Preparation of Polychlorinated Phenoxyphenols as Model Compounds of Impurities in Technical Chlorophenol Formulations

Tarmo Humppi

Research Centre of Finnish Defence Forces, Box 5, SF-34111 Lakiala, Finland

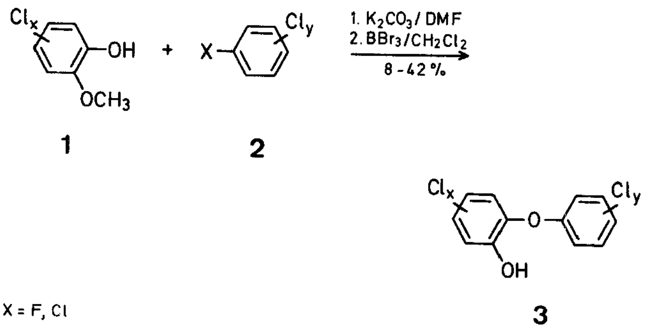
The synthesis of polychlorinated phenoxyphenols (PCPPs) by three methods is described: condensation of chlorinated guaiacols with chlorobenzene or chlorofluorobenzenes in the presence of base, followed by *O*-demethylation; reaction of chlorinated diphenyliodonium salts with chlorinated guaiacols, or of 4,4'-dimethoxydiphenyliodonium salts with chlorophenols, followed by *O*-demethylation; chlorination of lower-chlorinated phenoxyphenols.

Studies on chlorophenol impurities have been focussed so far on the neutral ones such as polychlorinated dibenzo-1,4-dioxins and dibenzofurans. Only minor attention has been paid to the polychlorinated phenoxyphenols (PCPPs), although these compounds have been found to be major impurities in chlorophenol formulations[1-6].

The synthesis of lower-chlorinated phenoxyphenols, mainly used as bactericides, has been described in several patents[7-11]. PCPPs most frequently present in technical chlorophenols have been shown to contain 5-9 Cl atoms[1-6]; however, only few of these PCPPs have been synthesized[12-18]. A published study on synthetic routes to higher-chlorinated phenoxyphenols[19] did not include those PCPPs which are most probably present in technical chlorophenols[17].

In the present paper, the syntheses of 31 different PCPPs (**3**, **7**, **9**) are reported. Only 7 of these compounds had been described earlier (except for one publication[17]). The PCPPs synthesized in this study have already been used in analytical examinations of impurities in commercial chlorophenols used as fungicides in Finnish sawmills[17,20]. The synthetic methods used are discussed below.

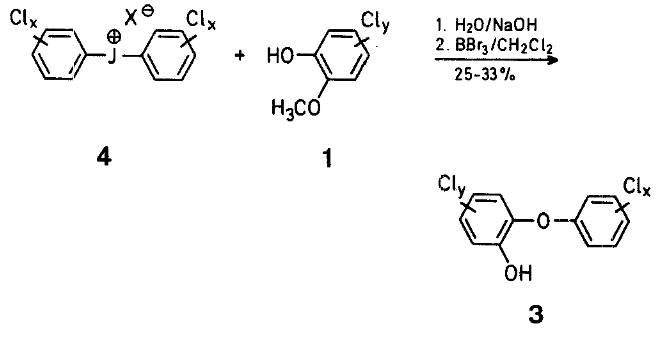
Method A: Nucleophilic displacement of fluorine or chlorine in a polychloro- or polychlorofluorobenzene (**2**) by the anion of a chloroguaiacol (**1**) followed by *O*-demethylation with boron tribromide.



