Polyhalogenoaromatic Compounds. Part 41.[1] Photochemical Dehalogenation and Arylation Reactions of Polyhalogenoaromatic and Polyhalogenoheteroaromatic Compounds

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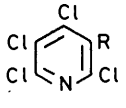
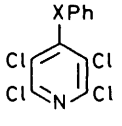
Photolysis of pentachloro- and pentabromo-pyridine in diethyl ether or methanol leads to loss of β-halogen. A product (9) derived from attack on diethyl ether was also identified. 4-Bromotetrachloropyridine also undergoes loss of bromine and tetrachloro-4-iodopyridine loses iodine exclusively. Photodehalogenation of some perhalogenothiophens, tetrachloropyrimidine, and hexachlorobenzene is also described. Photolysis of pentachloroiodobenzene, tetrachloroiodopyridines, and trichloro-5-iodothiophen in benzene gives the corresponding polychloroaryl- or polychloroheteroaryl-benzenes.

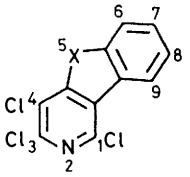
Photolysis of tetrachloro-4-(phenylthio)pyridine (3) gives 1,3,4-trichloro[1]benzothieno[3,2-*c*]pyridine (6), and the analogous perchloro(phenylthio)pyridine (37) gives the corresponding perchlorobenzothienopyridine (61). The scope of this type of photocyclisation has been explored; starting materials investigated include various arylthiopolyhalogenopyridines, some arylamino- and aryloxy-tetrachloropyridines, and 4-anilinotrichloropyrimidine.

THE broad outlines of the photochemical reactions of halogenoaromatic compounds are related to the relative strength of the bonds involved: Ph–F > Ph–H > Ph–Cl > Ph–Br > Ph–I. Thus, fluoroaromatic compounds can undergo a variety of fascinating photoisomerisation and photoaddition reactions without the loss of fluorine (see ref. 2 for recent examples). Photoreactions of the other halogenoaromatic compounds, on the other hand, almost invariably involve loss of halogen from the ring giving rise to aryl radicals which may be exploited in synthesis. Moreover, such photodehalogenation reactions are of importance in the environmental degradation of compounds such as polyhalogenobiphenyls [3] and polyhalogeno-pesticides and -herbicides.[4]

We have shown that photolysis of pentachloropyridine leads to loss of a chlorine atom in the 3-position and that the resulting radical can abstract a hydrogen atom from a suitable solvent to give 2,3,4,6-tetrachloropyridine (1),







(1) R = H
(2) R = Ph
(9) R = CH(Me)OEt
(10) R = Br
(23) R = I

(3) X = S
(4) X = O
(5) X = NH
(55) X = CH_2

(6) X = S
(7) X = O
(8) X = NH

or attack benzene to give tetrachloro-5-phenylpyridine (2).[5] Photolysis of substituted tetrahalogenopyridines, *e.g.* (3)—(5), gave tricyclic compounds, *e.g.* (6)—(8), by intramolecular arylation.[6] We now report experiments on the regioselectivity of dehalogenation in various polyhalogenoaromatic systems and on inter- and intramolecular arylation by the radicals so produced, including full details of the results published in preliminary form.[6]

RESULTS AND DISCUSSION

Our experiments on the photodehalogenation of some pentahalogenopyridines are summarised in Table 1. Irradiation of pentachloropyridine under various conditions failed to improve on our earlier maximum yield of 2,3,4,6-tetrachloropyridine (1) (43%),[5] but revealed that reactions in diethyl ether gave an additional product (9) in 8% yield. Its formation involved coupling of tetrachloro-3-pyridyl radicals with radicals derived from hydrogen abstraction from the solvent, but the selectivity of the coupling (no bipyridyls were observed) requires explanation. Analogous products have been observed in the photolysis of pyridines in the presence of ether and amines,[7] and further examples are described below. U.v.-[8] or γ-irradiation [9] of polychlorobenzenes in alcohols give products of this type. Photolysis of pentachloropyridine in diethyl ether in the presence of triethylamine (*cf. e.g.* ref. 10) gave much triethylammonium chloride, but only small yields of all three tetrachloropyridines. We found that photolysis of pentachloropyridine in bromoform was very slow, and after 196 h gave 3-bromotetrachloropyridine (10) in only 8% yield, together with a trace of 2,3,4,6-tetrachloropyridine (1).

In the case of 4-bromotetrachloropyridine (11) in diethyl ether the photo-fission of the comparatively weak C–Br bond was competitive with that of the photolabile C-3–Cl bond, giving 2,3,5,6-tetrachloropyridine (12) (17%) and 4-bromo-2,3,6-trichloropyridine (13) (6%). In tetrachloro-4-iodopyridine (14), photo-cleavage of the C–I bond giving 2,3,5,6-tetrachloropyridine (12) in high yield was the only reaction observed, while irradiation of pentabromopyridine in diethyl ether gave 2,3,4,6-tetrabromopyridine (15) (12%) and 2,4,5-tribromopyridine (16) (3%). We are aware of no other authenticated example of photochemical cleavage of a 2-pyridyl–halogen bond, although it may also have

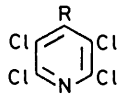
TABLE 1

Photodehalogenation of pentahalogenopyridines

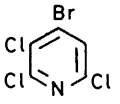
Starting material	Lamp [a]	Filter [b]	Solvent	Time/h	Starting material recovered (%)	Products isolated [yield %]
Pentachloropyridine	A	P	Et_2O	46	50	(1), [40]; (9), [8]
	A	Q	Et_2O	28	13	(1), [40]
	A	Q	Et_2O [c]	31	60	(1), [4]; (12), [1]; 2,3,4,5-tetrachloropyridine, [4]; (9) and an isomer, [7]
	B	P	MeOH [d]	139	16	(1), [40]; (12), [2]; 2,3,4,5-tetrachloropyridine, [7]; unidentified, [*ca.* 35]
	A	Q	MeOH	14	3	(1), [20]; (12), [trace]; 2,3,4,5-tetrachloropyridine, [trace]
	B	P	MeCN	139	96	(1), [4]
	B	P	CH_2Cl_2	139	95	(1), [5]
	C	P	$CHBr_3$	196	91	(1), [1]; (10), [8]
4-Bromotetrachloropyridine (11)	C	P	Et_2O	71	49	(12), [17]; (13), [6]
Tetrachloro-4-iodopyridine (14)	B	P	Et_2O	19	0	(12), [87]
Pentabromopyridine	C	P	Et_2O	41	13	(15), [12]; (16), [3]

[a] A, Hanovia medium-pressure mercury; B, Rayonet photochemical mini-reactor, 300-nm medium-pressure mercury lamp; C, Hanau medium-pressure mercury. [b] P, Pyrex; Q, quartz. [c] Containing 1 equiv. Et_3N. [d] EtOH and Pr^iOH gave mainly unidentified products.

accompanied the photocyclisation of compound (42) described below (see Table 4). Irradiation of 3,5-dichlorotrifluoropyridine gave a mixture of products, probably formed by photo-isomerisation as well as dehalogenation, which was not analysed.



