Polyhalogenoaromatic Compounds. Part 40.[1] Synthesis and Thermal Rearrangements of Some Polychloropyridines

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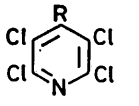
The ethers (1), (2), and (7)—(10) were prepared by alkylation of tetrachloro-4(or 2)-hydroxypyridine. Alkylation of the 2-hydroxy-compound also gave the 1-alkyltetrachloro-2-pyridones (15)—(18) (Table). Allyl (3) and propargyl (4) tetrachloro-4-pyridyl sulphides were prepared similarly, and the latter rearranged to allenyl tetrachloro-4-pyridyl sulphide (5). Allylamine reacted with pentachloropyridine 1-oxide by displacement of an α-chlorine atom, sodium benzyloxide and allyloxide gave only the 1-alkoxytetrachloro-2-pyridones (12) and (13), whilst under the same conditions sodium propargyloxide gave a mixture of (14) and the 1-oxide of ether (10). Allyl tetrachloro-4-pyridyl ether (1) underwent a Claisen rearrangement to give a mixture of 4,6,7-trichloro-2-methyl (and chloromethyl)-2,3-dihydrofuro[3,2-*c*]pyridine, (22) and (23), 3-allyl-2,5,6-trichloro-4-hydroxypyridine (21) (major product), and tetrachloro-4-hydroxypyridine. In *NN*-diethylaniline at 230 °C, propargyl tetrachloro-4-pyridyl ether (2) gave tetrachloro-4-hydroxypyridine and tetrachloro-4-ethoxypyridine; the latter product was shown to arise by attack of the hydroxy-compound on the solvent. Allyl tetrachloro-2-pyridyl ether (7) rearranged thermally to give only 1-allyltetrachloro-2-pyridone (15), whilst the corresponding crotyl (8) and dimethylallyl (9) ethers gave only tetrachloro-2-hydroxypyridine and starting material. Attempts to thermally rearrange compounds (3), (4), (6), (10), and (11) gave either starting material or an intractable product.

In continuation of our studies on polyhalogenopyridines [1] we have become interested in derivatives of polyhalogenohydroxypyridines, some of which, for example, 2,3,5-trichloro-4-hydroxypyridine (pyriclor) and 3,5-dichloro-2,6-dimethyl-4-hydroxypyridine (clopidol), are of interest as pesticides and herbicides.[2] Initially we synthesised some allyloxypolyhalogenopyridines that were of commercial interest and decided to study their Claisen rearrangements.

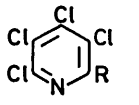
The first recorded example of a pyridine Claisen rearrangement was that of allyl 2,6-dimethyl-4-pyridyl ether to give 3-allyl-2,6-dimethyl-4-pyridone.[3] An attempt to rearrange allyl 4-pyridyl ether in *NN*-diethylaniline at 250 °C gave an intractable product, whilst its 2-isomer yielded both 1- and 3-allyl-2-pyridone.[4] Since the completion of our work thermal rearrangements of allyl 3-pyridyl ether and allyl 2-methyl-3-pyridyl ether have been reported [5] to give 2-methyl-2,3-dihydrofuro[3,2-*b*]pyridine and 2,7-dimethyl-2,3-dihydrofuro-[2,3-*c*]pyridine, respectively. The literature contains several examples of Claisen rearrangements carried out on allyl aryl ethers in which the *ortho*- or *para*-positions, or both, are blocked by halogen atoms.[6-9] An allyl group can rearrange with displacement of halogen, which is either lost or migrates to another position. Allyl 2,4,6-tribromophenyl ether, for example, rearranges to give mainly 2-allyl-4,6-dibromophenol but also some 5,7-dibromo-2,3-dihydro-2-methylbenzo[*b*]furan and 2,4,6-tribromophenol.[7] Thermolysis of allyl pentafluorophenyl ether in the vapour phase at 365 °C allows the intermediate, 4-allyl-2,3,4,5,6-pentafluorocyclohexa-2,5-dienone, to be isolated.[8] In some cases rearrangement of an allyl group results in displacement of other groups,[9] for example carboxy [10,11] or allyloxy.[12] To our knowledge rearrangements of similarly substituted allyl pyridyl ethers have not been investigated.

RESULTS AND DISCUSSION

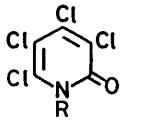
When allyl 2,3,5,6-tetrahydro-4-pyridyl ether (1) was heated at 190 °C for 90 min in sulpholan under nitrogen, it gave a complex mixture of products, which were separated by column chromatography. The isolable products were identified as 4,6,7-trichloro-2,3-dihydro-2-methylfuro[3,2-*c*]pyridine (22) (10.5%), 4,6,7-trichloro-



(1) R = $OCH_2CH=CH_2$
(2) R = $OCH_2C\equiv CH$
(3) R = $SCH_2CH=CH_2$
(4) R = $SCH_2C\equiv CH$
(5) R = $SCH=C=CH_2$
(6) R = $NHCH_2CH=CH_2$