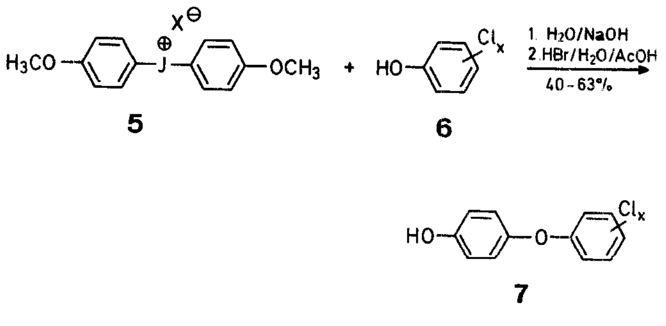
1 **2** **3**

This method has been used earlier[16]; however, in the present work the use of acetonitrile + catalytic amounts of 18-crown-6 as solvent system led to only low conversion of the starting materials into the desired products **3**. The use of sodium hydroxide/dimethyl sulfoxide[15] led to some complications such as formation of polymeric material; besides, there is a considerable hazard of dioxin formation due to the strongly basic reaction medium. In the present work, the boiling dimethylformamide/potassium carbonate system proved to be the most versatile medium for the reaction. The reactivity of the starting material appeared to depend mainly on the number of chlorine substituents. Increasing chlorine substitution in chlorobenzenes **2** afforded higher yields while for the chloroguaiacols **1** the effect was reversed. Thus, hexachloro-, 2,3,4,6-tetrachlorofluoro-, and 2,4,6-trichlorofluorobenzenes afforded fairly good results when 4-chloroguaiacol was used as substrate, but with 3,5-dichloroguaiacol the reaction proceeded less satisfactorily and it failed when tetrachloroguaiacol was used. This behaviour proves the role of the guaiacol as the nucleophilic reactant. The condensation of 1,3,5-trichlorobenzene with 4-chloroguaiacol afforded only a fair yield of **3c** and required more forcing conditions such as the use of sodium hydroxide in place of potassium carbonate, and longer reaction times.

Method B: Reaction of chlorinated diphenyliodonium salts (**4**) with chloroguaiacols (**1**) or of 4,4'-dimethoxydiphenyliodonium salts (**5**) with chlorophenols (**6**), followed by *O*-demethylation to give the polychlorinated 2-phenoxyphenols **3** or the 4-(chlorophenoxy)-phenols **7**, respectively.



4 **1** **3**

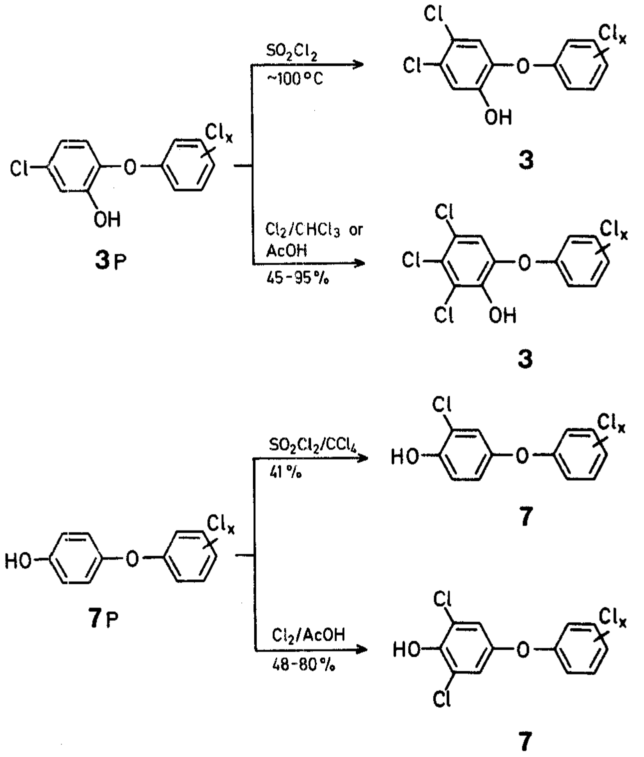


5 **6** **7**

The procedure used was adapted from Ref.[19]. Although the method seems to be of general utility, one serious drawback was observed: Attempts to perform the synthesis and/or coupling reaction of 2,2′,4,4′,6,6′-hexa-, 2,2′,3,3′, 4,4′, 6,6′-octa- and decachlorodiphenyliodonium salts failed. This means that the method has little synthetic value of those PCPPs which are expected to be present in chlorophenols[17].

It appears that Method B (complemented by Method C) might be extended to include the PCPPs expected in chlorophenols by using chlorinated methoxy-substituted diphenyliodonium salts. However, these iodonium salts have hitherto not been described and all attempts to prepare them failed.

Method C: Direct chlorination of ("parent") phenoxyphenols (3P, 7P).



The direct chlorination of phenoxyphenols has been shown to be a convenient route to PCPPs, provided that suitable starting materials are available[19]. In the present work, a number of PCPPs were prepared by this method from lower-chlorinated phenoxyphenols (with respect to the phenol part of the molecule, prepared by Methods A and B). Chlorination of 2-phenoxyphenols having no Cl-atoms in the phenol part afforded complex mixtures, but chlorination of 5-chloro-2-(chlorophenoxy)-phenols (compounds **3a,c,g,l,o,s** in Table 1) afforded 4,5,6-trichloro-2-(chlorophenoxy)-phenols in rather pure state. The chlorination reaction can be catalyzed by Lewis acids such as aluminum chloride[19]. Chlorination of the phenoxy group was not observed except for 5-chloro-2-(3,5-dichlorophenoxy)-phenol (**3c**) which was converted into 4,5,6-trichloro-2-(3,4,5-trichlorophenoxy)-phenol (**3d**). Monochlorination of 5-chloro-2-(chlorophenoxy)-phenols (for example **3s**→**3t**) could be achieved by simply allowing the starting compounds to stand in sulfuryl chloride solution for several hours; formation of other, isomeric PCPPs was not observed.

In the case of 4-phenoxyphenols (**7a,d,f**), the reaction with elemental chlorine in acetic acic led to chlorination in both positions *ortho* to the hydroxy group whereas in chloroform as solvent, decomposition of the starting material occurred. Attempts to further chlorinate the products (*meta* position) resulted mainly in decomposition. Monochlorination of the parent 4-(chlorophenoxy)-phenols (**7P**) could be achieved by using sulfuryl chloride in boiling tetrachloromethane. 3-(Pentachlorophenoxy)-phenol (**9a**, obtained from **8** and **2** by Method A) could be chlorinated with elemental chlorine in acetic acid to give either the 4,6-dichloro derivative (**9b**; under G.L.C. control) or the 2,4,6-trichloro derivative (**9c**; prolonged reaction time in the presence of iodine).

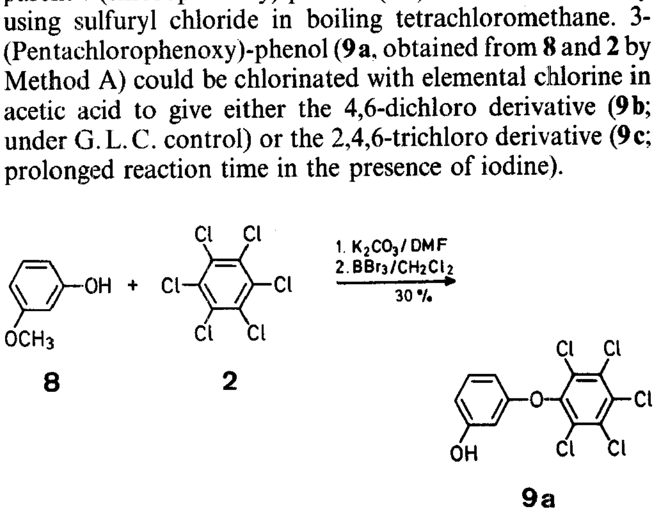


Table 1. Synthesis of Polychlorinated Phenoxyphenols (3, 7, 9)

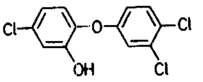
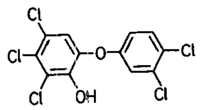
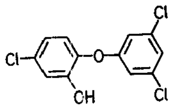
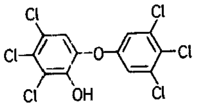
Starting Materials (Reagents or Types thereof)	Method	Reaction Conditions// Purification[a]	Product		Yield [%]	m.p. [°C]	Molecular Formula[b] or Lit. m.p. [°C]
4[c] + 1	B	1. reflux in NaOH/H_2O, 4h; 2. demethylation//F.C.		**3a**	26	95–96°	103–104°[17]
3a	C	Cl_2/AcOH, 20°C//F.C.		**3b**	56	115–116°	$C_{12}H_5Cl_5O_2$ (358.4)
1 + 2	A	1. reflux in DMF with NaOH, 20h; 2. demethylation//F.C.		**3c**	8	75–78°	$C_{12}H_7Cl_3O_2$ (289.6)
3c	C	$Cl_2/AcOH/AlCl_3$, 20°C, 18h//F.C.		**3d**	45	146–149°	$C_{12}H_4Cl_6O_2$ (392.9)

Table 1. (continued)

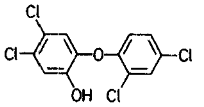
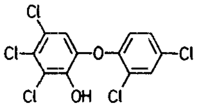
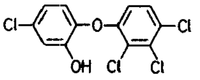
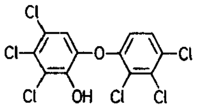
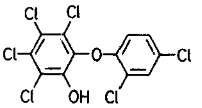
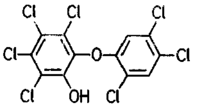
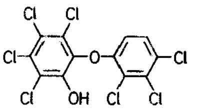
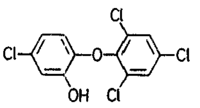
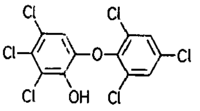
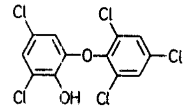
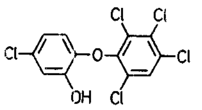
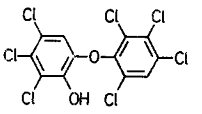
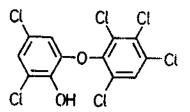
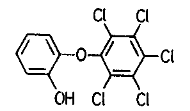
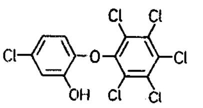
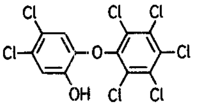
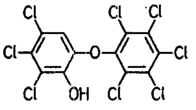
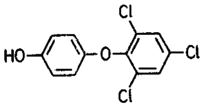
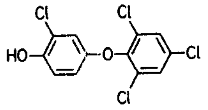
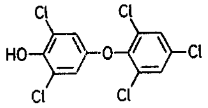
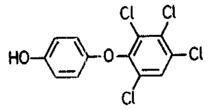
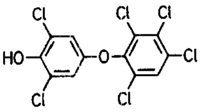
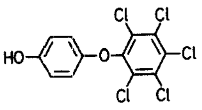
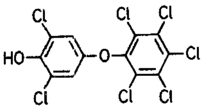
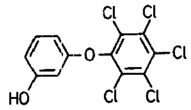
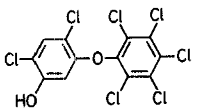
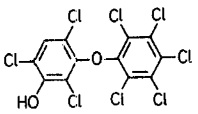
Starting Materials (Reagents or Types thereof)	Method	Reaction Conditions// Purification[a]	Product	Yield [%]	m.p. [°C]	Molecular Formula[b] or Lit. m.p. [°C]
5-chloro-2-(2,4-dichlorophenoxy)-phenol[d]	C	stirring in SO_2Cl_2, 20 °C, overnight//recryst. hexane	 **3e**	100	84–85°	88.0–88.5°[19]
(as **3P**)	C	$Cl_2/CHCl_3$, 20 °C//recryst. hexane	 **3f**	56	99–100°	103.5–104.0°[19]
1 + **2**[e]	A	1. reflux in DMF with K_2CO_3, 3h; 2. demethylation//F.C.	 **3g**	33	104–105°	$C_{12}H_6Cl_4O_2$ (324.0)
3g	C	$Cl_2/CHCl_3$, 20 °C//recryst. hexane/benzene	 **3h**	95	141–143°	$C_{12}H_4Cl_6O_2$ (392.9)
4[f] + **1**	B	1. reflux in $NaOH/H_2O$, 3h; 2. demethylation//F.C.	 **3i**	25	116–117°	$C_{12}H_4Cl_6O_2$ (392.9)
4[g] + **1**	B	1. reflux in $NaOH/H_2O$, 4h; 2. demethylation//F.C.	 **3j**	31	147–148°	$C_{12}H_3Cl_7O_2$ (427.3)
4[h] + **1**	B	1. reflux in $NaOH/H_2O$, 4h; 2. demethylation//F.C.	 **3k**	33	173–175°	$C_{12}H_3Cl_7O_2$ (427.3)
1 + **2**[i]	A	1. reflux in DMF with K_2CO_3, 3h; 2. demethylation//F.C.	 **3l**	36	95–97°	$C_{12}H_6Cl_4O_2$ (324.0)
3l	C	$Cl_2/AcOH$, 20 °C//recryst. hexane/benzene	 **3m**	90	131–132°	$C_{12}H_4Cl_6O_2$ (392.9)
1 + **2**[i]	A	1. reflux in DMF with K_2CO_3, 8h; 2. demethylation//F.C.	 **3n**	21	111–113°	$C_{12}H_5Cl_5O_2$ (358.4)
1 + **2**[j]	A	1. reflux in DMF with K_2CO_3, 2h; 2. demethylation//F.C.	 **3o**	42	122–124°	$C_{12}H_5Cl_5O_2$ (358.4)
3o	C	$Cl_2/CHCl_3$, 20 °C//recryst. hexane/benzene	 **3p**	65	179–180°	$C_{12}H_3Cl_7O_2$ (427.3)
1 + **2**[j]	A	1. reflux in DMF with K_2CO_3, 3h; 2. demethylation//F.C.	 **3q**	39	149–151°	$C_{12}H_4Cl_6O_2$ (392.9)
1 + **2**	A	1. reflux in DMF with K_2CO_3, 4h; 2. demethylation//F.C.	 **3r**	23	149–150°	154°[16]
1 + **2**	A	1. reflux in DMF with K_2CO_3, 4h; 2. demethylation//F.C.	 **3s**	33	135–137°	$C_{12}H_4Cl_6O_2$ (392.9)