(11) R = Br
(12) R = H
(14) R = I
(22) R = Ph
(47) R = OC_6Cl_5
(52) R = PPh_2
(54) R = $NHCH_2CH=CH_2$



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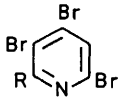
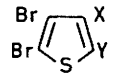


(15) R = Br
(16) R = H

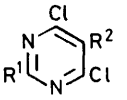
The results of our experiments on the photodehalogenation of two perhalogenothiophens, tetrachloropyrimidine, and hexachlorobenzene are summarised in Table 2.

Tetrachlorothiophen was photo-stable to the conditions used, but tetrabromothiophen gave 2,3,4-tribromothiophen (17) (58%) and 2,3,5-tribromothiophen (18) (20%). The greater lability of the Br-2 is in line with the observations recently reported for the monobromothiophens.[11]

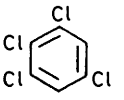
Photolysis of tetrachloropyrimidine in diethyl ether gave, remarkably, a mixture (35% yield) of isomeric ethers as the only isolable products, besides starting material (46%). The mixture was inseparable, but its ^{13}C spectrum was most consistent with the presence of compounds (19) and (20), although the signal for C-5 in (19) was at unexpectedly low field (see Experimental section for assignments).



(17) X = Br, Y = H
(18) X = H, Y = Br



(19) R^1 = Cl, R^2 = CH(Me)OEt
(20) R^1 = CH(Me)OEt, R^2 = Cl
(29) R^1 = H, R^2 = Br
(30) R^1 = Cl, R^2 = Br
(31) R^1 = H, R^2 = Ph
(32) R^1 = Cl, R^2 = Ph



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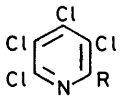


(25) R = I
(26) R = Ph
(42) R = SPh
(46) R = OPh
(50) R = NHPh

Plimmer has reported that photolysis of hexachlorobenzene in hexane gives pentachlorobenzene and a tetrachlorobenzene tentatively identified as the 1,2,3,5-

TABLE 2

Photodehalogenation of perhalogenothiophens, tetrachloropyrimidine, and hexachlorobenzene in diethyl ether

Starting material	Lamp [a]	Filter [b]	Time/h	Starting material recovered (%)	Products isolated, [yield %]
Tetrachlorothiophen	C	Q	30	100	
Tetrabromothiophen	B	P	26	22	(17), [58]; (18), [20]
Tetrachloropyrimidine	C	Q	72	46	(19) + (20), [35]
Hexachlorobenzene	C	Q	17	43	pentachlorobenzene, [47]; (21), [10]

[a,b] As for footnotes to Table 1.

isomer (21).[8] We have obtained similar results in diethyl ether, and have confirmed the identity of the tetrachlorobenzene by g.l.c. and ^{1}H n.m.r. spectroscopy.

Photolysis of iodoaromatic compounds in aromatic solvents has long been recognised as a useful method of preparing biaryls. In many cases yields are surprisingly high, possibly as a result of a mechanism involving charge-transfer complexation.[12] On the other hand, it has recently been reported that photolysis of pentachloroiodobenzene in benzene gives 2,3,4,5,6-pentachlorobiphenyl in only 22% yield.[13] However, we have obtained high yields from the same reaction, and from analogous reactions of polychloroiodohetarenes, as

As previously reported,[6] the 4-substituted tetrachloropyridines (3)—(5) may be photocyclised to the tricyclic compounds (6)—(8). Further studies have shown that reactions of this type have a wide scope, though some limitations have been encountered. The results for a series of arylthiohalogenopyridines are summarised in Table 4. The cyclisation of tetrachloro-4-(phenylthio)-pyridine (3) is envisaged as proceeding *via* loss of 3-Cl followed by intramolecular homolytic arylation as represented in the Scheme. The elemental analysis and spectroscopic properties of the product (see Table 6) are consistent with the structure (6).

The analogous cyclisation of the α-naphthylthio-

TABLE 3

Biaryls from photolysis of polychloroiodoaromatic compounds in benzene

Iodo-compound	Lamp [a]	Time of photolysis/h	Starting material recovered (%)	Biaryl, [yield %]	M.p. °C (lit. M.p.)
C_6Cl_5I	C	50	0	C_6Cl_5Ph, [95]	125—126 (124—125) [b]
6-I-C_5Cl_4N (25)	B	64	47	6-Ph-C_5Cl_4N (26), [40]	111—112 (113—114) [c]
5-I-C_5Cl_4N (23)	B	90	0	5-Ph-C_5Cl_4N (2), [86]	98 (98) [d]
4-I-C_5Cl_4N (14)	C	25	26	4-Ph-C_5Cl_4N (22), [74]	138—139 (137—138) [e]
5-I-C_4Cl_3S (27)	A	9	0	5-Ph-C_4Cl_3S (28), [98]	62—63 (63—64) [f]

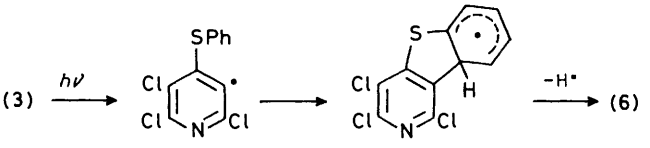
[a] As for footnote to Table 1; all with Pyrex filter. [b] O. Hutzinger, S. Safe, and V. Zitko, *Bull. Environ. Contam. Toxicol.*, 1971, **6**, 209. [c] A. Roedig, H.-A. Reuk, V. Schaal, and D. Scheutzow, *Chem. Ber.*, 1974, **107**, 1136. [d] Ref. 5. [e] R. A. Fernandez, H, Heaney, J. M. Jablonski, K. G. Mason, and T. J. Ward, *J. Chem. Soc.* (*C*), 1969, 1908. [f] M. R. Smith, M. Rahman, and H. Gilman, *Organomet. Chem. Synth.*, 1971, 295.

isted in Table 3, although in some cases conversion was incomplete even after prolonged irradiation. In order to obtain high yields and significant conversions it was essential to carry out the reactions in the presence of sodium thiosulphate, to remove the iodine formed.

