Polyhalogenoaromatic Compounds. Part 43.[1] Inter- and Intra-molecular Reactions of Polychloroaromatic Compounds with Copper

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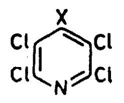
The reaction of polychloroiodoarenes with copper in dimethylformamide gives good yields of the biaryls. 4-Bromotetrachloropyridine gives products of halogen exchange and reduction as well as coupling. Pentachloropyridine gave only tetrachloropyridines. Evidence against free radical or pyridyne intermediates is presented, and it is postulated that the reactions proceed *via* pyridylcopper compounds, although an electron transfer mechanism is not excluded. On reaction with copper, some 4-(*o*-halogenophenoxy)- and 4-(*o*-halogenothiophenoxy)-tetrahalogenopyridines give products of cyclisation, reduction, and halogen transfer. Copper reacts initially, at least in part, with the pyridyl group rather than with the *o*-halogenoaryl group. The results are again consistent with a reaction pathway involving a pyridylcopper intermediate.

The products of nucleophilic substitution in pentahalogenopyridines by some phenols, thiophenols, and anilines are reported.

THE Ullmann reaction is a well established method for preparing biaryls, but its mechanism is uncertain although there is some evidence for organocopper intermediates.[2,3] It is most successful with iodoarenes, less so with bromoarenes, and rarely so with chloroarenes. Heterocyclic as well as homocyclic arenes can be used, and cyclisations *via* intramolecular Ullmann reactions have been achieved. Temperatures from 150 to 300 °C are commonly required. The reaction is often carried out without a solvent, but lower temperatures and less copper are required with a dipolar, aprotic solvent such as dimethylformamide (DMF).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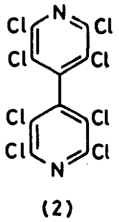
(9) X = Br
(10) X = Cu
(12) X = COPh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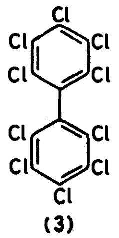
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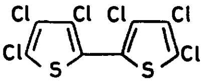
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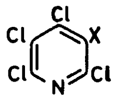
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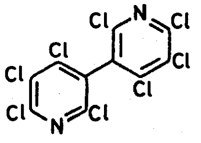
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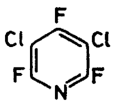
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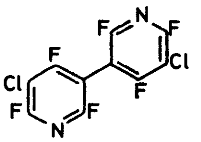
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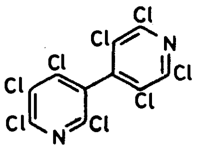
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In this paper we describe reactions of some polychloroaromatic and -heteroaromatic compounds with copper, which provide syntheses of some biaryls and tricyclic systems, and furnish some information concerning the mechanism of the Ullmann reaction.

Several polyfluoroiodo-aromatic and -heteroaromatic compounds have been converted into the corresponding biaryls in fair to good yields.[4-7] Some polychlorobiphenyls have been prepared in this way,[8] and a reaction of tetrachloro-4-iodopyridine (1) with copper without solvent at 200 °C gave octachloro-4,4′-bipyridyl (2) (40%).[9] By reactions with copper bronze in DMF at 150 °C we have prepared decachlorobiphenyl (3) (81%) from pentachloroiodobenzene and hexachloro-2,2′-bithienyl (4) (75%) from trichloro-5-iodothiophen. Under these conditions, however, tetrachloro-4-iodopyridine (1) gave pentachloropyridine (4%) and 2,3,5,6-tetrachloropyridine (5) (22%) as well as the bipyridyl (2) (52%). Similarly tetrachloro-5-iodopyridine (6) gave octachloro-3,3′-bipyridyl (7) (71%), a trace of pentachloropyridine, and 2,3,4,6-tetrachloropyridine (8) (3%). Halogen exchange and reductive dehalogenation as side reactions have been noted previously in Ullmann reactions in DMF;[2,3] they are discussed below.

The results of some reactions of 4-bromotetrachloropyridine (9) with copper in DMF at 150 °C are summarised in Table 1. In every case, octachloro-4,4′-bipyridyl (2) was obtained in only low yields, and was accompanied by pentachloropyridine, two tetrachloropyridines (5) and (8), and another octachlorobipyridyl. The m.p. of the last product differed from those of the previously known 2,2′-, 2,3′-, 2,4′-, and 4,4′-isomers[10] and of the 3,3′-isomer described in this paper. It was possible to rationalise the formation of all of these products by the reactions shown in Scheme 1; according to this Scheme the unknown octachlorobipyridyl would be the 3,4′-isomer (15). We have carried out a number of experiments designed to test the validity of Scheme 1, in particular the intermediacy of tetrachloro-4-pyridylcopper (10).