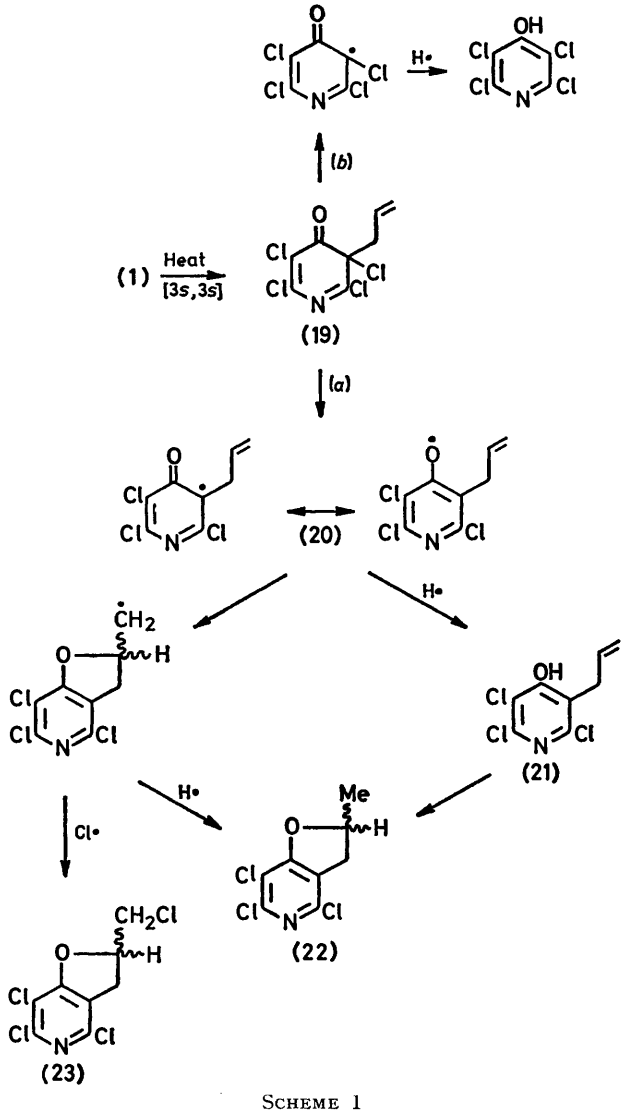
(7) R = $OCH_2CH=CH_2$
(8) R = $OCH_2CH=CHMe$
(9) R = $OCH_2CH=CMe_2$
(10) R = $OCH_2C\equiv CH$
(11) R = $NHCH_2CH=CH_2$



(12) R = OCH_2Ph
(13) R = $OCH_2CH=CH_2$
(14) R = $OCH_2C\equiv CH$
(15) R = $CH_2CH=CH_2$
(16) R = $CH_2CH=CHMe$
(17) R = $CH_2CH=CMe_2$
(18) R = $CH_2C\equiv CH$

2-chloromethyl-2,3-dihydrofuro[3,2-*c*]pyridine (23) (6%), 3-allyl-2,5,6-trichloro-4-hydroxypyridine (21) (26%), and tetrachloro-4-hydroxypyridine (6%) (see Scheme 1). The structures of (21)—(23) were confirmed by i.r., ^1H, and ^{13}C n.m.r. spectroscopy (^{13}C n.m.r. spectra will be reported later). In addition, the position of the allyl group in compound (21) was proved by the fact that it cyclised readily to give the furopyridine (22) with hydrogen bromide in acetic acid. In the ^1H n.m.r. spectrum of compound (22) (recorded in carbon tetrachloride at 60 MHz) the methyl group appeared as a

doublet at τ 8.42 (J 6.5 Hz). The asymmetry of the carbon atom to which it is attached renders the adjacent methylene protons non-equivalent. The signals for these protons both appear as a doublet of doublets at τ 6.51 and 7.13, with a J_{gem} 16.0 Hz and J_{vic} 9.5 and 7.0 Hz, respectively. We made no attempt to assign these two signals unambiguously. The methine proton

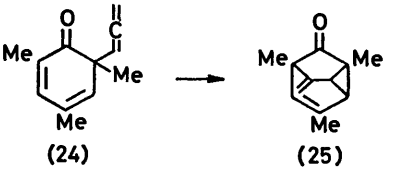


SCHEME 1

on C-2 appeared at τ 4.73 as a multiplet which it was not possible to resolve. The ^{1}H n.m.r. spectrum of the chloromethyl compound (23) was similar to that of the methyl compound (22). We can find no reference in the literature to the formation of chloromethyl derivatives during Claisen rearrangements of *allyl* aryl ethers of this type.