5-Phenylpyrimidines have recently been obtained in good yield by photolysis of 5-iodopyrimidines in benzene.[14] We have similarly obtained the corresponding 5-phenylpyrimidines (31) and (32) from the 5-bromopolychloropyrimidines (29) and (30), although in the former case the conversion was low. Compound (30) gave no 2-phenyl derivative in the product, in contrast to the photolysis of tetrachloropyrimidine described above.

The starting materials for studies on the preparation of tricyclic systems by intramolecular arylation were the substituted pyridines and pyrimidine (3)—(5) and (33)—(57). Most of these were prepared by nucleophilic substitution of the appropriate pentahalogenopyridine. We have described previously the synthesis of compounds (3), (40)—(45), (50),[15] (4) and (46),[16] and (38).[17] Compounds (5) and (42),[18] (51),[19] (52) and (53),[20] (55),[21] and (56) [22] have been reported by others. In most cases the orientation of the substituent in the new compounds was established by the use of 4-bromotetrachloropyridine (10),[23] where the bromine atom served as a marker; use was also made of ^{13}C (ref. 24) and ^{19}F n.m.r. spectroscopy. The bipyridyl (57) was obtained by the reaction of hexachloro-5,5′-dilithio-4,4′-bipyridyl [25] with iodine.

compound (33) would give the naphthothienopyridine (58). However, in this case attack at the 8-position of the naphthyl group could give the naphthothiopyranophenanthrene (59).* The product from the photolysis of (33) was so sparingly soluble in organic solvents that even using Fourier-transform only a very weak ^{1}H



SCHEME

n.m.r. spectrum could be obtained. The spectrum was more consistent with structure (58) in view of the low-field doublets, attributed to H-5 and H-6.

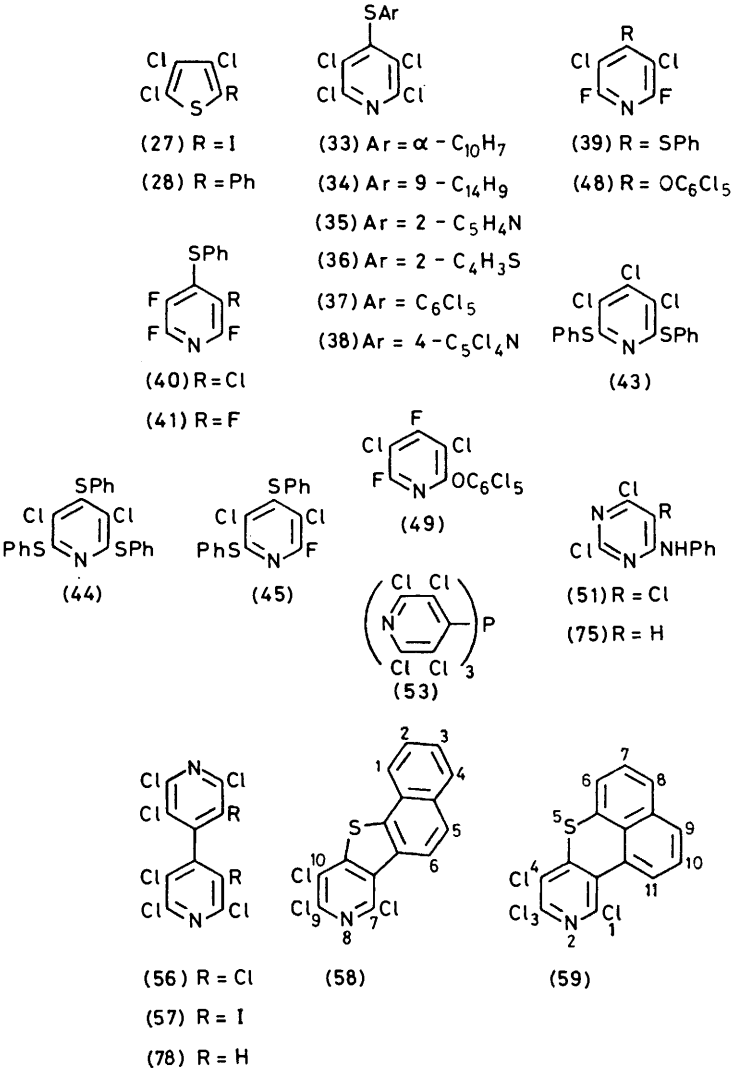
In the case of the 9-anthrylthio-compound (34) only attack at a *peri*-position was possible but no cyclised product was isolated.

A modest yield of cyclised product (60) was obtained from the pyridylthio-derivative (35). The reaction in this case was complicated by the formation of a solid of high m.p., containing chloride ions, whose mass spectrum indicated that it was polymeric. The thienylthio-derivative (36) was surprisingly photostable and

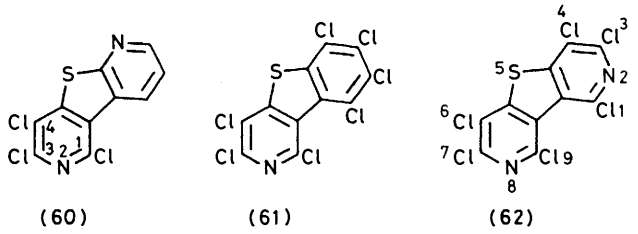
* Various 1-(2-halogenopenyl)naphthalenes prefer to react on photolysis in benzene by cyclisation in the *peri*-position, although mixtures of products are obtained (W. A. Henderson and A. Zweig, *J. Amer. Chem. Soc.*, 1967, **89**, 6778; W. A. Henderson, R. Loprets, and A. Zweig, *J. Amer. Chem. Soc.*, 1969, **91**, 6049).

gave no cyclised product. In 1965, Kharasch and Ariyan reported that photolysis of di(pentachlorophenyl) sulphide gave octachlorodibenzothiophen,[26] but no analogous cases have since been described, although solvent, and the isolation of pentachloropyridine indicates that some homolysis of C–S bonds occurs.