The formation of pentachloropyridine is readily accounted for, if copper(I) chloride is formed in any of the reactions, since on treatment with copper(I) chloride in

DMF 4-bromotetrachloropyridine gave pentachloropyridine in 95% yield (*cf.* ref. 11). Interestingly, a trace of octachloro-4,4'-bipyridyl (2) was also obtained from this reaction, indicating that an organocopper intermediate could again be involved (*cf.* ref. 12, but see ref. 13).

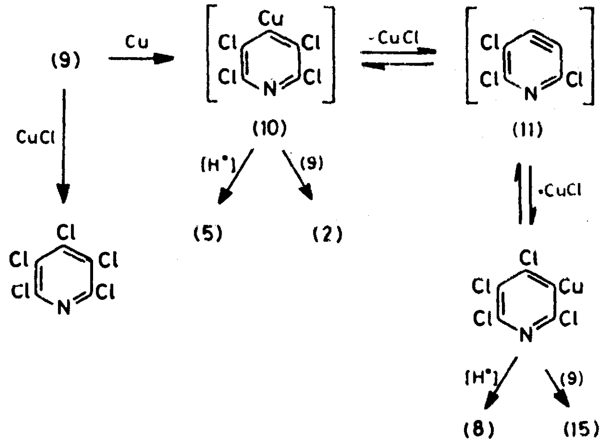
TABLE 1

Reactions of 4-bromotetrachloropyridine (9) with copper in DMF at 150 °C

				Products (yield %)				
Expt. No.	Proportion of Cu to substrate (at eq.)	Time (h)	Special conditions	Octachloro-4,4' 1-bipyridyl (2)	Pentachloro-pyridine	2,3,5,6-Tetra-chloropyridine (5)	2,3,4,6-Tetra-chloropyridine (8)	Unidentified octachloro-bipyridyl [a]
(1)	5	0.5		8	10	10	Trace	9
(2)	1	0.5		14	21	17	*b*	8
(3)	1	1	Solvent comprised DMF (10 ml) and *p*-xylene (1.0 g)	18	15	42	5	4
(4)	1	1	Solvent comprised DMF (10 ml) and cumene (1.2 g)	17	16	63	15	Trace
(5)	5	0.5	Benzoyl chloride (excess) added before work-up	15	*b*	61	24	Trace

[a] Probably the 3,4'-isomer (15); see text. [b] Not observed.

The possible intermediacy of a pyridyne (11) was



SCHEME 1

examined by experiments (3) and (4) in which the reaction took place in the presence of an aromatic hydrocarbon (*p*-xylene or cumene). Unfortunately only approximately one equivalent of the hydrocarbon could be used as higher proportions inhibited the reaction, but no adducts of the pyridyne (11)[14] were obtained. The absence of bicumyl among the products of experiment (4)[15] also indicated that free radicals were not involved.

The reduction products (5) and (8) could arise from hydrolysis of the organocopper intermediate on work-up. Gilman has prepared tetrachloro-4-pyridylcopper (10) and shown that it reacts with benzoyl chloride to give 4-benzoyltetrachloropyridine (12).[16] However, experiment (5), involving addition of benzoyl chloride before work-up, showed that no pyridylcopper intermediate had survived the reaction conditions. On the other hand, the presence of traces of water in DMF is almost unavoidable,[17] and in any case DMF itself is capable of acting as a proton donor.[18]

Further evidence on the possible intermediacy of tetrachloro-4-pyridylcopper (10) came from experiments on this compound, prepared *via* the Grignard reagent as described by Gilman.[16] The results are summarised in Table 2. Experiment (1) confirmed that it could be trapped by benzoyl chloride and that the product (12) was stable in boiling DMF. Experiment (2) demonstrated the remarkable thermal stability of tetrachloro-4-pyridylcopper (10), some of which survived 21 h in boiling *p*-xylene. The decomposition products isolated were from coupling and reduction (see refs. 13 and 19 for recent work on thermolysis of arylcopper compounds)

