Kirk-Othmer Encyclopedia of Chemical Technology.

CHLOROPHENOLS

The chlorophenols make up an important class of industrial chemical compounds. They are used as either intermediates in the synthesis of agrochemicals, dyestuffs, and pharmaceuticals or directly in formulations.

1. Physical Properties

The main characteristics and physical properties of the chlorophenols are brought together in Table 1. With the exception of *o*-chlorophenol, they are all solids at room temperature. The refractive indexes of the monochlorophenols, C_6H_5ClO, are as follows: ortho, 1.5524; meta, 1.5565; para, 1.5579. The pK_a values of chlorophenols depend on the number and the position of the substituents.

2. Preparation

2.1. Chlorination of Phenols

Industrially, the phenols are chlorinated without solvent. Chlorine reacts rapidly with phenol and with the chlorophenols, which makes it difficult to determine the relative reaction rates because of the superchlorination that sometimes results from an unsatisfactory chlorine dispersion. Studies have yielded the relative reaction rates indicated in Figure 1.

2.1.1. Monochlorophenols

Chlorination of phenol [108-95-2] between 50 and 120°C gives a para/ortho ratio of 1.65. To improve the selectivity in the para position, it is possible to use dialkyl sulfides, diaryl sulfides (12), or alkyl and aryl sulfides combined.(**1, 2**) Sulfides are active only at low temperatures ($\leq 50^{\circ}C$), because at high temperatures the active species decomposes into sulfur and chlorine.

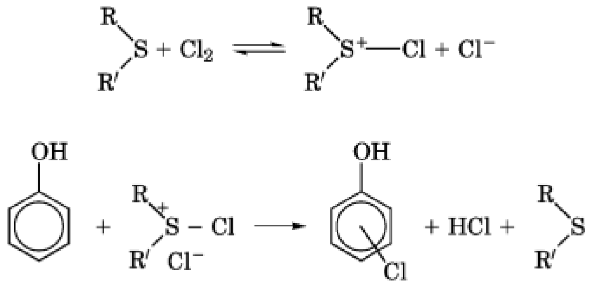


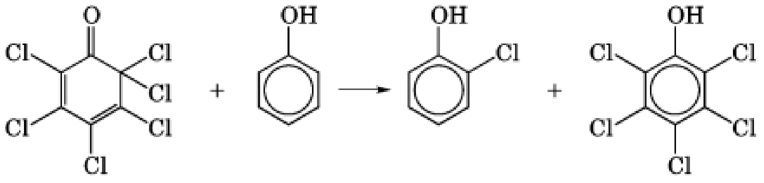
Table 1. Physical Properties of the Chlorophenols

				pK_a		
Compound	CAS Registry Number	Mp, °C	Bp, °C	Water[a]	Methanol/water[b]	Density, g/mL
2-chlorophenol[c]	[95-57-8]	8.7	175–176	8.5–8.52	9.13	1.2634^{20°
3-chlorophenol	[108-43-0]	32.8	215–217	8.97–9[d]	9.53	1.27
4-chlorophenol[e]	[106-48-9]	40–41	219	9.37–9.44[f]	9.70	1.265
2,3-dichlorophenol	[576-24-9]	58	206	7.4–7.71	8.52	
2,4-dichlorophenol	[120-83-2]	42.8	210	7.9[g]–7.9	8.51	1.388^{50°
2,5-dichlorophenol	[583-78-8]	58	212–213	7.5–7.51	7.69	
2,6-dichlorophenol	[87-65-0]	67	219–220	6.8[h]–6.80	7.15	
3,4-dichlorophenol	[95-77-2]	65	253	8.6[f]–8.62	8.87	
3,5-dichlorophenol	[591-35-5]	68	233	8.2[i]–8.25	8.54	
2,3,4-trichlorophenol	[15950-66-0]	83.5		6.97[j]–6.97	7.34	
2,3,5-trichlorophenol	[933-78-8]	62	255	6.43	6.92	
2,3,6-trichlorophenol	[933-75-5]	101	272	5.8[j]–5.80	6.10	
2,4,5-trichlorophenol	[95-95-4]	68	245–246	6.72–7.3[k]	7.20	
2,4,6-trichlorophenol	[88-06-2]	68	244.5	5.99–6.2[h]	6.51	1.49
3,4,5-trichlorophenol	[609-19-8]	101	275	7.55–7.8[f]	7.57	
2,3,4,5-tetrachlorophenol	[4901-51-3]	115–117		5.64[j]–5.64	5.92	
2,3,4,6-tetrachlorophenol	[58-90-2]	69–70		5.22[f]–5.22	5.53	
2,3,5,6-tetrachlorophenol	[935-95-5]	115		5.02[j]–5.03	5.76	
pentachlorophenol	[87-86-5]	190	309–310	4.74–4.8	4.93	1.98