Photolysis of the dichlorodifluoro-compound (39) gave the expected product (63) in good yield. The



examples of intramolecular homolytic arylation with displacement of halogen are known.[27] We can now report the synthesis of the heptachlorobenzothienopyridine (61) and the hexachlorodipyridothiophen (62) by



this type of reaction. The solvent for these photolyses was carbon tetrachloride; the isolation of hexachloroethane from the products of these reactions is consistent with radical intermediates abstracting chlorine from the chlorotrifluoro-analogue (40) gave the product (64) in which Cl-3 rather than F-5 had been lost, as expected because of the greater strength of the C–F bond. It was thus not unexpected that tetrafluoro-4-(phenylthio)-pyridine (41) was stable to irradiation through Pyrex, and only a little decomposition was observed after prolonged irradiation through quartz. Indeed, we have never observed photolytic loss of fluorine from a pyridine ring, although Russian workers have recently reported the photocyclisation of tetrafluoro-4-(*N*-methylanilino)-pyridine to the carboline (65).[28]

The photolyses of compounds (42) and (43) demonstrate that cyclisation involving α-arylthio-groups can occur. It is of interest that in the case of the 6-(phenylthio)-compound (42) irradiation through Pyrex gave the cyclised product (66) in high yield *via* loss of Cl-5, without observable loss of Cl-3; the concepts discussed recently

TABLE 4

Photolysis of arylthiohalogenopyridines

Starting material	Solvent	Lamp [a] (filter) [b]	Time/h	Cyclised product	Yield (%)	Other products [%]
(3)	EtOH	C(P)	24	(6)	68	
(33)	THF	C(P)	3	(58) [c]	83	starting material [8]
(34)	THF	C(P)	up to 65	*d*		starting material + tar
(35)	THF + EtOH	C(P)	6	(60) [e]	13	pentachloropyridine [39], polymer [36]
(36)	THF or EtOH	C(P) or D(Q) [g]	up to 115	*d*		starting material + tar
(37)	CCl_4	D(Q) [g]	40	(61)	36	pentachloropyridine (trace), CCl_3CCl_3
(38)	CCl_4	D(Q) [g]	24	(62)	44	pentachloropyridine [6.5], starting material [15]
(39)	EtOH	C(P)	24	(63)	83	
(40)	EtOH	C(P)	20	(64)	48	starting material [40]
(41)	EtOH	C(P) or A(Q)	24	*d*		starting material + unidentified
(42)	EtOH	C(P)	24	(66)	87	
	EtOH	A(Q)	24	(66)	34	a dichloro[1]benzothieno[2,3-*b*]pyridine [38] [h]
(43)	EtOH	C(P)	24	(68)	26	
	EtOH	A(Q)	24	(68)	40	
(44)	EtOH	C(P)	24	(69)	30	
(45)	EtOH	C(P)	24	(70)	66	

[a,b] As for footnotes to Table 1. [c] Product partly precipitated during irradiation; chromatography on alumina. [d] Not obtained. [e] Isolated by h.p.l.c. [f] See text. [g] Hanovia low-pressure mercury. [h] Possibly (67): see Table 6.

by Schultz *et al.*[29] could perhaps account for the observed regiospecificity. On irradiation of compound (42) through quartz, some loss of a second chlorine was observed, but the chemical shift of the pyridine ring proton in the product (τ 1.50) suggests that it is located at an α- rather than a β-position (*cf.* ref. 30). In the photolysis of compound (43) no cyclisation involving both phenylthio-groups was observed.

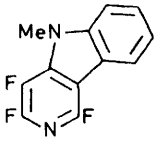
In the cases of compounds (44) and (45), cyclisation of the 2- and the 4-phenylthio-groups are in competition. The product from irradiation of compound (44) was identical with the product from reaction of compound (6) with an excess of thiophenoxide, and therefore had structure (69). Reaction of the product from irradiation of compound (45) with thiophenoxide also gave compound (69). Thus, in both cases cyclisation of the 4-phenylthio-group is preferred. Reaction of compound (63) with one molar equivalent of thiophenoxide gave a product which differed from the product of irradiation of (45). In the ^{19}F n.m.r. spectrum of compound (63) the signal at δ 1.4 p.p.m. is assigned to F-1 and that at −6.8 p.p.m. to F-3 [*cf.* compound (39), δ_F −9.2 p.p.m.]. The product from irradiation of compound (45) had δ_F −9.5 p.p.m. and is therefore assigned structure (70); the product from reaction of compound (63) with thiophenoxide had δ_F −1.2 p.p.m. and is assigned structure (71).

In a less extensive study of aryloxy- and arylamino-polyhalogenopyridines we have observed several analogous photocyclisations. Our results are summarised in Table 5. Photocyclisation of 4-anilinotrichloropyrimidine (51) was also observed, giving the pyrimidoindole (74) in 17% yield, but was accompanied by dechlorination, giving 4-anilino-2,6-dichloropyrimidine (75).

Preliminary experiments on the photolyses of some related compounds failed to give cyclised products. In

(63) R = Cl

(64) R = F



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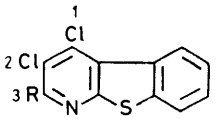


(66) R = Cl

(67) R = H

(68) R = PhS

(69) R = PhS

(70) R = F

the cases of the phosphines (52), its *P*-oxide, and (53), and 4-allylaminotetrachloropyridine (54), only multicomponent mixtures of uncharacterised decomposition products were obtained. The main product from photo-

TABLE 5

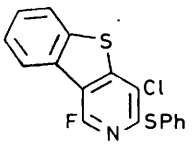
Photolysis of arylamino- and aryloxy-polyhalogenopyridines

Starting material	Solvent	Lamp [a] (filter) [b]	Time/h	Cyclised product	Yield (%)	Other products
(4)	EtOH	C(P)	24	(7)	54	
(46)	THF	C(P)	5	(72)	38	
(47)	CCl_4	D(Q)	148			starting material (quantitative)
(48)	THF	D(Q)	76			multicomponent mixture
(49)	CCl_4	D(Q)	103			starting material (quantitative)
(5)	EtOH	C(P)	24	(8)	79	
(50)	THF	C(P)	24	(73)	12	

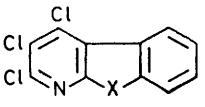
[a,b] As for footnotes to Tables 1 and 4.

lysis of 4-benzyltetrachloropyridine (55) in THF was the tetrahydrofuryl derivative (76).