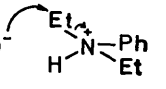
Our results can be rationalised as shown in Scheme 1. An initial [3*s*,3*s*] sigmatropic rearrangement yields intermediate (19) which reacts further, either by loss of a chlorine atom [pathway (*a*)] or by loss of an allyl radical [pathway (*b*)]. Loss of an allyl radical followed by hydrogen abstraction from the solvent explains the formation of tetrachloro-4-hydroxypyridine. A similar process explains the formation of 3-allyl-2,5,6-trichloro-4-hydroxypyridine (21). Alternatively, cyclisation of the intermediate radical (20) followed by either hydrogen or chlorine abstraction (or reaction with a chlorine atom) explains the formation of compounds (22) and (23), respectively. Similar mechanisms can be postulated to account for the migration of halogen already described in the literature and mentioned above. An alternative explanation for the formation of tetrachloro-4-hydroxypyridine would be hydrolysis of the ether (1) by any hydrogen chloride present in the reaction mixture. However, we were unable to isolate any allyl chloride. Several fates for the ejected allyl radical are possible. It may abstract hydrogen to give propene, eliminate hydrogen to give allene, or polymerise. Our work-up procedures allowed low boiling materials to escape and further work is necessary to confirm the proposed mechanism (Scheme 1). However, a similar mechanism has been proposed to account for the products obtained on rearrangement of 2,6-dichlorophenyl propargyl ether.[13]

Propargyl 2,4,6-tribromophenyl ether is reported [13] to rearrange thermally to give only 5,7-dibromo-2-methyl- and 5,7-dibromo-2-bromomethyl-benzo[*b*]furan, whilst propargyl 2,4,6-trimethylphenyl ether rearranges initially to give an intermediate (24), which undergoes an intramolecular Diels–Alder reaction to yield (25).[14] The



thermolysis of allyl pentafluorophenyl ether, mentioned before, also yields a product whose formation can be explained by involving a reaction step similar to (24)→(25).[8]

These results prompted us to study the thermolysis of propargyl 2,3,5,6-tetrachloro-4-pyridyl ether (2). However, when this ether was heated in sulpholan at 190 °C for 60 or 90 min, it gave only starting material and tetrachloro-4-hydroxypyridine. In *NN*-diethylaniline, heated at 230 °C for 60 min, it gave the tetrachlorohydroxypyridine and, surprisingly, tetrachloro-4-ethoxypyridine as the only isolable products. That the latter product is formed by a process similar to that shown in Scheme 2 (a radical process cannot be excluded) was supported by g.l.c. examination of the solvent before and after the experiment, which showed the presence of *N*-ethylaniline only after the reaction, and by the fact



SCHEME 2

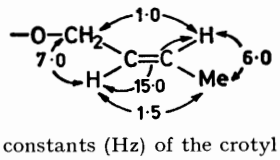
that, when tetrachloro-4-hydroxypyridine and *NN*-diethylaniline were heated together, they formed tetrachloro-4-ethoxypyridine and *N*-ethylaniline. Since the completion of our work, rearrangement of propargyl 3-pyridyl ether in DMF at 208 °C in a sealed tube has been reported [5] to yield a mixture of 2-methylfuro-[3,2-*b*]- and -[2,3-*c*]-pyridine. In decane at 208 °C, 2*H*-pyrano[3,2-*b*]pyridine is the main product apart from the two above furano-compounds. Similar products are obtained from 2-methyl-3-pyridyl propargyl ether but, if propargyl 3-pyridyl ethers substituted in both *ortho*-positions to the ether moiety are rearranged, intermediates are formed which undergo intramolecular Diels–Alder reactions.[5]

Attempts to rearrange allyl (3) or propargyl (4) 2,3,5,6-tetrachloro-4-pyridyl sulphide thermally gave only intractable products, whilst 4-allylamino-2,3,5,6-tetrachloropyridine (6) resisted rearrangement under all the conditions tried; for example, in sulpholan at 211 °C for 3 h it gave only starting material (84% recovery).

Thermal rearrangement of allyl 3,4,5,6-tetrachloro-2-pyridyl ether (7) under a variety of conditions gave, as expected, 1-allyl-3,4,5,6-tetrachloro-2-pyridone (15) in moderate yield. The corresponding crotyl (8) and dimethylallyl (9) ethers give only tetrachloro-2-hydroxypyridine. Propargyl 3,4,5,6-tetrachloro-2-pyridyl ether (10) failed to yield isolable rearranged products in sulpholane at 211 °C for 2 h, 55% of the starting material being recovered, whilst 2-allylamino-3,4,5,6-tetrachloropyridine (11) similarly gave a 74% recovery of starting material under the same conditions.

Synthesis of Starting Materials, and Thermal Rearrangement of Some 2-Alkoxy-3,4,5,6-tetrachloropyridine 1-Oxides.—Tetrachloro-4-hydroxypyridine and the corresponding thiol reacted with allyl or propargyl bromide (Finkelstein conditions reduce reaction times) to give the ether (1) and (2) and sulphides (3) and (4), respectively. 1-Substituted tetrachloro-4-pyridones could not be detected in the crude products. The sulphide (4) rearranged to allenyl 2,3,5,6-tetrachloro-4-pyridyl sulphide (5) on sequential treatment with sodium hydride and propan-2-ol.