[a] At 25°C from Ref. 1 unless otherwise noted.
[b] 60% CH_3OH/40% H_2O at 20°C (2).
[c] pK_a in pyridine = 12.1 (3).
[d] Ref. 4.
[e] pK_a in DMSO = 16.1 (5)
[f] Ref. 6.
[g] Ref. 7.
[h] Ref. 8.
[i] Ref. 9.
[j] Ref. 10.
[k] Ref. 11.

The use of phosphine has also been described (13). The para/ortho ratios obtained with sulfur catalysis vary between 1.8 and 2.1, according to the nature of the disulfide, but the best para isomer selectivity is obtained by using sulfuryl chloride as the chlorinating agent. Sulfuryl chloride has also been used in the presence of sulfides and Lewis acids (14–16). Ortho chlorination is generally favored by using a nonpolar solvent (17). *o*-Chlorophenol can be obtained with a selectivity in the vicinity of 90% by chlorinating the phenol in a halogenated solvent with traces of amines present (18).

Other chlorinating agents, such as pentachlorocyclohexadienone, have been subjected to laboratory study to make it possible to select each of the isomers (19). The use of 2,3,4,5,6,6-hexachlorocyclohexa-2,4-dien-1-one [21306-21-8] makes **chlorination possible in the ortho position**.



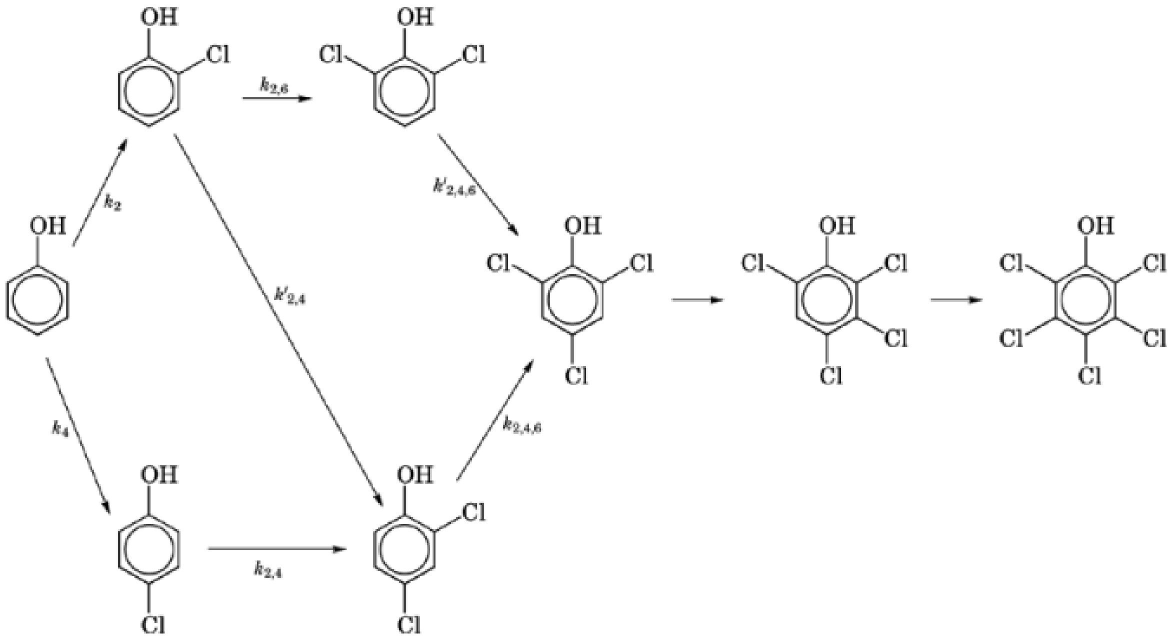
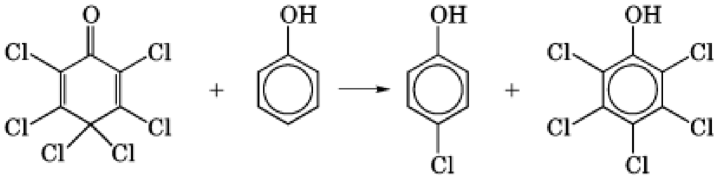