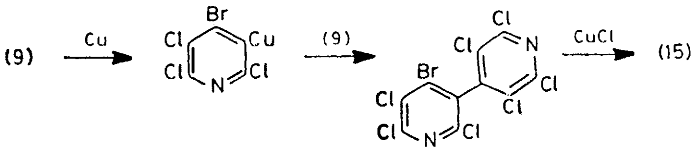
TABLE 2

Reactions of tetrachloro-4-pyridylcopper (10)

		Products (yield %)				
Experiment No.	Reaction conditions	Octachloro-4,4'-bipyridyl (2)	Pentachloro-pyridine	2,3,5,6-Tetrachloro-pyridine (5)	4-Benzoyl-tetrachloro-pyridine (12)	Other
(1)	i, PhCOCl, DMF; ii, reflux ½ h	*a*	*a*	9	72	*a*
(2)	i, *p*-xylene; ii, reflux 23 h; iii, PhCOCl	2.5	1	12	13	2 [b]
(3)	i, DMF; ii, reflux 1 h; iii, PhCOCl	1	*a*	13.5	*a*	4 [b]
(4)	i, 4-bromotetrachloropyridine, DMF; ii, reflux 1 h; iii, PhCOCl	16	24 [c]	14	*a*	7 [d]

[a] Not observed. [b] Mixture of two heptachlorobipyridyls; see text. [c] Contained some 4-bromotetrachloropyridine. [d] Probably octachloro-3,4'-bipyridyl (15); see text.

but not from pyridyne formation, since no adduct with the solvent was obtained. The heptachlorobipyridyls were presumably formed *via* the reaction of octachlorobipyridyl with copper produced in the coupling or *via* displacement of chlorine in tetrachloro-4-pyridylcopper (10) by another molecule of the same compound. Experiment (3) showed that decomposition was more rapid in DMF, none of the starting material surviving 1 h under reflux. Finally experiment (4) showed that tetrachloro-4-pyridylcopper (10) reacted with 4-bromotetrachloropyridine (9) in DMF to give a similar range of products to those obtained from the reaction of the bromo-compound (9) with copper (see Table 1).

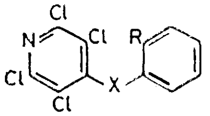


SCHEME 2

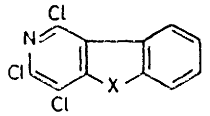
If, as shown above, pyridynes are not involved in these reactions, the copper(I) chloride required for the formation of pentachloropyridine must come from direct reaction of copper at a chlorine-substituted position. That this can indeed occur was shown by the reaction of copper with pentachloropyridine. The reaction was slow, and gave the three tetrachloropyridines, the 2,3,4,6-isomer (8) predominating. [A reaction of 3,5-dichlorotrifluoropyridine (13) with copper in DMF gave the bipyridyl (14) in 15% yield, together with polymeric material (*cf.* ref. 20).] The unknown octachlorobipyridyl, noted in Tables 1 and 2, could be the 3,4′-isomer (15) formed as shown in Scheme 2.

The simplest rationalisation of all the results described above is that the reaction between copper and a pentahalogenopyridine leads initially to the formation of a tetrahalogenopyridylcopper intermediate. One possibility that cannot be excluded is that formation of the pyridylcopper intermediate is preceded by electron transfer from copper to the polyhalogenopyridine (by analogy with the formation of a Grignard reagent [21]) and that the products are formed *via* a relatively long-lived radical anion. However, magnesium reacts with pentachloropyridine to give tetrachloro-4-pyridylmagnesium halide almost exclusively,[22] and it has very recently been shown that electroreduction of pentachloropyridine leads to tetrachloro-4-pyridyl derivatives,[23] whereas the reaction with copper occurred mainly at the 3-position.

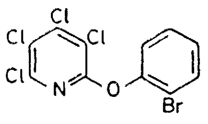
We have investigated the possible use of intramolecular Ullmann reactions for preparing some tricyclic compounds, similar to those synthesised photochemically.[24,25] These experiments met with limited success, but they provided further information on the reaction mechanisms. The starting materials for this study were prepared by nucleophilic substitution in a pentahalogenopyridine by the appropriate *o*-halogenophenol, -thiophenol, or -aniline. The position(s) of substitution were determined by ^{13}C (or ^{19}F where appropriate) n.m.r. spectroscopy [1] and/or by reactions with 4-bromotetrachloropyridine, where the bromine acted as a ' marker ' (*cf.* ref. 24). Details are given in the Experimental section, together with a note of the preparation and properties of related new compounds, prepared but not used in this study.