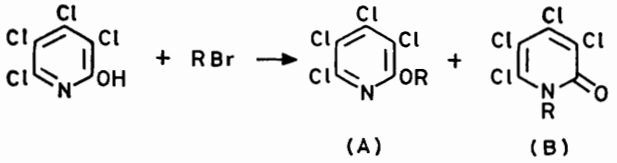
By contrast, tetrachloro-2-hydroxypyridine reacted with allyl, crotyl, or propargyl bromide, and with 1-bromo-3-methylbut-2-ene, to give mixtures of the corresponding ether (7)—(10) and 2-pyridone (15)—(18), respectively (Table). The crotyl ether (8) was shown to be the *trans*-isomer by an examination of its 220 MHz



Coupling constants (Hz) of the crotyl ether (8)

^{1}H n.m.r. spectrum in deuteriochloroform; the coupling constants shown in the Figure were measured after the two complex multiplets for the olefinic protons at τ 4.13 and 4.28 had been amplified and expanded. In both the 60 and 100 MHz ^{1}H n.m.r. spectra of this compound, signals are insufficiently resolved for these coupling constants to be measured.

TABLE



(A) (B)

R	Yields (%) (A)	(B)
$CH_2CH=CH_2$	86	12
$CH_2CH=CHMe$	56	9
$CH_2CH=CMe_2$	28	11
$CH_2C\equiv CH$	32	17

2-Substituted tetrachloropyridines are available by reaction of pentachloropyridine 1-oxide with the appropriate nucleophile followed by deoxygenation of the product with phosphorus trichloride. 2-Allylamino-3,4,5,6-tetrachloropyridine (11) was prepared in this way; its isomer (6) was prepared as described elsewhere.[15] When pentachloropyridine 1-oxide is treated with sodium allyloxide, however, it gives only 1-allyloxy-3,4,5,6-tetrachloro-2-pyridone (13). The structure of this compound was established by comparison of its i.r., u.v., and ^{1}H and ^{13}C n.m.r. spectra (^{13}C n.m.r. spectra will be reported later) with those of 3,4,5,6-tetrachloro-1-methoxy-2-pyridone, a known compound.[16] Pentachloropyridine 1-oxide reacts similarly with sodium benzyloxide, to give 1-benzyloxy-3,4,5,6-tetrachloro-2-pyridone (12), but with sodium propargyloxide it gives a mixture of the 1-oxide of propargyl 3,4,5,6-tetrachloro-2-pyridyl ether (10) (major product) and 3,4,5,6-tetrachloro-1-propargyloxy-2-pyridone (14). The rearrangement of 2-alkoxypyridine 1-oxides to 1-alkoxy-2-pyridones is well known but the mechanism of these reactions is still being investigated.[17]

EXPERIMENTAL

^{1}H N.m.r. spectra * were recorded on Varian A60 or EM360 instruments (with $SiMe_4$ as internal standard), i.r. spectra on a Perkin-Elmer 257 spectrometer, mass spectra on A.E.I. MS12 or MS902S instruments, and u.v. spectra on a Pye–Unicam SP200 spectrometer. All the mass spectra recorded exhibited the correct isotopic abundance ratios for the number of chlorine atoms contained in them, and reported molecular weights are given for the isotopes ^{35}Cl and ^{79}Br. G.l.c. analysis was carried out with a Pye 104 chromatograph fitted with a katharometer detector and a 5-ft × 5-mm i.d. column packed with 10% Carbowax 20M on brickdust and operating at 174 °C with hydrogen as the carrier gas (40 ml min^{-1}).

All the rearrangements reported in this paper were carried out in anhydrous solvents under nitrogen with the apparatus heated by a vapour-bath. Light petroleum had b.p. 60—80 °C unless stated otherwise.

The following compounds were prepared by literature

* ^{1}H N.m.r. data are available as Supplementary Publication No. SUP 22605 (6 pp.). For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1978, Index issue.

procedures: 1-bromo-3-methylbut-2-ene (36%), b.p. 37—39 °C at 15 mmHg (lit.,[18] b.p. 50—51 °C at 40 mmHg); tetrachloro-4-hydroxypyridine (91%),[19] tetrachloro-2-hydroxypyridine (78%),[20] 2,3,5,6-tetrachloropyridine-4-thiol (88%),[21] 4-(*N*-allylamino)-2,3,5,6-tetrachloropyridine (6) (73%),[15] pentachloropyridine 1-oxide (91%),[22] and 3,4,5,6-tetrachloro-1-methoxy-2-pyridone (82%).[16] Tetrachloro-4-ethoxypyridine (46%) was prepared by alkylation of the hydroxy-compound with ethyl iodide in acetone in the presence of potassium carbonate and had m.p. 56—57 °C (from light petroleum) (lit.,[23] 58—59 °C).