Table 1. (continued)

Starting Materials (Reagents or Types thereof)	Method	Reaction Conditions// Purification[a]	Product		Yield [%]	m.p. [°C]	Molecular Formula[b] or Lit. m.p. [°C]
3s	C	stirring in SO_2Cl_2, 20°C, 5h//crude		**3t**	100	209–211°	216°[16]
3s	C	Cl_2/AcOH//recryst. hexane/benzene		**3u**	80	173–175°	$C_{12}H_2Cl_8O_2$ (461.8)
5^k + 6	B	1. reflux in $NaOH/H_2O$, 2h; 2. demethylation//F.C.		**7a**	46	134–135°	$C_{12}H_7Cl_3O_2$ (289.6)
7a	C	1.2 equiv SO_2Cl_2/CCl_4, overnight//F.C.		**7b**	41	105–107°	$C_{12}H_6Cl_4O_2$ (324.0)
7a	C	Cl_2/AcOH, 20°C//recryst. hexane		**7c**	57	128–129°	$C_{12}H_5Cl_5O_2$ (358.4)
5^k + 6	B	1. reflux in $NaOH/H_2O$, 3h; 2. demethylation//recryst. hexane/benzene		**7d**	40	147–152°	$C_{12}H_6Cl_4O_2$ (324.0)
7d	C	Cl_2/AcOH//recryst. AcOH		**7e**	80	135–152°	$C_{12}H_4Cl_6O_2$ (392.9)
5^k + 6	B	1. reflux in $NaOH/H_2O$, 3h; 2. demethylation//recryst. AcOH		**7f**	63	186–187°	170°[16]
7f	C	Cl_2/AcOH//F.C. and recryst. AcOH		**7g**	48	184–186°	$C_{12}H_3Cl_7O_2$ (427.3)
8 + **2**	A	1. reflux in DMF with K_2CO_3, 4h; 2. demethylation//F.C. and recryst. hexane/benzene		**9a**	30	135–136°	134°[16]
9a	C	Cl_2/AcOH//recryst. hexane/benzene		**9b**	64	150–152°	$C_{12}H_3Cl_7O_2$ (437.3)
9a	C	Cl_2 (+ J_2)/AcOH, overnight//recryst. hexane/benzene		**9c**	80	140–142°	$C_{12}H_2Cl_8O_2$ (461.8)

---

[a] F.C. = flash chromatography.

[b] The high-resolution mass spectra (m/e of M^+) were in satisfactory agreement with the calculated values.

[c] 3,3',4,4'-Tetrachlorodiphenyliodonium chloride[22].

[d] Commercial product from Ciba Geigy (Irgasan DP 300).

[e] 2,3,4-Trichlorofluorobenzene, prepared by Schieman reaction from the corresponding aniline.

[f] 2,2',4,4'-Tetrachlorodiphenyliodonium chloride[22].

[g] 2,2',4,4',5,5'-Hexachlorodiphenyliodonium chloride[22].

[h] 2,2',3,3',4,4'-Hexachlorodiphenyliodonium chloride[22].

[i] 2,4,6-Trichlorofluorobenzene, prepared by Schiemann reaction from the corresponding aniline.

[j] 2,3,4,6-Tetrachlorofluorobenzene, prepared by Schiemann reaction from the corresponding aniline.

[k] Prepared according to Ref.[23].