(16) X = O, R = Br
(18) X = O, R = Cl
(19) X = S, R = Br
(21) X = S, R = Cl
(22) X = NH, R = Br
(23) X = O, R = H



(17) X = O
(20) X = S



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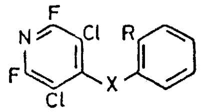
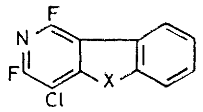
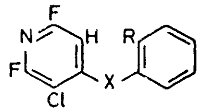


(25) X = S, R = Br
(28) X = S, R = H
(30) X = O, R = Br
(31) X = O, R = Cl



(26) X = S
(32) X = O



(27) X = S, R = Cl
(29) X = S, R = H
(33) X = O, R = Cl

The reaction of the *o*-bromophenoxy-derivative (16) with copper in DMF gave the benzofuranopyridine (17) in 41% yield, accompanied by the *o*-chlorophenoxy-derivative (18) (16%). Similarly, the sulphur analogue (19) gave compounds (20) (28%) and (21) (6%). The corresponding amine (22) gave only tars. The formation of compounds (18) and (21) suggested that some reaction had occurred initially at the pyridyl ring, leading to the formation of copper(I) chloride, which was then available for halogen exchange. The *o*-chlorophenoxy-compound (18) reacted with copper in DMF only very slowly, giving the cyclised product (17) in 4% yield after 10 h. The 2-(*o*-bromophenoxy)-compound (24) gave only tars. Possibly in this case it is unfavourable for the *o*-bromophenoxy-group to adopt the conformation necessary for cyclisation, and copper could react at the 3- as well as the 5-position of the pyridyl group.

Further confirmation of reaction at the pyridyl ring came from experiments on dichlorodifluoro-derivatives. The sulphide (25) gave the cyclised product (26) (24%) and compound (27) (35%) in which both reduction at the pyridyl group and halogen exchange at the phenyl group had occurred.* Compound (28), lacking the *o*-halogen, gave the reduced product (29) in 25% yield. The fact that no cyclised product (26) was obtained again tended to rule out a radical intermediate, since the analogous photocyclisation, which is believed to involve this intermediate, proceeds in good yield.[24]

The results of experiments with the ethers (30) and (31) are summarised in Table 3. These experiments were complicated by replacement of fluorine atoms by dimethylamino-groups during prolonged heating in DMF (*cf.* ref. 26). However, the pattern was again similar, with initial reaction at the pyridine leading to reduction, cyclisation, and halogen exchange.

TABLE 3

Reactions of 4-aryloxypolyhalogenopyridines (30) and (33) with copper in DMF

Starting material	Reaction time (h)	Products (yield %) (32)	(31)	(33)	Starting material (%)
(30)	5	15	55	*a*	*a*
(30)	8	34	36	*a*	17 [b]
(30)	13	1	31 [b]	7 + 34 [b]	*a*
(33)	13	27	13		12

[a] Not observed. [b] One F replaced by NMe_2: see text and Table 4.

We suggest that the reactions with copper of the substituted tetrahalogenopyridines, like those of the pentahalogenopyridines, proceed by initial formation of pyridylcopper intermediates, although again the possibility of an electron transfer pathway must be considered.

EXPERIMENTAL

All n.m.r. spectra were recorded in deuteriochloroform unless otherwise stated. For ^1H spectra $SiMe_4$ was used as internal reference: for ^{19}F spectra trifluoroacetic acid was used as external reference. For ^{13}C spectra, see ref. 1. Mass spectroscopic data refer to ions containing ^{35}Cl and/or ^{79}Br only; the isotopic distribution for the composition given in parentheses was observed.

Dimethylformamide (DMF) was a commercial grade, specified as 99+%, stored over 4A molecular sieve. The use of less pure material led to increased side-reactions involving replacement of halogens by dimethylamino-groups. Light petroleum refers to the fraction b.p. 60—80 °C.

Pentachloropyridine and 3,5-dichlorotrifluoropyridine were gifts from I.C.I. Ltd., Mond Division. The other pentahalogenopyridines,[27] pentachloroiodobenzene,[28] and trichloro-5-iodothiophen [28] were prepared according to the references cited.