Allyl 2,3,5,6-Tetrachloro-4-pyridyl Ether (1).—(*a*) A mixture of tetrachloro-4-hydroxypyridine (23.3 g, 0.1 mol), allyl bromide (12.1 g, 0.1 mol), potassium iodide (10 g), potassium carbonate (10 g), and acetone (150 ml) was stirred and heated under reflux for 24 h. The solvent was distilled off under reduced pressure, water (200 ml) was added to the residue, and extraction with ether gave *allyl 2,3,5,6-tetrachloro-4-pyridyl ether* (1) (21.0 g, 77%), m.p. 55—56 °C (from aqueous ethanol) (Found: C, 34.7; H, 1.9; N, 5.05%; M^+, 271. $C_8H_5Cl_4NO$ requires C, 35.2; H, 1.85; N, 5.1%; *M*, 271).

(*b*) A mixture of tetrachloro-4-hydroxypyridine (1.16 g, 5.0 mmol), allyl bromide (0.6 g, 5.0 mmol), potassium carbonate (2.0 g), and acetone (10 ml) was stirred and heated under reflux for 7 days. Work-up as described in (*a*) gave the product (1) (0.85 g, 94% at 65% conversion). Starting material (0.40 g) was recovered by acidification of the aqueous layer.

In a manner similar to that described in (*b*) the following compounds were prepared (reaction times in parentheses): *propargyl 2,3,5,6-tetrachloro-4-pyridyl ether* (2) (1 week) (94%), m.p. 85—86 °C (sublimed at 80 °C and 0.005 mmHg); $\nu_{max.}$ (Nujol) 3 300 (≡CH) and 2 140 cm^{-1} (C≡C) (Found: C, 35.6; H, 1.2; N, 5.0%; M^+, 269. $C_8H_3Cl_4NO$ requires C, 35.45; H, 1.1; N, 5.2%; *M*, 269); *allyl 2,3,5,6-tetrachloro-4-pyridyl sulphide* (3) (24 h) (89%) as an oil, which solidified after distillation, b.p. (Kugelrohr apparatus) 97 °C at 0.005 mmHg, m.p. 42—43 °C (Found: C, 33.3; H, 1.9; N, 4.8%; M^+, 287. $C_8H_5Cl_4NS$ requires C, 33.25; H, 1.7; N, 4.85%; *M*, 287); *propargyl 2,3,5,6-tetrachloro-4-pyridyl sulphide* (4) (24 h) (86%), m.p. 76—77 °C (from light petroleum); $\nu_{max.}$ (Nujol) 3 300 (≡CH) and 2 120 cm^{-1} (C≡C) (Found: C, 33.35; H, 1.2; N, 5.2%; M^+, 285. $C_8H_3Cl_4NS$ requires C, 33.5; H, 1.1; N, 4.9%; *M*, 285).

Allenyl 2,3,5,6-Tetrachloro-4-pyridyl Sulphide (5).—A stirred mixture of propargyl 2,3,5,6-tetrachloro-4-pyridyl sulphide (4) (0.68 g, 2.5 mmol), sodium hydride (0.1 g, 4.0 mmol), and anhydrous tetrahydrofuran (10 ml) was heated under reflux for 30 min, then the mixture was cooled to ambient temperature and propan-2-ol (30 ml) was added dropwise with cooling. The mixture was stirred for a further 5 min, the solvent was distilled off under reduced pressure, the residue was extracted with light petroleum, and distillation gave the *product* (5) (0.4 g, 57%), b.p. (Kugelrohr apparatus) 75 °C at 0.005 mmHg, $\nu_{max.}$ (liquid film) 1 940 cm^{-1} (C=C=C) (Found: M^+, 284.873 2. $C_8H_3Cl_4NS$ requires *M*, 284.873 8).

Reaction of Tetrachloro-2-hydroxypyridine with Allyl Bromide.—A mixture of the tetrachlorohydroxypyridine (23.3 g, 0.1 mol), allyl bromide (12.1 g, 0.1 mol), potassium carbonate (10 g), potassium iodide (10 g), and acetone (150 ml) was stirred and heated under reflux for 24 h. The solvent was distilled off under reduced pressure and the residue chromatographed on alumina. Light petroleum eluted *allyl 3,4,5,6-tetrachloro-2-pyridyl ether* (7) (21.1 g, 78%), m.p. 53—54 °C (from aqueous ethanol) (Found: C, 35.2; H, 1.6; N, 5.4%; M^+, 271. $C_8H_5Cl_4NO$ requires C, 35.2; H, 1.85; N, 5.1%; *M*, 271), and chloroform eluted *1-allyl-3,4,5,6-tetrachloro-2-pyridone* (15) (3.1 g, 11.5%), m.p. 108—110 °C (from light petroleum); $\nu_{max.}$ (Nujol) 1 670 cm^{-1} (CO); $\lambda_{max.}$ 337.5 nm (ε 5 800) (Found: C, 34.8; H, 1.7; N, 5.05%; M^+, 271).