Table 2. Mass- and ^{1}H-N.M.R.-Spectral Data of the PCPPs **3**, **7**, and **9**

PCCP	M.S.[a] *m/e* (rel. Int., %)	^{1}H-N.M.R. (acetone-d_6/TMS$_{\text{int}}$)[b] δ [ppm]
3a	292 (32), 290 (98), 288 (100), 220 (16), 218 (49), 148 (32), 146 (50), 145 (18), 143 (28)	6.80–7.59 (m, 6H); 8.98 (s, OH)
3b	362 (20), 360 (65), 358 (100), 356 (65), 290 (22), 288 (55), 286 (50), 148 (53), 146 (82)	6.94–7.64 (m, 3H); 7.33 (s, 1H); – (OH)
3c	292 (40), 290 (100), 288 (100), 218 (47), 145 (18), 143 (38)	6.88–7.22 (m, 6H); 9.04 (s, OH)
3d	396 (37), 394 (82), 392 (100), 390 (50), 324 (39), 322 (80), 320 (58), 184 (19), 182 (44), 180 (42)	7.32 (s, 2H); 7.44 (s, 1H); 9.56 (br. s, OH)
3e	328 (10), 236 (47), 324 (100), 322 (82), 256 (8), 254 (46), 252 (71), 148 (89), 146 (86)	6.89–7.58 (m, 5H); – (OH)
3f	362 (11), 360 (34), 358 (50), 356 (30), 290 (11), 288 (32), 286 (33), 150 (12), 148 (67), 146 (100)	7.14 (s, 1H); 7.19–7.64 (m, 3H); – (OH)
3g	328 (12), 326 (50), 324 (100), 322 (78), 256 (10), 254 (52), 252 (80), 184 (11), 182 (35), 180 (37)	6.74–7.56 (s, 2H); 6.95–7.17 (m, 3H); 9.08 (s, OH)
3h	396 (27), 394 (65), 392 (82), 390 (42), 324 (36), 322 (67), 320 (50), 184 (41), 182 (100), 180 (97)	7.03–7.64 (q, 2H); 7.27 (s, 1H); – (OH)
3i	396 (14), 394 (36), 392 (45), 390 (19), 324 (13), 322 (25), 320 (20), 148 (67), 146 (100)	6.76–7.62 (m, 3H); – (OH)
3j	432 (16), 430 (36), 428 (68), 426 (67), 424 (30), 360 (12), 358 (31), 356 (50), 184 (30), 182 (99), 180 (100)	7.21 (s, 1H); 7.80 (s, 1H); – (OH)
3k	data not available	6.80–7.55 (q, 2H); – (OH)
3l	328 (13), 326 (50), 324 (100), 322 (79), 254 (38), 252 (56), 184 (13), 182 (40), 180 (42)	6.43–7.05 (m, 3H); 7.66 (s, 2H); 8.83 (s, OH)
3m	396 (26), 394 (60), 392 (72), 390 (40), 324 (32), 322 (68), 320 (44), 184 (44), 182 (99), 180 (100)	6.83 (s, 1H); 7.69 (s, 2H); – (OH)
3n	362 (18), 360 (54), 358 (83), 356 (52), 290 (20), 288 (58), 286 (59), 184 (31), 182 (94), 180 (100)	6.56–7.20 (q, 2H); 7.69 (s, 2H); 9.18 (s, OH)
3o	362 (20), 360 (64), 358 (100), 356 (62), 290 (16), 288 (48), 286 (50), 218 (26), 216 (52), 214 (40)	6.50–7.06 (m, 3H); 7.88 (s, 1H); 9.04 (s, OH)
3p	432 (8), 430 (20), 428 (36), 426 (36), 424 (16), 394 (34), 392 (80), 290 (100), 218 (34), 216 (75), 214 (62)	6.99 (s, 1H); 7.92 (s, 1H); – (OH)
3q	396 (12), 394 (30), 392 (34), 390 (18), 360 (34), 358 (66), 356 (100), 354 (66), 218 (18), 216 (36), 214 (29)	6.71–7.21 (q, 2H); 7.92 (s, 1H); – (OH)
3r	362 (22), 360 (65), 358 (100), 356 (64), 327 (6), 325 (23), 323 (49), 321 (40), 290 (26), 288 (79), 286 (76), 254 (7), 252 (18), 250 (29), 248 (16)	6.59–7.02 (m, 4H); 8.46 (s, OH)
3s	396 (35), 394 (86), 392 (100), 326 (8), 324 (32), 322 (63), 320 (48), 254 (10), 252 (31), 250 (48), 248 (30)	6.68–7.07 (m, 3H); – (OH)
3t	432 (8), 430 (42), 428 (88), 426 (86), 424 (43), 394 (40), 392 (83), 390 (100), 388 (51), 254 (14), 252 (46), 250 (70), 248 (46)	6.97 (s, 1H); 7.20 (s, 1H); – (OH)
3u	466 (2), 464 (8), 462 (11), 460 (10), 458 (5), 430 (18), 428 (52), 426 (99), 424 (100), 422 (42), 254 (4), 252 (9), 250 (15), 248 (8)	7.06 (s, 1H); – (OH)
7a	292 (33), 290 (98), 288 (99), 220 (34), 218 (100), 109 (35)	6.74–6.76 (d, 4H); 7.64 (s, 2H); 8.20 (br. s, OH)
7b	328 (11), 326 (49), 324 (100), 322 (76), 256 (8), 254 (85), 145 (7), 143 (13)	6.61–7.08 (m, 3H); 7.67 (s, 2H); 8.58 (s, OH)
7c	362 (23), 360 (63), 358 (98), 356 (62), 290 (33), 288 (98), 286 (100), 145 (7), 143 (15)	6.97 (s, 2H); 7.68 (s, 2H); – (OH)
7d	328 (10), 326 (42), 324 (89), 322 (66), 256 (14), 254 (68), 252 (100)	6.75 (s, 4H); 7.82 (s, 1H); – (OH)
7e	396 (25), 394 (55), 392 (73), 390 (41), 326 (12), 324 (49), 322 (100), 320 (78)	7.02 (s, 2H); 7.88 (s, 1H); – (OH)
7f	362 (15), 360 (51), 358 (80), 356 (51), 290 (30), 288 (96), 286 (100), 109 (32)	6.79 (s, 4H); 8.19 (s, OH)
7g	432 (12), 430 (35), 428 (60), 426 (63), 424 (28), 360 (24), 358 (64), 356 (100), 354 (57), 179 (17), 177 (21)	7.09 (s, 2H); – (OH)
9a	362 (6), 360 (18), 358 (28), 356 (16), 325 (19), 323 (19), 321 (15), 290 (32), 288 (92), 286 (100)	6.27–7.30 (m, 4H); 8.57 (s, OH)
9b	432 (6), 430 (22), 428 (37), 426 (44), 424 (19), 360 (20), 358 (67), 356 (100), 354 (62)	6.41 (s, 1H); 7.56 (s, 1H); – (OH)
9c	466 (10), 464 (25), 462 (36), 460 (29), 458 (9), 394 (38), 392 (79), 390 (100), 388 (51)	7.55 (s, 1H); 9.46 (s, OH)