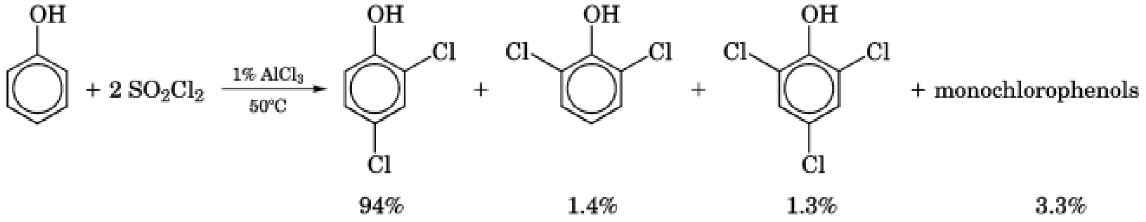
Fig. 1. Kinetics of the chlorination of phenol. Relative rate constants are $k_2=1090$; $k_{2,6}=16$; $k_4=1910$; $k_{2,4,6}=0.9$; $k_{2,4}=124$; $k'_{2,4,6}=0.7$; and $k'_{2,4}=61$.

The 2,3,4,4,5,6-hexachlorocyclohexa-2,5-dien-1-one [599-52-0] **gives the para isomer**.



2.1.2. Dichlorophenols

Among all the dichlorophenols, $C_6H_4Cl_2O$, it is 2,4-dichlorophenol that is produced in greatest quantity. 2,4-Dichlorophenol is used in manufacturing 2,4-dichlorophenoxyacetic acid [94-75-7] (2,4-D) and 2-(2,4-dichlorophenoxy)propionic acid [720-36-5] (2,4-DP). Industrially, 2,4-dichlorophenol can be obtained by chlorinating phenol, *p*-chlorophenol, *o*-chlorophenol, or a mixture of these compounds in cast-iron reactors. The chlorinating agent may be chlorine or sulfuryl chloride in combination with a Lewis acid. For example:



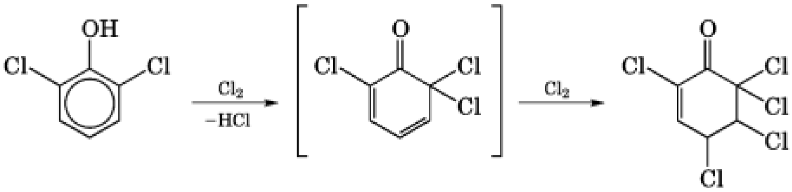
Chlorination with SO_2Cl_2, which is favorable to the para isomer at the monochlorination stage, gives an excellent yield of 2,4-dichlorophenol. Starting with *o*-chlorophenol, it is possible to attain a selectivity for 2,4-dichlorophenol of 98%, if chlorination is carried out in liquid SO_2 at low temperature (20). 2,6-Dichlorophenol is also used as an intermediate. It is obtained by chlorinating *o*-chlorophenol in the presence of a catalytic quantity of an amine, with or without a solvent medium (21, 22), giving a yield of 90%.

2.1.3. 2,4,6-Trichlorophenol

Although 2,4,6-trichlorophenol, $C_6H_3Cl_3O$, can be prepared directly from phenol, the two real precursors are 2,4-dichlorophenol and 2,6-dichlorophenol. The chlorination of these two chlorophenols presents several problems. First, in the chlorination of 2,4-dichlorophenol there is the formation of 2,4,5-trichlorophenol, which is exceedingly troublesome even if present only in trace quantities. The formation of 2,4,5,6,6-pentachloro-2-cyclohexen-1-one is a problem for the 2,6 isomer. Still another problem consists in stopping the process precisely at the tri stage and preventing the formation of tetrachlorophenol or gem-chlorinated cyclohexadienones.

In the chlorination of 2,4-dichlorophenol it has been found that traces of amine (23), onium salts (24), or triphenylphosphine oxide (25) are excellent catalysts to further chlorination by chlorine in the ortho position with respect to the hydroxyl function. During chlorination (80°C, without solvent) these catalysts cause traces of 2,4,5-trichlorophenol ($\sim 500 - 1000$ ppm) to be transformed into tetrachlorophenol. Thus these techniques leave no 2,4,5-trichlorophenol in the final product, yielding a 2,4,6-trichlorophenol of outstanding quality. The possibility of chlorination using SO_2Cl_2 in the presence of Lewis catalysts has been discussed (26), but no mention is made of 2,4,5-trichlorophenol formation or content.