Reaction of tetrachloro-2-hydroxypyridine with propargyl or crotyl bromide or with 1-bromo-3-methylbut-2-ene, and chromatography of the products on alumina similarly gave the following compounds (reaction times and elution solvents given in parentheses): *propargyl 3,4,5,6-tetrachloro-2-pyridyl ether* (10) (4 h, eluted with light petroleum, 32% yield), m.p. 119—120 °C (from aqueous ethanol); $\nu_{max.}$ (Nujol) 3 300 (≡CH) and 2 160 cm^{-1} (C≡C) (Found: C, 35.4; H, 1.0; N, 5.1%; M^+, 269. $C_8H_3Cl_4NO$ requires C, 35.45; H, 1.1; N, 5.2%; *M*, 269); and *3,4,5,6-tetrachloro-1-propargyl-2-pyridone* (18) (eluted with light petroleum–chloroform, 17% yield), m.p. 177—178 °C (from methanol); $\nu_{max.}$ (Nujol) 3 260 (≡CH), 2 160 (C≡C), and 1 660 cm^{-1} (CO) (Found: C, 35.5; H, 1.1; N, 5.2%; M^+, 269): *crotyl* trans-*3,4,5,6-tetrachloro-2-pyridyl ether* (8) (24 h, eluted with light petroleum, 56%), m.p. 58—59 °C (from aqueous ethanol) (Found: C, 37.5; H, 2.35; N, 4.9%; M^+, 285. $C_9H_7Cl_4NO$ requires C, 37.7; H, 2.5; N, 4.9%; *M*, 285); and *3,4,5,6-tetrachloro-1-crotyl-2-pyridone* (16) (eluted with light petroleum–chloroform, 9%), an oil, b.p. 116—121 °C at 0.001 mmHg; $\nu_{max.}$ (liquid film) 1 670 cm^{-1} (CO) (Found: C, 37.9; H, 2.5; N, 5.0%; M^+, 285): *3-methylbut-2-enyl 3,4,5,6-tetrachloro-2-pyridyl ether* (9) (6 h, eluted with light petroleum, 28% yield at 59% conversion), m.p. 78—79 °C (from aqueous ethanol) (Found: C, 39.9; H, 2.9; N, 4.6%; M^+, 299. $C_{10}H_9Cl_4NO$ requires C, 39.9; H, 3.0; N, 4.65%; *M*, 299); and *3,4,5,6-tetrachloro-1-(3-methylbut-2-enyl)-2-pyridone* (17) (11% at 24% conversion), m.p. 108.5—109.5 °C (from methanol); $\nu_{max.}$ (Nujol) 1 675 cm^{-1} (CO) (Found: C, 39.9; H, 3.2; N, 4.4%; M^+, 299).

2-Allylamino-3,4,5,6-tetrachloropyridine 1-Oxide.—A stirred mixture of pentachloropyridine 1-oxide (5.4 g, 20.0 mmol), allylamine (2.28 g, 40.0 mmol), and chloroform (25 ml) was heated under reflux for 16 h. The mixture was cooled, washed successively with 4M-hydrochloric acid (200 ml) and water, the organic layer dried ($MgSO_4$), and the solvent distilled off under reduced pressure to yield the *product* (5.50 g, 95%), m.p. 110—111 °C (from aqueous ethanol); $\nu_{max.}$ (Nujol) 3 230 cm^{-1} (NH) (Found: C, 33.3; H, 2.0; N, 9.7%; M^+, 286. $C_8H_6Cl_4N_2O$ requires C, 33.4; H, 2.1; N, 9.7%; *M*, 286).

2-Allylamino-3,4,5,6-tetrachloropyridine (11).—A mixture of 2-allylamino-3,4,5,6-tetrachloropyridine 1-oxide (2.89 g, 10 mmol), phosphorus trichloride (1.4 g, 10 mmol), and chloroform (20 ml) was stirred at ambient temperature for 1 h. Water (50 ml) was added and stirring continued for a further 5 min. The organic layer was separated, dried ($MgSO_4$), and passed down an alumina column, to yield 2-allylamino-3,4,5,6-tetrachloropyridine (11) (2.58 g, 95%), m.p. 58—59 °C (from aqueous ethanol) (lit.,[15] m.p. 45 °C), with an i.r. spectrum identical with that of an authentic sample.

Reaction of Pentachloropyridine 1-Oxide with Sodium Allyloxide.—Sodium (0.23 g, 10.0 mmol) was added to anhydrous allyl alcohol (15 ml) with stirring, and when reaction was complete, the resulting solution was added dropwise to a stirred suspension of pentachloropyridine

1-oxide (2.67 g, 10.0 mmol) in allyl alcohol (15 ml). The mixture was stirred at ambient temperature for 16 h, then filtered and the residue [pentachloropyridine 1-oxide (1.2 g)] washed with ether (10 ml). The combined filtrate and washings were distilled under reduced pressure to give 1-*allyloxy*-3,4,5,6-*tetrachloro*-2-*pyridone* (13) (1.2 g, 42%), m.p. 113—114 °C (from light petroleum); $\nu_{max.}$ (Nujol) 1 675 cm^{-1} (CO) [1 675 cm^{-1}]; $\lambda_{max.}$ (MeOH) 334 nm (ε 7 000) [333 nm (6 700)] (figures in square brackets for 3,4,5,6-tetrachloro-1-methoxy-2-pyridone) (Found: C, 33.2; H, 1.65; N, 4.75%; M^+, 286.907 8. $C_8H_5Cl_4NO_2$ requires C, 33.3; H, 1.7; N, 4.8%; *M*, 286.907 3).