---

[a] The G.L.C.-inlet EI mass spectra were recorded at 70 eV on a Finnigan MAT 212 mass spectrometer connected to a Varian Series 3700 gas chromatograph which was equipped an SE-54 quartz capillary column (20 m × 0.3 I.D.), operating with the temperature program 60–260 °C at 10 °C/min and then held at the final temperature for 25 min.

[b] Recorded on a JEOL FX-60 spectrometer.

Polychlorinated Phenoxyphenols (PCPP; 3, 7, 9); General Procedures:

Method A: Equimolecular amounts of polychloro- or polychlorofluorobenzene and chloroguaiacol are refluxed in dimethylformamide with potassium carbonate (4-6 equiv) for several hours. The mixture is allowed to cool and water is added. The solid formed is extracted with diethyl ether. The ethereal layer is washed with diluted sodium hydroxide solution and water and is dried with sodium sulfate. The ether is removed by evaporation and the residue is demethylated with boron tribromide according to Ref.[16]. Flash chromatography (F.C.) is used for purification of the crude product according to Ref.[21] operating with a 2 × 40 cm glass column packed with Kieselgel 60 (230-400 mesh, Merck) and using petroleum ether (b.p. 60-60 °C) diethyl ether (80/20) as solvent system.

Method B: A mixture of equimolecular amounts of the diphenyliodonium salt (**4**, **5**), chloroguaiacol (**1**) or chlorophenol (**6**), and sodium hydroxide is refluxed in water for several hours, and then allowed to cool. The mixture is extracted with ether and the ether extract is dried with sodium sulfate and evaporated to dryness. The residual product is demethylated with boron tribromide[16] (for products **3**) or with 47% hydrobromic acid[8] (for products **7**). The crude products thus obtained are purified by flash chromatography and/or recrystallization. (Examples and more detailed descriptions of this procedure are given in Ref.[17]).

Method C:

Chlorination with Elemental Chlorine: Chlorine gas is passed for a few minutes through a solution of the parent PCPP (**3**P, **7**P; 50-200 mg) in glacial acetic acid (20-50 ml) (or chloroform). The chlorination reaction is monitored by G.L.C. After all of the substrate has reacted, the reaction is stopped by the addition of 20% sodium hydrogen sulfite solution (10-20 ml). The solid product formed is isolated by suction and dried. When chloroform is used as solvent the crude product is isolated by separating the organic layer of the mixture, drying this layer with sodium sulfate, and evaporation. The crude product is purified by flash chromatography and/or recrystallization.