Reactions of Pentachloropyridine with Nucleophiles.—A typical experiment is described. The following compounds were prepared by similar experiments: 2- and 4-(o-*chlorophenoxy*)*tetrachloropyridine* (18), 2- and 4-(*o*-bromoanilino)-tetrachloropyridine (22), 2- and 4-(p-*bromoanilino*)-*tetrachloropyridine*, 2- and 4-(o-*chloroanilino*)*tetrachloropyridine*, 4-(2,4,6-*tribromoanilino*)*tetrachloropyridine*, 4-(o-*bromothiophenoxy*)*tetrachloropyridine* (19), and 4-(o-*chlorothiophenoxy*)*tetrachloropyridine* (21). The yields and properties of these compounds are recorded in Table I.† A mixture of pentachloropyridine (5.0 g, 0.02 mol), *o*-bromophenol (3.45 g, 0.02 mol), anhydrous sodium carbonate (2.29 g), and DMF (20 ml) was stirred under reflux during 3 h. The mixture was cooled, poured into water (250 ml), and extracted with chloroform (3 × 75 ml). The combined extracts were dried ($MgSO_4$) and evaporated (Büchi) and adsorbed on silica. Chromatography on silica (gradient elution with chloroform and light petroleum) gave successively 2-(o-*bromophenoxy*)*tetrachloropyridine* (24) and 4-(o-*bromophenoxy*)*tetrachloropyridine* (16), whose yields and properties are recorded in Table I.†

Reactions of 3,5-*Dichlorotrifluoropyridine with Nucleophiles.*—The reactions were carried out by a procedure similar to that for pentachloropyridine, except that the nucleophile was added at room temperature (exothermic reaction in some cases) to the reaction mixture, which was then stirred at room temperature for 1 h before being heated at 100–120 °C for 1 h. The yields and properties of the resulting compounds, *viz.* 4-(o-*bromophenoxy*)-3,5-*dichloro*-2,6-*difluoropyridine* (30), 4-(o-*chlorophenoxy*)-3,5-*dichloro*-2,6-*difluoropyridine* (25), and 4-(o-*chlorothiophenoxy*)-3,5-*dichloro*-2,6-*difluoropyridine* are recorded in Table II.†

Intermolecular Ullmann Reactions.—The general procedure for reaction and work-up was as follows. A suspension of the polyhalogeno-compound (6—20 mmol) and copper bronze (1—5 equiv.) in DMF (10—20 ml) was stirred under reflux during the time required. The mixture was cooled and poured into a dilute solution of ammonium hydroxide and ammonium chloride in water (200—300 ml). The mixture was filtered. The filter was washed well with chloroform (*ca.* 200 ml) and the filtrate was extracted with chloroform (3 × 75 ml). The combined chloroform solutions were washed with water (4 × 150 ml), dried ($MgSO_4$), reduced to a small volume (Büchi), and adsorbed on silica for chromatography (silica column, gradient elution with light petroleum and chloroform). The conditions used in, and the products from, the experiments are summarised below and in Table 1.

(a) Pentachloroidobenzene (10 mmol) and copper bronze (50 mmol) gave decachlorobiphenyl (81%), m.p. 308—309 °C (lit.,[10] m.p. 309 °C) identical (i.r.) to an authentic sample.

(b) Trichloro-5-iodothiophen (10 mmol) and copper bronze (50 mmol) gave hexachloro-2,2′-bithienyl (75%), m.p. 187—189 °C (lit.,[28] m.p. 189.5—190 °C), M^+ at m/e 370 (Cl_6).

(c) Tetrachloro-4-iodopyridine (5.8 mmol) and copper bronze (42 mmol) gave, in order of elution, (i) pentachloropyridine (4%), (ii) 2,3,5,6-tetrachloropyridine (22%), and (iii) octachloro-4,4′-bipyridyl (52%). The products were identified by comparison with authentic specimens.

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* The ^1H n.m.r. spectrum of compound (27) showed a doublet, assigned to the proton on the pyridyl group, at remarkably high field: τ 4.1. Presumably the preferred conformation of the compound is such that the proton concerned is located within the shielding cone of the phenyl group. The i.r. spectra of this and related compounds also showed a peak at *ca.* 3 100 cm^{-1}.

† Tables I, II, and III are deposited in Supplementary Publication No. SUP 22751 (5 pp). For details see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1979, Index issue.

(d) Tetrachloro-5-iodopyridine (3.3 mmol) and copper bronze (16.8 mmol) gave, in order of elution, (i) pentachloropyridine (trace), (ii) 2,3,4,6-tetrachloropyridine (3%), identified by comparison with an authentic specimen, and (iii) *octachloro*-3,3′-*bipyridyl* (71%), m.p. 148—149 °C (from light petroleum), M^+ at m/e 428 (Cl$_8$) (Found: C, 28.1; N, 6.5. $C_{10}Cl_8N_2$ requires C, 27.8; N, 6.5%).

(e) The experiments on reactions of 4-bromotetrachloropyridine with copper are summarised in Table 1. Octachloro-4,4′-bipyridyl and the tetrachloropyridines were identified by comparison with authentic specimens. The unidentified octachlorobipyridyl (possibly the 3,4′-isomer) had m.p. 204—205 °C (from light petroleum), M^+ at m/e 428 (Cl$_8$).

TABLE 4

Intramolecular Ullmann and related reactions

Starting material [mmol]	Copper bronze (mmol)	DMF (ml)	Time (h)	Products [a]	Yield (%)	M.p. (°C) [lit. m.p.]
4-(*o*-Bromophenoxy)tetrachloropyridine (16). [5.2]	26	15	6	4-(*o*-Chlorophenoxy)tetrachloropyridine (18)	16	135—136 [135—136] [b]
				1,3,4-Trichlorobenzo[*b*]furano[3,2-*c*]pyridine (17)	41	127 [130] [25]
4-(*o*-Chlorophenoxy)tetrachloropyridine (18), [10]	50	20	10	Starting material	4	
				1,3,4-Trichlorobenzo[*b*]furano[3,2-*c*]pyridine (17)	4	127—128 [130] [25]
4-(*o*-Bromothiophenoxy)tetrachloropyridine (19), [12.5]	62.5	10	5	4-(*o*-Chlorothiophenoxy)tetrachloropyridine (21)	14	123—125 [123—125] [b]
				1,3,4-Trichlorobenzo[*b*]thieno[3,2-*c*]pyridine (20)	25	177—178 [185] [25]
4-(o-Bromophenoxy)-3.5-dichloro-2.6-difluoropyridine (30), [8.5]	42	20	13	4-(*o*-Chlorophenoxy)-3,5-dichloro-2,6-difluoropyridine (31)	7	54—56 [54—56] [c]
				4-*Chloro*-1,3-*difluorobenzo*[b]*furano*-[3,2-c]*pyridine* (32)	1	117—118
				4-(*o-Chlorophenoxy*)-3,5-*dichloro*-2-*dimethylamino*-6-*fluoropyridine*	34	94—95
				4-(o-*Chlorophenoxy*)-3-*chloro*-2-*dimethylamino*-6-*fluoropyridine*	31	95—96
4-(*o*-Chlorophenoxy)-3,5-dichloro-2.6-difluoropyridine (31), [10]	50	10	13	Starting material	12	
				4-Chloro-1,3-difluorobenzo[*b*]furano[3,2-*c*]pyridine (32)	27	117—118
				4-(o-*Chlorophenoxy*)-3-*chloro*-2,6-*difluoropyridine* (33)	13	110—112
				4-(o-Chlorophenoxy)-3,5-dichloro-2-dimethylamino-6-fluoropyridine	Trace	
4-(*o*-Bromothiophenoxy)-3,5-dichloro-2,6-difluoropyridine (25), [2.7]	13.5	10	10	Starting material	7	
				4-Chloro-1,3-difluorobenzo[*b*]thieno[3,2-*c*]pyridine (26)	24	158—159 [159] [25]
				4-(o-*Chlorothiophenoxy*)-3-*chloro*-2,6-*difluoropyridine* (27)	35	80—81
3,5-Dichloro-2,6-difluoro-4-(thiophenoxy)pyridine (28), [10]	50	10	5	Starting material	20	
				3-*Chloro*-2,6-*difluoro*-4-*thiophenoxy*)*pyridine* (29)	35	76—77

[a] In order of elution. In each case intractable oils followed the products listed. [b] This work: see Table I.* [c] This work: see Table II.* [d] For conditions for other experiments, see Table 3. A product from the 8 h reaction was 4-(o-*bromophenoxy*)-3,5-*dichloro*-2-*dimethylamino*-6-*fluoropyridine* (17%), m.p. 74—75 °C.