Reaction of Pentachloropyridine 1-*Oxide with Sodium Benzyloxide*.—A solution of sodium benzyloxide [prepared from sodium (0.57 g, 25.0 mmol)] in anhydrous benzyl alcohol (20 ml) was added dropwise to a stirred solution of the 1-oxide (6.62 g, 25.0 mmol) in benzyl alcohol (20 ml) at ambient temperature and the mixture was stirred at this temperature for 16 h. It was then filtered and the filtrate was evaporated under reduced pressure (temperature not exceeding 35 °C to prevent rearrangement, if possible) to give a viscous oil (1.95 g) which was triturated with methanol to yield 1-*benzyloxy*-3,4,5,6-*tetrachloro*-2-*pyridone* (12) (1.73 g, 20%), m.p. 129.5—130.5 °C (from methanol); $\nu_{max.}$ 1 685 cm^{-1} (CO) (Found: C, 42.8; H, 2.05; N, 4.15%; M^+, 337. $C_{12}H_7Cl_4NO_2$ requires C, 42.5; H, 2.1; N, 4.1%; *M*, 337). The residue from the filtration was washed with water and dried to give starting material (4.2 g).

Reaction of Pentachloropyridine 1-*Oxide with Sodium Propargyloxide*.—A solution of sodium propargyloxide (17.4 mmol) in propargyl alcohol (10 ml) was added dropwise to a stirred solution of the 1-oxide (4.64 g, 17.4 mmol) in propargyl alcohol (10 ml) at ambient temperature and the mixture was stirred for 2 h at this temperature. The mixture was filtered and the solvent evaporated off under reduced pressure to give a white solid (4.70 g) which was chromatographed on alumina. Chloroform–light petroleum eluted 3,4,5,6-*tetrachloro*-2-*propargyloxypyridine* (10) 1-*oxide* (3.7 g, 74%), m.p. 126—128 °C (from methanol); $\nu_{max.}$ (Nujol) 3 250 (≡CH) and 2 120 cm^{-1} (C≡C) (Found: C, 33.9; H, 1.05; N, 4.9%; M^+, 285. $C_8H_3Cl_4NO_2$ requires C, 33.5; H, 1.05; N, 4.9%; *M*, 285): and 3,4,5,6-*tetrachloro*-1-*propargyloxy*-2-*pyridone* (14) (0.8 g, 16%), m.p. 129.5—130 °C (from methanol); $\nu_{max.}$ (Nujol) 3 255 (≡CH), 2 140 (C≡C), and 1 680 cm^{-1} (CO) (Found: C, 33.5; H, 1.0; N, 4.9%; M^+, 285).

Attempted Rearrangement of 2-*Allylamino*-3,4,5,6-*tetrachloropyridine* 1-*Oxide*.—A mixture of the pyridine (0.6 g, 2.1 mmol) and diglyme (5 ml) was heated at 160 °C for 30 min; it was then cooled and the solvent distilled off at 75 °C and 0.005 mmHg to give starting material (0.5 g).

Rearrangement of Allyl 2,3,5,6-*Tetrachloro*-4-*pyridyl Ether* (1).—The ether (6.5 g, 24.0 mmol) was heated for 90 min in sulpholan (40 ml) at 190 °C. The mixture was then poured into water (1 l), and extraction with chloroform gave a brown oil which was chromatographed on silica gel. Chloroform eluted three fractions: (*i*) an oil (1.07 g), which was rechromatographed on silica gel using light petroleum to elute 4,6,7-*trichloro*-2,3-*dihydro*-2-*methylfuro*[3,2-c]-*pyridine* (22) (0.6 g, 10.5%), m.p. 62—63 °C (from aqueous ethanol) (Found: C, 39.9; H, 2.6; N, 5.6%; M^+, 236.952 0. $C_8H_6Cl_3NO$ requires C, 40.3; H, 2.5; N, 5.9%; *M*, 236.951 3) and 4,6,7-*trichloro*-2-*chloromethyl*-2,3-*dihydrofuro*-[3,2-c]*pyridine* (23) (0.4 g, 6%), b.p. (Kugelrohr apparatus) 105 °C at 0.005 mmHg (Found: C, 35.45; H, 1.8; N, 5.0%; M^+, 270.913 3. $C_8H_5Cl_4NO$ requires C, 35.2; H, 1.85; N, 5.1%; *M*, 270.912 3); (*ii*) 3-*allyl*-2,5,6-*trichloro*-4-*hydroxypyridine* (21) (1.5 g, 26%), m.p. 110—111 °C (from carbon tetrachloride) (Found: C, 40.4; H, 2.2; N, 5.6%; M^+, 237); and (*iii*) a brown oil (0.75 g), which t.l.c. showed to be a complex mixture containing at least eight components. Methanol eluted tetrachloro-4-hydroxypyridine (0.37 g, 6%) as a fourth fraction with m.p. and i.r. spectrum identical with those of an authentic sample.