Chlorination of Compounds **3**P *with Sulfuryl Chloride*: A mixture of the parent 5-chloro-2-(chlorophenoxy)-phenol (**3**P; 20-50 mg) and sulfuryl chloride (1-2 ml) is allowed to stand for several hours, with occasional shaking. The crude product is obtained by evaporation.

Chlorination of Compounds **7**P *with Sulfuryl Chloride*: A solution of the parent 4-(chlorophenoxy)-phenol (**7**P; 20-50 mg) and sulfuryl chloride (1.2 equiv) in tetrachloromethane is refluxed for the time given in Table 1. The product is isolated by flash chromatography.

This work was supported financially by the Maj and Tor Nessling Foundation. I am grateful to Ms. M. Lahtiperä and A. Pippuri for running the mass spectra and Ms. L. Virkki for the ^{1}H-N.M.R. spectra.

Received: August 28, 1984
(Revised form: April 19, 1985)

---

[1] Jensen, S., Renberg, L. *Ambio* **1972**, *1*, 62.

[2] Rappe, C., Nilsson, C.A. *J. Chromatogr.* **1972**, *67*, 247.

[3] Nilsson, C.A., Renberg, L. *J. Chromatogr.* **1974**, *89*, 325.

[4] Levin, J.O., Nilsson, C.A. *Chemosphere* **1977**, *6*, 443.

[5] Deinzer, M., Griffin, D., Miller, T., Skinner, R. *Biomed. Mass Spectrom.* **1979**, *6*, 301.

[6] Deinzer, M., Lamberton, J., Griffin, D., Miller, T. *Biomed. Mass Spectrom.* **1978**, *5*, 566.

[7] Belgian Patent 659 636 (1965), J.R. Geigy; *C.A.* **1966**, *64*, 2010.

[8] Model, E., Bindler, J. *U.S. Patent* 3 904 696 (1975), Ciba-Geigy, *C.A.* **1975**, *83*, 205924.

[9] Darsow, G., Schnell, H., Bottenbruch, L. *German Patent (DBP)* 1 911 799 (1970), Bayer AG; *C.A.* **1970**, *73*, 120321.

[10] Darsow, G., Schnell, H. *German Patent (DBP)* 1 930 256 (1970), Bayer AG; *C.A.* **1971**, *74*, 64907.

[11] Biller, E., Haas, B., Schlegel, R., Schmook, F.P. *German Patent (DBP)* 2 117 690 (1972), Union Rheinische Braunkohlen-Kraftstoff AG; *C.A.* **1973**, *78*, 15783.

[12] Deinzer, M., Miller, T., Arbogast, B., Lamberton, J. *J. Agric. Food Chem.* **1981**, *29*, 679.

[13] Campbell, J.A.O., Deinzer, M.L., Miller, T.L., Rohrer, D.C., Strong, P.E. *J. Org. Chem.* **1982**, *47*, 4968.

[14] Deinzer, M., Miller, T., Lamberton, J., Arbogast, B. *J. Org. Chem.* **1981**, *46*, 4800.

[15] Göthe, R., Wachtmeister, C.A. *Acta Chem. Scand.* B **1976**, *30*, 796.

[16] Kolonko, K., Deinzer, M., Miller, T. *Synthesis* **1981**, 133.

[17] Humppi, T., Laitinen, R., Kantolahti, E., Knuutinen, J., Paasivirta, J., Tarhanen, J., Lahtiperä, M., Virkki, L. *J. Chromatogr.* **1984**, *291*, 135.

[18] Newsome, W., Shields, J. *Int. J. Environ. Anal. Chem.* **1983**, *14*, 299.

[19] Nilsson, C.A. *Dissertation*, University of Umeå, 1977.
Nilsson, C.A., Andersson, K. *Chemosphere* **1977**, *6*, 249.

[20] Humppi, T., Knuutinen, J., Paasivirta, J. *Chemosphere* **1984**, *13*, 1235.

[21] Still, W., Kahn, M., Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

[22] Nilsson, C.A., Norström, Å., Hansson, M., Andersson, K. *Chemosphere* **1977**, *6*, 599.

[23] Beringer, F.M., Falk, R.A., Karniol, M., Lillien, I., Masulla, G., Mausner, M., Sommer, E. *J. Am. Chem. Soc.* **1958**, *81*, 342.