It was hoped that irradiation of octachloro-4,4'-bipyridyl (56) might give the diazabiphenylene (77) (*cf.* ref. 17). However, photolysis in ethanol resulted in dehalogenation, and the ^{1}H n.m.r. spectrum of the product [τ 2.96(s), 2.90(s), and 1.60(s)] indicated that chlorine had been lost from both α- and β-positions, while starting material was recovered almost quantitatively from irradiation in carbon tetrachloride. In order to ensure loss of halogen from β-positions exclusively, the hexachlorodi-iodobipyridyl (57) was synthesised. Photolysis in diethyl ether gave the hexachlorobipyridyl (78) quantitatively, but photolysis in carbon tetrachloride again gave octachloro-4,4'-bipyridyl (56). Presumably, although the required radical intermediates were formed, steric hindrance presented them from adopting the conformation necessary for cyclisation before they abstracted hydrogen or chlorine from the solvent.

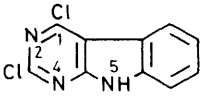


(71)

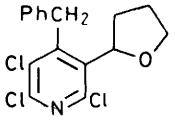


(72) X = O

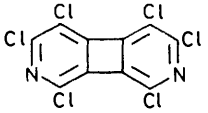
(73) X = NH



(74)



(76)



(77)

EXPERIMENTAL

Photolyses were carried out using the commercial apparatus specified in the footnotes to Table 1. ^{1}H N.m.r. spectra were recorded at 60 or 90 MHz, with tetramethylsilane as internal reference, in deuteriochloroform unless otherwise stated. ^{19}F N.m.r. spectra were recorded using trifluoroacetic acid as external reference. ^{13}C N.m.r. spectra of many of the compounds are recorded in ref. 24. Mass spectra refer to ions containing ^{35}Cl and/or ^{79}Br only; the isotope pattern for the composition given in parentheses was observed. Light petroleum refers to the fraction of b.p. 60—80 °C unless otherwise stated.

Photolysis of Pentahalogenopyridines.—Pentachloropyridine was a gift from I.C.I. Limited, Mond Division; pentabromopyridine,[31] 4-bromotetrachloropyridine,[23] and the tetrachloroiodopyridines [23] were prepared as described in the references cited. Details of the photolyses are given in Tables 1 and 3; photolyses of iodo-compounds were carried out in the presence of solid sodium thiosulphate. The products were worked up by conventional methods and analysed by chromatography on silica and/or by gas chromatography. Known products, *viz.* compounds (1),[5] (2),[5] (10),[23] (12),[30] (15),[32] [τ 2.25(s); $\nu_{max.}$ 3 112 cm^{-1}], (16) [32] [τ 1.56(s) and 2.27(s)], (22) (see Table 3), (24) (see Table 3), and (26) (see Table 3), were identified by comparison with authentic specimens or with literature data. The properties of new compounds were as follows: 1-*ethoxy*-1-(*tetrachloro*-3-*pyridyl*)*ethane* (9), m.p. 84—86 °C (from aqueous ethanol); τ 4.6(q, 1 H), 6.6(q, 2 H), 8.4(d, 3 H), and 8.75(t, 3 H); *m/e* 287 (M^+) (Cl_4) (Found: C, 37.4; H, 3.1; N, 4.8. $C_9H_9Cl_4NO$ requires C, 37.4; H, 3.1; N, 4.85%); 4-*bromo*-2,3,6-*trichloropyridine* (13), m.p. 60—62 °C (from aqueous ethanol); τ 2.45(s); *m/e* 259 (M^+) ($BrCl_3$) (Found: C, 22.5; H, 0.3; N, 5.2. C_5HBrCl_3N requires C, 22.9; H, 0.4; N, 5.4%).

Photolysis of Perhalogeno-pyrimidines, -thiophens, and -benzenes.—Tetrachlorothiophen, tetrabromothiophen, and hexachlorobenzene were commercial materials; trichloro-5-iodothiophen was prepared as described previously; [33] the polyhalogenopyrimidines were a gift from Drs. J. Clark and R. Colman. Details of the photolyses are given in Tables 2 and 3. Compounds (17),[34] (18),[34] (21), (28) (see Table 3), (31),[35] and (32) [35] were identified by comparison with authentic samples or with literature data. The properties of new compounds were as follows: mixture of 1-ethoxy-1-(trichloropyrimidin-5-yl)ethane (19) and 1-ethoxy-1-(trichloropyrimidin-2-yl)ethane (20), an oil; τ 5.0(q) overlapping 5.3(q) (integration 1 : 1), 6.5(dq), 8.5(d), and 8.6(t); δ_C 157.8 [C-2 in (19)], 160.7 [C-4 in (19)], 169.2 [C-5 in (19)], 171.6 [C-2 in (20)], 160.0 [C-4 in (20)], and 127.1 [C-6 in (20); *m/e* 254 (M^+) (Cl_3).*

Reactions of 4-Bromotetrachloropyridine with Thiols.—(*a*) A mixture of 4-bromotetrachloropyridine (2.96 g, 10 mmol), naphthalene-1-thiol [36] (1.6 g, 10 mmol), and pyridine (25 ml) was heated under reflux in a nitrogen atmosphere during 30 min. The resulting mixture was poured into 4M-hydrochloric acid (200 ml). Extraction with chloroform gave *tetrachloro*-4-(1-*naphthylthio*)*pyridine* (33) (3.0 g, 80%), m.p. 140—141 °C (from light petroleum, b.p. 80—100 °C); τ 1.5—1.9 (m, 1 H) and 2.0—2.8 (m, 6 H); *m/e* 373 (M^+) (Cl_4) (Found: C, 47.7; H, 1.9; N, 3.3. $C_{15}H_7Cl_4NS$ requires C, 48.0; H, 1.9; N, 3.7%).

(*b*) An analogous reaction with anthracene-9-thiol [37] gave, after chromatography (silica, carbon tetrachloride), 9,9'-dianthracenyl disulphide (10%), m.p. 218–220 °C (lit.,[38] m.p. 223 °C) and 4-(9-*anthracenylthio*)*tetrachloropyridine* (34) (28%), m.p. 191—192 °C (from light petroleum, b.p. 80—100 °C); τ 1.35—2.7 (m) (Found: C, 53.7; H, 2.1; N, 3.2%; M^+ 422.918 6. $C_{19}H_9Cl_4NS$ requires C, 53.7; H, 2.1; N, 3.3%; *M* 422.920 6).

(*c*) An analogous reaction with thiophen-2-thiol [39] gave *tetrachloro*-4-(2-*thienylthio*)*pyridine* (36) (2.3 g, 70%), m.p. 98—99 °C (from light petroleum, b.p. 100—120 °C); τ 2.4—2.6 (m, 2 H), and 2.9 (dd, 1 H, *J* 6 and 4 Hz) [Found: C, 32.7; H, 1.0; N, 4.2%; M^+ 328.846 7 (Cl_4). $C_9H_3Cl_4NS$ requires C, 32.6; H, 0.9; N, 4.2%; M^+ 328.845 9].

Tetrachloro-4-(2-*pyridylthio*)*pyridine* (35).—A mixture of 4-bromotetrachloropyridine (3.0 g), pyridine-2-thione (1.1 g), potassium carbonate (1.4 g), and acetone (20 ml) was heated under reflux during 2 h. The solvent was evaporated under reduced pressure and the residue was washed with water. Extraction with chloroform and conventional work-up gave *tetrachloro*-4-(2-*pyridylthio*)*pyridine* (1.3 g, 39%), m.p. 121—122 °C (from light petroleum, b.p. 100—120 °C); τ 1.5 (ddd, 1 H, $J_{6.5}$ 5, $J_{6.4}$ 2, $J_{6.3}$ 1.2 Hz; H-6), 2.2 (ddd, 1 H, $J_{4.3}$ 8.5, $J_{4.5}$ 7, $J_{4.6}$ 2 Hz; H-4), 2.6 (dt, 1 H, $J_{3.4}$ 8.5, $J_{3.5}$ 1.3, $J_{3.6}$ 1.2 Hz; H-3), and 2.7 (ddd, 1 H, $J_{5.4}$ 7, $J_{5.6}$ 5,

* See also ref. 24.

$J_{5,3}$ 1.3 Hz, H-5) (Found: C, 36.5; H, 1.2; N, 8.6. $C_{10}H_4Cl_4N_2S$ requires C, 36.8; H, 1.2; N, 8.6%).

Tetrachloro-4-(pentachlorophenylthio)pyridine (37).—A mixture of pentachloropyridine (5.0 g), pentachlorothiophenol (5.64 g), sodium carbonate (2.2 g), and dimethylformamide (50 ml) was stirred and heated under reflux during 2 h. Conventional work-up followed by chromatography (silica, 10% chloroform–light petroleum) gave pentachloropyridine (0.36 g, 7%) and *tetrachloro-4-(pentachlorophenylthio)pyridine* (2.5 g, 25%), m.p. 226—227 °C (from light petroleum), *m/e* 493 (M^+) (Cl_9) (Found: C, 26.5; N, 2.9. $C_{11}Cl_9NS$ requires C, 26.6; N, 2.8%).

Tetrachloro-4-(pentachlorophenoxy)pyridine (47).—A mixture of potassium pentachlorophenoxide (3.66 g), 4-bromotetrachloropyridine (2.96 g), 18-crown-6 (0.2 ml), and dry acetonitrile (50 ml) was stirred under reflux during 5 d, filtered, and evaporated. Water (100 ml) was added and the resulting solution was extracted with chloroform (2 × 100 ml). The extract was dried and concentrated. Chromatography (silica, light petroleum) gave successively (i) *4-bromo-3,5,6-trichloro-2-(pentachlorophenoxy)pyridine* (0.50 g, 11%), m.p. 213—215 °C (from light petroleum); *m/e* 521 (M^+) ($BrCl_8$) (Found: C, 26.5; H, 0.17; N, 2.6. $C_{11}BrCl_8NO$ requires C, 26.1; N, 2.7%); (ii) 4-bromotetrachloropyridine (0.84 g, 29%); and (iii) *tetrachloro-4-(pentachlorophenoxy)pyridine* (1.68 g, 36%), m.p. 182—183 °C (from light petroleum); *m/e* 477 (M^+) (Cl_9) (Found: C, 27.2; N, 2.8. $C_{11}Cl_9NO$ requires C, 27.5; N, 2.9%).

Reaction of Pentachloropyridine with Aniline (cf. *ref.* 18).—A solution of pentachloropyridine (5.0 g) and aniline (3.5 g) in dimethylformamide (25 ml) was heated under reflux during 2.5 h. The solvent was evaporated under reduced pressure and water (100 ml) was added to the residue. Work-up *via* chloroform extraction and chromatography (silica, light petroleum) gave successively *2-anilinotetrachloropyridine* (50) (2.2 g, 36%), m.p. 106—107 °C (Found: C, 42.9; H, 2.2; N, 8.9. $C_{11}H_6Cl_4N_2$ requires C, 42.9; H, 2.0; N, 9.1%) and 4-anilinotetrachloropyridine (8) (3.8 g, 62%), m.p. 100 °C (lit.,[18] m.p. 103—104 °C).

Reaction of 3,5-Dichlorotrifluoropyridine with Potassium Pentachlorophenoxide.—A solution of 3,5-dichlorotrifluoropyridine (10.05 g), potassium pentachlorophenoxide (15.1 g), and 18-crown-6 (0.4 ml) in acetonitrile (200 ml) was heated under reflux during 20 h. The resulting suspension was filtered and evaporated. Conventional work-up and chromatography (silica, light petroleum; difficult separation) gave successively (i) *3,5-dichloro-2,4-difluoro-6-(pentachlorophenoxy)pyridine* (49) (8.43 g, 38%), m.p. 174—175 °C (from light petroleum); δ_F −8.4(s) and −8.6(s) p.p.m.; *m/e* 445 (M^+) (Cl_7) (Found: C, 29.85; N, 2.85. $C_{11}Cl_7F_2NO$ requires C, 29.5; N, 3.1%) and (ii) *3,5-dichloro-2,6-difluoro-4-(pentachlorophenoxy)pyridine* (48) (2.5 g, 11%), m.p. 136—137 °C (from light petroleum), δ_F −9.36(s) p.p.m.; *m/e* 445 (M^+) (Cl_7) (Found: C, 29.5; N, 3.2. $C_{11}Cl_7F_2NO$ requires C, 29.5; N, 3.1%).

Allylaminotetrahalogenopyridines.—(*a*) A mixture of pentachloropyridine (3.0 g), allylamine (2.0 ml), and dimethylformamide (10 ml) was heated at 100 °C during 6 h. The solvent was evaporated *in vacuo* and the residue was chromatographed (silica, light petroleum) to give 2-allylaminotetrachloropyridine (0.85 g, 26%), m.p. 45 °C (lit.,[1] m.p. 58—59 °C) (Found: C, 35.8; H, 2.6; N, 10.0. $C_8H_6Cl_4N_2$ requires C, 35.3; H, 2.2; N, 10.3%) followed by *4-allylaminotetrachloropyridine* (54) (2.0 g, 62%), m.p. 59 °C (Found: C, 35.4; H, 2.2; N, 10.2%).

(*b*) A similar reaction with 4-bromotetrachloropyridine gave *2-allylamino-4-bromotrichloropyridine* (19%), m.p. 56 °C (Found: C, 30.7; H, 2.2; N, 9.4. $C_8H_6BrCl_3N_2$ requires C, 30.4; H, 1.9; N, 8.9%) and 4-allylaminotetrachloropyridine (54) (65%), identical to the material described in (*a*).

Hexachloro-5,5′-di-iodo-4,4′-bipyridyl (57).—2M-n-Butyllithium in hexane (60 ml) was added slowly to a suspension of octachloro-4,4′-bipyridyl (21.4 g) in diethyl ether (1 l) at −75 °C. The mixture was allowed to warm to room temperature, stirred for 1 h, and re-cooled to −75 °C. Iodine (30.5 g) was added in one portion. The mixture was allowed to warm to room temperature and poured into aqueous sodium thiosulphate. Conventional work-up followed by chromatography (silica, light petroleum) gave a mixture of heptachloro-5-iodo-4,4′-bipyridyl [*m/e* 520 (M^+) (Cl_7)] and the di-iodo-compound (total 10.0 g) followed by *hexachloro-5,5′-di-iodo-4,4′-bipyridyl* (15.0 g, 50%), m.p. 248—250 °C (from light petroleum, b.p. 80—100 °C); *m/e* 612 (M^+) (Cl_6) (Found: C, 19.9; N, 4.5. $C_{10}Cl_6I_2N_2$ requires C, 19.5; N, 4.6%).

Photocyclisation and Attempted Photocyclisation Reactions.—The conditions used for most of the photolyses are listed in Tables 4 and 5. 4-Anilino-2,5,6-trichloropyrimidine (51) was irradiated for 74 h in THF with the Hanovia lamp and Pyrex filter. 4-Benzyltetrachloropyridine (55) [21] was irradiated for 88 h in THF with the Hanau lamp and Pyrex filter. Octachloro-4,4′-bipyridyl (56) was irradiated under the following conditions: (*a*) 24 h, CCl_4, Hanau lamp, Pyrex filter; (*b*) 24 h, EtOH, Hanau lamp, quartz filter; and (*c*) 117 h, CCl_4, Hanovia lamp, quartz filter. Hexachloro-5,5′-di-iodo-4,4′-bipyridyl (57) was irradiated in the presence of sodium thiosulphate under the following conditions: (*a*) 90 h, Et_2O, Rayonet reactor, Pyrex filter; and (*b*) 87 h, CCl_4, Rayonet reactor, Pyrex filter. The products were isolated by conventional work-up followed by column chromatography on silica unless otherwise stated. The properties of the new products are given in Table 6. 1,1′,2,2′,6,6′-Hexachloro-4,4′-bipyridyl (78) was identified by comparison with an authentic specimen.[25]

Reactions of Benzothienopyridines with Thiophenoxide.—(*a*) A mixture of 1,3,4-trichloro[1]benzothieno[3,2-*c*]pyridine (6) (0.6 g), anhydrous potassium carbonate (0.45 g), and thiophenol (20 ml) was heated at 150 °C during 18 h. The mixture was allowed to cool and stirred with an excess of 30% aqueous sodium hydroxide during 48 h. The solid product was filtered off and recrystallised from ethanol to give 4-chloro-1,3-bis(phenylthio)[1]benzothieno[3,2-*c*]pyridine (69), identical to the material recorded in Table 6.

(*b*) A solution of 4-chloro-1,3-difluoro[1]benzothieno[3,2-*c*]pyridine (63) (0.50 g) in pyridine (5 ml) was maintained at 0 °C while a solution of sodium thiophenoxide (0.25 g) in pyridine (5 ml) was added. After a further 30 min at 0 °C the solution was allowed to warm to room temperature and poured into an excess of 5% hydrochloric acid. The solid product, recovered by filtration, was *4-chloro-1-fluoro-3-(phenylthio)[1]benzothieno[3,2-c]pyridine* (71) (0.54 g), m.p. 152—153 °C (from ethanol); τ 1.3 (m, 1 H, H-9), 2.2 (m, 1 H, H-6), and 2.6 (m, 7 H, H-7, H-8, Ph); δ_F −1.2 p.p.m. (s) (Found: C, 59.2; H, 2.7; N, 3.9. $C_{17}H_9ClFNS_2$ requires C, 59.1; H, 2.6; N, 4.1%).

(*c*) A mixture of 4-chloro-3-fluoro-1-(phenylthio)[1]benzothieno[3,2-*c*]pyridine (70) (0.20 g), anhydrous potassium carbonate (0.08 g), and thiophenol (5 ml) was heated at