(f) Pentachloropyridine (20 mmol) and copper bronze (20 mmol) gave, after 20 h reaction, a liquid mixture which was analysed by g.l.c., and shown to contain 2,3,4,5-tetrachloropyridine (2%), 2,3,4,6-tetrachloropyridine (22%), 2,3,5,6-tetrachloropyridine (3%), pentachloropyridine (30%), and tetrachloro-4-dimethylaminopyridine (13%).

(g) 3,5-Dichlorotrifluoropyridine (20 mmol) and copper bronze (100 mmol) gave, after 5 h reaction, 3,3′-*dichlorohexafluoro*-5,5′-*bipyridyl* (15%), m.p. 78—79 °C (from aqueous ethanol), ^{19}F δ −14.5 (m, 2 F), −13 (dd, J 21 Hz and 8.5 Hz, 2 F), and +13 p.p.m. (ddd, J 21 Hz, 14.5 Hz and 2.5 Hz); M^+ at m/e 332 (Cl$_2$) (Found: C, 36.0; N, 8.4. $C_{10}Cl_2F_6N_2$ requires C, 36.1; N, 8.4%).

Reaction of 4-*Bromotetrachloropyridine with Copper*(I) *Chloride*.—A mixture of 4-bromotetrachloropyridine (5 mmol), copper(I) chloride (5 mmol), and DMF (10 ml) was stirred under reflux during 30 min and worked up as for the Ullmann reactions described above, to give pentachloropyridine (95%), a mixture (trace) of starting material and pentachloropyridine, and octachloro-4,4′-bipyridyl (trace).

Reactions of Tetrachloro-4-*pyridylcopper*.—Solutions (*ca.* 0.5M) of tetrachloro-4-pyridylcopper in tetrahydrofuran (THF) were prepared from pentachloropyridine *via* tetrachloro-4-pyridylmagnesium chloride and copper(I) iodide.[16] In the case of reaction (d) 4-bromotetrachloropyridine was used as starting material, since the use of pentachloropyridine led to conversion of 4-bromotetrachloropyridine into pentachloropyridine by the chloride ions produced.

(a) Solvent was evaporated under reduced pressure under nitrogen from a solution (100 ml) of tetrachloro-4-pyridylcopper in THF. DMF (100 ml) was added. The solution was cooled to −10 °C as benzoyl chloride (10 ml) was added dropwise. The solution was heated under reflux during 30 min and worked up as described for the Ullmann reactions to give, in order of elution, (i) 2,3,5,6-tetrachloropyridine (0.97 g, 9%) and (ii) 4-benzoyltetrachloropyridine (11.45 g, 72%), m.p. 133—135 °C (lit.,[30] m.p. 134—135 °C), $\nu_{max.}$ 1 680 cm^{-1}.

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* See note † on p. 1685.

(b) Solvent was evaporated from a solution (100 ml) of tetrachloro-4-pyridylcopper in THF. *p*-Xylene (115 ml) was added and the mixture was heated under reflux during 21 h, then allowed to cool. Benzoyl chloride (7.0 g) was added, and the mixture was stirred during 1 h and worked up as in (a) to give the products listed in Table 2, including the mixture of heptachlorobipyridyls, τ 1.9(s), 2.3(s); M^+ at m/e 394 (Cl_7).

(c) The experiment was carried out as described in (a), except that the solution in DMF was heated under reflux during 1 h *before* the addition of benzoyl chloride. The products are listed in Table 2.

(d) The solvent in a 0.33 M-solution (30 ml) of tetrachloro-4-pyridylcopper in THF was replaced by DMF (30 ml). 4-Bromotetrachloropyridine (2.93 g, 10 mmol) was added and the resulting mixture was stirred under reflux during 1 h and worked up as in (a) to give the products listed in Table 2.

Intramolecular Ullmann and Related Reactions.—The reactions and work-up were carried out as described for the intermolecular Ullmann reactions.

Details of the conditions and the products are given in Tables 3 and 4. Known compounds were identified by comparison with authentic specimens. Spectroscopic and analytical data for the new compounds are recorded in Table III.†

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* See note † on p. 1685.

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