Chlorination of 2,6-dichlorophenol by chlorine at 70°C gives a yield of only 85%. Fifteen percent of the mixture is made up of 2,4,5,6,6-pentachloro-2-cyclohexen-1-one, the formation of which can be explained by **the following mechanism**:



To avoid the formation of this kind of by-product, a direct attack by chlorine in the para position must be encouraged. This can be achieved by using catalysis based on a strong acid (27), or on a sulfur (28), an amine (29), or an onium salt (30). The yields can go as high as 98%.

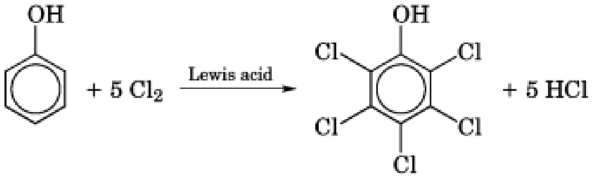
The catalytic systems described thus far have the advantage of preventing large quantities of gem-chlorinated cyclohexadienones from forming. This type of by-product can, however, always be eliminated with reducing agents (25, 31, 32) or acids (33).

2.1.4. Tetrachlorophenol

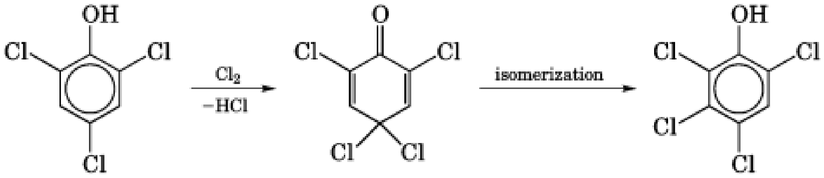
Pure 2,3,4,6-tetrachlorophenol, $C_6H_2Cl_4O$, is not sold commercially because of the difficulty encountered in adjusting the chlorination at the tetra stage. It is found in combination with pentachlorophenol. However, there are patents which describe the use of zirconium tetrachloride (34) or of aluminum trichloride-amine complex (35) as the catalyst to get a yield of 85% for this chlorophenol.

2.1.5. Pentachlorophenol

Because of the high melting temperature of pentachlorophenol, C_6HCl_5O, its preparation makes it necessary to **raise the temperature progressively throughout chlorination. The presence of Lewis acid catalysts is essential.** The most commonly used of these are $AlCl_3$ and $FeCl_3$.

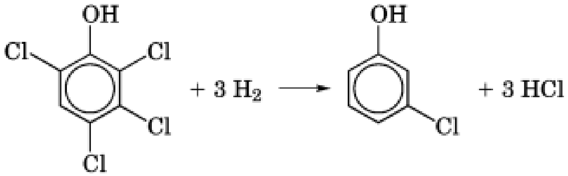


Much research has been done to improve pentachlorophenol selectivity, either by using a solvent or by seeking more effective catalysts (36–40). A recent study has demonstrated the catalytic role of gem-chlorinated cyclohexadienones in the process of by-product formation, in particular for the formation of chlorinated phenoxyphenols. Insofar as the gem-chlorinated cyclohexadienones constitute an **essential intermediate step to the heavier chlorophenols**, their presence during chlorination also explains the quantities of chlorinated phenoxyphenols present in pentachlorophenol.



2.2. Hydrodechlorination

The polychlorophenols can be broken back down into lighter chlorophenols by catalytic hydrogenation with Pd (41, 42), CO (43) in liquid or in gaseous phase (44). This technique is particularly valuable for giving access to phenols chlorinated in the meta position (3-chlorophenol, 3,5-dichlorophenol), because certain conditions yield a **regioselective hydrodechlorination** (45–47)



2.3. Sandmeyer Reaction

This general reaction allows the phenol function to be introduced. The technique complements chlorination insofar as it makes it possible to produce chlorophenols chlorinated in the meta position from the corresponding meta-chlorinated anilines.

2.4. Polyhalogenobenzene Hydrolysis

The chlorobenzenes can be transformed into chlorophenols by hydrolysis in a liquid-phase basic medium. The two most commonly used techniques are treatment in aqueous alkali medium at a temperature between 200 and 350°C (48), or a milder hydrolysis (200–250°C) treatment with dilute sodium hydroxide in the presence of copper. The hydrolysis may be carried out in the vapor phase (250–400°C) on solid catalysts based on rare-earth phosphates (49) or copper-bearing silica.

2.5. Sulfonation–Desulfonation of Chlorobenzenes

Sulfonation of chlorobenzenes can also be used to produce chlorophenols. