethiolate (4·2 g, 4 mol. equiv.) under similar conditions, *3-chlorotetrakisphenylthiopyridine 1-oxide* (2·0 g, 50%), m.p. 158°, was obtained (Found: C, 61·9; H, 3·9; N, 2·2. $C_{29}H_{20}ClNOS_4$ requires C, 62·0; H, 3·6; N, 2·5%). Excess of sodium benzenethiolate (6·0 g) gave under similar conditions, when the reaction mixture was kept at 60° for 4 h, a mixture of penta- and tetra-substituted products (analysed by mass spectrometry). Separation attempts led to decomposition and isolation of some tetrasubstituted product.

Deoxygenation of the tetrasubstituted 1-oxide (0·5 g) with phosphorus trichloride (1 ml) in chloroform (25 ml) by heating for 0·5 h was followed by addition of water (50 ml) and extraction with chloroform. The residue obtained on evaporation was chromatographed (silica; petroleum) to give *3-chlorotetrakisphenylthiopyridine* (0·3 g, 59%), m.p. 116° (from methanol) (Found: C, 63·3; H, 3·8; N, 2·3. $C_{29}H_{10}ClNS_4$ requires C, 63·8; H, 3·7; N, 2·6%). By a similar procedure *3,4,5-trichloro-2,6-bisphenylthiopyridine* (72%), m.p. 125°, was obtained from the corresponding *N*-oxide (Found: C, 50·8; H, 2·6; N, 3·4. $C_{17}H_{10}NS_2$ requires C, 51·2; H, 2·5; N, 3·5%).

(b) *4-Bromotetrachloropyridine 1-oxide.* This *N-oxide*, m.p. 198° (Found: C, 19·3; N, 4·4. C_5BrCl_4NO requires C, 19·2; N, 4·5%), was obtained (95%) by oxidation[28] in acetic acid–sulphuric acid with 87% hydrogen peroxide. When treated with sodium benzenethiolate (4 mol. equiv.) in propan-2-ol as described for the pentachloropyridine 1-oxide (a) it gave 3-chlorotetrakisphenylthiopyridine (72%).

Reactions of Polyhalogenopyridines with Sodium Nitrite.—(*a*) Pentachloropyridine (2·0 g), sodium nitrite (5·0 g), and dimethylformamide (25 ml) were stirred at room temperature for 15 min. The mixture was then poured into water (200 ml) and the unchanged pentachloropyridine (0·4 g) was removed. The filtrate was acidified with hydrochloric acid and the tetrachloropyridine-4-ol (1·3 g, 73%) filtered off.

(*b*) 3,5-Dichlorotrifluoropyridine was treated in a similar way. Starting material was extracted with chloroform after addition of water to the mixture, and 3,5-dichloro-2,6-difluoropyridin-4-ol (80%) was filtered off after acidification.

(*c*) Pentafluoropyridine was treated as in (*a*). Tetrafluoropyridin-4-ol was obtained by extraction of the acidified reaction mixture with chloroform.

(*d*) Pentachloropyridine 1-oxide was treated as in (*a*). Tetrachloro-2-hydroxypyridine 1-oxide (50%) separated on diluting the mixture with water.

(*e*) Tetrachloro-4-phenylsulphonylpyridine was treated as in (*a*) to give tetrachloropyridin-4-ol (70%).

(*f*) Tetrachloro-2-phenylsulphonylpyridine gave *3,5,6-trichloro-2-phenylsulphonylpyridin-4-ol* (70%), m.p. 160° (Found: C, 38·9; H, 1·8; N, 4·3. $C_{11}H_6Cl_3NO_3S$ requires C, 39·1; H, 1·8; N, 4·1%).

Reaction of Pentachloropyridine with Trimethyl and Triethyl Phosphites.—(*a*) The pyridine (5·0 g) was refluxed in trimethyl phosphite (10·5 ml) under nitrogen for 24 h. Excess of solvent was driven off, leaving *dimethyl 2,3,5,6-tetrachloro-4-pyridylphosphonate* (2·5 g), m.p. 109° (Found: C, 25·8; H, 1·8; N, 4·2. $C_7H_6Cl_4NO_3P$ requires C, 25·8; H, 1·9; H, 4·3%$_6$. The 4-bromotetrachloropyridine gave the same product.

(*b*) Reaction with triethyl phosphite was similar. After removal of solvent under reduced pressure, 2,3,5,6-tetrachloropyridine (5%) sublimed into the condenser. The residue was diethyl 2,3,5,6-tetrachloro-4-pyridylphosphonate[21] (50%), m.p. 45°. Refluxing this with sodium (1 mol. equiv.) in methanol for 72 h gave 3,5,6-trichloro-2-methoxypyridine (10).

Reactions of Dimethyl 2,3,5,6-Tetrachloro-4-pyridylphosphonate.—(*a*) The phosphonate (1·5 g), sodium hydroxide (3·0 g), and water (50 ml) were refluxed for 24 h. The solution was neutralised with hydrochloric acid and the precipitated solid was extracted with chloroform. Evaporation of the dried ($MgSO_4$) extracts gave 2,3,5,6-tetrachloropyridin-4-ol (0·6 g).

(*b*) The phosphonate (2·0 g) was refluxed with sodium (1 mol. equiv.) dissolved in an excess of methanol for 16 h. Water was added and the mixture was extracted with chloroform. The residue obtained from removal of the

[28] G. E. Chivers and H. Suschitzky, *J. Chem. Soc.* (*C*), 1971, 2867.

chloroform was chromatographed on silica with petroleum (b.p. 60—80°) to give 2,3,5,6-tetrachloropyridine (1·2 g), followed by 3,5,6-*trichloro*-2-*methoxypyridine* (0·4 g), m.p. 58° (Found: C, 34·0; H, 2·0; N, 6·8. $C_6H_4Cl_3NO$ requires C, 34·0; H, 1·9; N, 6·6%).

Refluxing the phosphonate (2·0 g) with excess of sodium (0·5 g) in methanol as before gave 3,5-*dichloro*-2,6-*dimethoxypyridine* (0·65 g) (Found: C, 49·0; H, 4·2; N, 8·0. $C_7H_7Cl_2NO_2$ requires C, 48·6; H, 4·1; N, 8·2%), also obtained from 2,3,5,6-tetrachloropyridine by refluxing in sodium methoxide solution.

Reactions of 2,3,5,6-*Tetrachloropyridyl(diphenyl)phosphine Oxide.*[29]—The phosphine oxide (1·0 g) was refluxed with sodium (1 mol. equiv.) dissolved in methanol (10 ml) for 24 h. The product was 3,5,6-trichloro-2-methoxypyridine (0·45 g). With an excess of sodium (3·0 g), 2,3,5,6-tetrachloropyridine (0·3 g) separated. On acidification diphenylphosphinic acid (0·6 g), m.p. 194° (lit.,[23] 191°), was obtained.

Reaction of Tetrachloro-4-nitrosopyridine with Triethyl Phosphite.—The nitroso-compound (5·0 g) was treated with triethyl phosphite (1 mol. equiv.) in dry ether at 0°. The mixture was then allowed to warm to room temperature. Starting material was filtered off, the filtrate was evaporated, and the residue was chromatographed (silica; benzene) to give 4-aminotetrachloropyridine (3·7 g).

Attempts at Prepararing a Grignard Reagent from Pentachloropyridine 1-Oxide.—The *N*-oxide and magnesium did not react in ether, tetrahydrofuran, or hexamethylphosphoramide even when a crystal of iodine and ethylene dibromide were added. A reaction occurred on heating hexamethylphosphoramide and magnesium at 150° for 2 h, then cooling the mixture and adding the *N*-oxide. The mixture yielded much tar and a little starting material only. Trapping (with tetraphenylcyclopentadienone) was of no avail. 2,6-Dichloropyridine 1-oxide behaved similarly

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[29] S. S. Dua, R. C. Edmondson, and H. Gilman, *J. Organometallic Chem.*, 1970, **24**, 703.