TABLE 6

Properties of products of photocyclisation reactions

Compound	M.p. (°C) (recrystallisation solvent)	^{1}H n.m.r. (τ)	Molecular formula	Found (Required) C%	H%	N%	M^+
1,3,4-Trichloro[1]benzothieno-[3,2-*c*]pyridine (6)	184—185 (EtOH–$CHCl_3$)	1.1 (m, 1 H, H-9), 2.1 (m, 1 H, H-6), 2.4 (m, 2 H, H-7, 8)	$C_{11}H_4Cl_3NS$	45.7 (45.8)	1.6 (1.4)	4.7 (4.7)	
7,9,10-Trichloronaphtho[1,2-*b*]-thieno[3,2-*c*]pyridine (58)	257—258 (CCl_4)	1.2 (d), 1.8 (d), 2.3 (m) [a]	$C_{15}H_6Cl_3NS$	52.9 (53.2)	2.1 (1.8)	4.0 (4.1)	336.9289 [b] (Cl_3)
1,3,4-Trichlorodipyrido[2,3-*b*; 3,4-*d*]thiophen (60)	183—185	1.1 (dd, 1 H, H-4), 1.3 (dd, 1 H, H-2), 2.55 (dd, 1 H, H-3)	$C_{10}H_3Cl_3N_2S$				287.9086 [c] (Cl_3)
Heptachloro[1]benzothieno-[3,2-*c*]pyridine (61)	213—214 (light petroleum)		$C_{11}Cl_7NS$	31.1 (31.0)		3.4 (3.3)	423 (Cl_7)
Hexachlorodipyrido[5,4-*b*; 3,4-*d*]thiophen (62)	175—176 (light petroleum, b.p. 100—120 °C)		$C_{10}Cl_6N_2S$	30.8 (30.6)		7.4 (7.1)	389.7878 [d] (Cl_6)
4-Chloro-1,3-difluoro[1]benzo-thieno[3,2-*c*]pyridine (63)	158—159 (EtOH)	1.7 (m, 1 H, H-9), 2.1 (m, 1 H, H-6), 2.4 (m, 2 H, H-7, 8)	$C_{11}H_4ClF_2NS$	51.9 (51.8)	1.9 (1.6)	5.2 (5.5)	
1,3,4-Trifluoro[1]benzothieno-[3,2-*c*]pyridine (64)	153—154	1.8 (m, 1 H, H-9), 2.24 (m), 1 H, H-6), 2.55 (m, 2 H, H-7, 8)	$C_{11}H_4F_3NS$	54.9 (55.2)	1.6 (1.7)	6.0 (5.9)	
1,2,3-Trichloro[1]benzothieno-[2,3-*b*]pyridine (66)	213—215 (EtOH–$CHCl_3$)	1.1 (m, 1 H, H-5), 2.0 (m, 1 H, H-8), 2.35 (m, 2 H, H-6, 7)	$C_{11}H_4Cl_3NS$	45.5 (45.8)	1.6 (1.4)	4.9 (4.7)	
Dichloro[1]benzothieno[2,3-*b*]-pyridine, possibly (67)	156—158	1.5 (s, 1 H, H-2 or 3), 1.95 (m, 2 H, H-5,8), 2.4 (m, 2 H, H-6,7)	$C_{11}H_5Cl_2NS$	50.3 (49.8)	2.2 (2.1)	5.4 (5.8)	
1,2-Dichloro-3-(phenylthio)[1]-benzothieno[2,3-*b*]pyridine (68)	220—222 (EtOH–$CHCl_3$)	1.2 (m, 1 H, H-5), 2.2 (m, 1 H, H-8), 2.45 (m, 2 H, H-6,7), 2.5 (s, 5 H, Ph)	$C_{17}H_9Cl_2NS_2$	55.9 (56.4)	2.7 (2.5)	3.7 (3.9)	
4-Chloro-1,3-di(phenylthio)[1]-benzothieno[3,2-*c*]pyridine (69)	117—118 (EtOH–$CHCl_3$)	1.2 (m, 1 H, H-9), 2.1 (m, 1 H, H-6), 2.4 (m, 2 H, H-7,8), 2.68 (5 H, Ph), 2.73 (s, 5 H, Ph)	$C_{23}H_{14}ClNS_3$	63.3 (63.4)	3.5 (3.2)	3.2 (3.2)	
4-Chloro-3-fluoro-1-(phenylthio)-[1]benzothieno[3,2-*c*]pyridine (70)	151—152	2.0 (m, 1 H, H-9), 2.3 (m, 1 H, H-6), 2.7 (m, 7 H, H-7,8, Ph) [e]	$C_{17}H_9ClFNS_2$	59.4 (59.1)	2.8 (2.6)	4.3 (4.1)	
1,3,4-Trichloro[1]benzofuro-[3,2-*c*]pyridine (7)	129—130	1.8 (m, 1 H, H-9), 2.6 (m, 3 H, H-6,7,8)	$C_{11}H_4Cl_3NO$	48.7 (48.6)	1.7 (1.5)	5.1 (5.2)	
2,3,4-Trichloro[1]benzofuro-[2,3-*b*]pyridine (72)	94—95	2.8 (m)	$C_{11}H_4Cl_3NO$	49.0 (48.6)	1.4 (1.5)	5.2 (5.2)	
1,3,4-Trichloro-5*H*-pyrido[4,3-*b*]-indole (8)	238—239	1.7 (m, 1 H, H-9), 2.6 (m, 3 H, H-6,7,8)	$C_{11}H_5Cl_3N_2$	48.4 (48.6)	1.8 (1.4)	10.2 (10.3)	
1,2,3-Trichloro-5*H*-pyrido[2,3-*b*]-indole (73)	302—304	1.4 (m, 1 H, H-5), 2.1—2.5 (m, 3 H, H-6,7,8), 3.6 (br, NH) [a]	$C_{11}H_5Cl_3N_2$				269.9519 (Cl_3) [f]
1,3-Dichloro-5*H*-pyrimido[4,5-*b*]-indole (74) [g]	314—315 ($CHCl_3$–Et_2O)	−1.9 (br, 1 H, NH), 1.8 (m, 1 H, H-9), 2.6 (m, 2 H, H-7,8)	$C_{10}H_5Cl_2N_3$	50.3 (50.45)	2.3 (2.1)	17.6 (17.65)	237 (Cl_2)
4-Anilino-2,6-dichloropyrimidine (75) [h]	137 [i]	2.6 (m, 6 H), 3.4 (s, NH)	$C_{10}H_7Cl_2N_3$	50.1 (50.2)	3.0 (2.6)	17.8 (17.6)	239 (Cl_2)
4-Benzyl-2,3,6-trichloro-5-(2-tetrahydrofuryl)pyridine (76)	175—180 [j]	2.8 (s, 5 H, Ph), 4.7 (t, 1 H, H-2′), 5.7 (s, 2 H, benzyl CH_2), 5.8—6.2 (m, 2 H, H-5′), 7.7—8.1 (m, 4 H, H-3′,4′)	$C_{16}H_{14}Cl_3NO$	56.4 (56.1)	4.3 (4.1)	3.9 (4.1)	341 (Cl_3)

[a] In Me_2SO. [b] Required 336.9285. [c] Required 287.9081. [d] Required 389.7910. [e] δ_F −9.55 p.p.m. (s). [f] Required 269.9518. [g] $\nu_{max.}$ 3 150 cm^{-1}. [h] $\nu_{max.}$ 3 200 cm^{-1}. [i] Lit., m.p. 137—138 °C (W. Winklemann, *J. prakt. Chem.*, 1927, **115**, 292). [j] Approx. b.p. at 0.005 mmHg (Kugelrohr apparatus).

120 °C during 18 h. A solution of potassium hydroxide (4.0 g) in water (20 ml) was added and the mixture was stirred for a further 2 h, poured into water (30 ml), and extracted with chloroform. The extract was dried and evaporated to yield an oil, which was dissolved in hot ethanol (30 ml). The solution was filtered to remove insoluble material, concentrated, and cooled, to yield crystalline 4-chloro-1,3-bis(phenylthio)[1]benzothieno-[3,2-*c*]pyridine (69) (0.09 g), identical to the material recorded in Table 6.

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