4,6,7-*Trichloro*-2,3-*dihydro*-2-*methylfuro*[3,2-c]*pyridine* (22).—A solution of hydrogen bromide in acetic acid (3 g of a 48% w/v solution) was added dropwise to a stirred solution of 3-allyl-2,5,6-trichloro-4-hydroxypyridine (21) (1.5 g, 6.3 mmol) in acetic acid (10 ml) and the mixture was heated under reflux for 3 h. It was then poured into water (100 ml) and the resulting solution was made alkaline with aqueous sodium hydrogencarbonate. Extraction with ether gave the product (22) (0.36 g, 24%), with m.p. and i.r. spectrum identical with those recorded for the sample prepared as described in the preceding experiment. By acidification of the aqueous layer with concentrated hydrochloric acid, starting material (0.84 g) was recovered.

Rearrangement of Propargyl 2,3,5,6-*Tetrachloro*-4-*pyridyl Ether* (12).—(*a*) The ether (6.5 g, 24.0 mmol) was heated in sulpholan (40 ml) at 190 °C (under nitrogen) for 60 min. Then the mixture was cooled and poured into aqueous sodium hydrogencarbonate (1 l, 4%). Extraction with chloroform gave a brown oil which was chromatographed on silica gel. Light petroleum eluted starting material (12) (3.2 g). Acidification of the aqueous layer with 4M-hydrochloric acid gave tetrachloro-4-hydroxypyridine (1.3 g, 23%).

(*b*) The ether (6.5 g, 24.0 mmol) was heated in *NN*-diethylaniline (40 ml) at 230 °C for 60 min. The solvent was distilled off under reduced pressure at 70 °C and 0.005 mmHg, and shown by g.l.c. analysis to contain *N*-ethylaniline (the *NN*-diethylaniline used was shown to be free of this material). The residue was chromatographed on silica gel. Light petroleum eluted tetrachloro-4-ethoxypyridine (1.3 g, 20%), m.p. 57—58 °C (from light petroleum) (lit.,[23] 58—59 °C) (Found: M^+, 259. $C_7H_5Cl_4NO$ requires *M*, 259), identical (m.p. and ^1H n.m.r. and mass spectra) with the sample prepared as described before. Methanol eluted tetrachloro-4-hydroxypyridine (2.4 g, 43%).

Reaction of Tetrachloro-4-*hydroxypyridine with* NN-*Diethylaniline*.—A mixture of the hydroxypyridine (1.2 g, 5.0 mmol) and the aniline (5 ml) was heated at 230 °C under nitrogen for 3 h. Then the mixture was poured into 4M-hydrochloric acid (500 ml) and extraction with ether gave a brown oil (0.8 g). This was re-dissolved in ether and the ethereal solution was washed with aqueous sodium hydrogencarbonate (2 × 50 ml, 4%), and then dried ($MgSO_4$). Distillation of the ether gave tetrachloro-4-ethoxypyridine (0.4 g, 30%), identical with an authentic sample (m.p. and i.r. spectrum). Acidification of the aqueous sodium hydrogencarbonate layer with 4M-hydrochloric acid gave tetrachloro-4-hydroxypyridine (0.2 g). The 4M-hydrochloric acid layer obtained at the beginning of the work-up procedure was made alkaline, extracted with ether, the ethereal extracts were combined and dried ($MgSO_4$), and distillation of the ether and g.l.c. examination of the residual amine showed that it consisted mainly of *NN*-diethylaniline with a minor *N*-ethylaniline component.

Rearrangement of Allyl 3,4,5,6-*Tetrachloro*-2-*pyridyl Ether* (7).—The ether (5.5 g, 20.0 mmol) was heated at 184 °C in

anhydrous sulpholan (30 ml) for 5 h under nitrogen (using an aniline vapour-bath). The mixture was then poured into water (750 ml) and extraction with light petroleum (b.p. 30—40 °C) gave a product which was chromatographed on alumina. Light petroleum eluted starting material (2.0 g), whilst light petroleum–chloroform eluted 1-allyl-3,4,5,6-tetrachloro-2-pyridone (15) (1.62 g, 30%), m.p. 108—110 °C [from light petroleum (b.p. 80—100 °C)], identical in all other respects with a sample prepared as described before.

Attempted Rearrangement of 3-Methylbut-2-enyl 3,4,5,6-Tetrachloro-2-pyridyl Ether (9).—A mixture of the ether (15.0 g, 50.0 mmol) and sulpholan (50 ml) was heated at 211 °C for 30 min (using a nitrobenzene vapour-bath), then poured into water (1 l). The precipitate (10.3 g, 89%) was filtered off and shown to be tetrachloro-2-hydroxypyridine (m.p. and i.r. spectrum identical with an authentic sample).

Similar treatment of crotyl 3,4,5,6-tetrachloro-2-pyridyl ether (8) gave tetrachloro-2-hydroxypyridine in 69% yield.

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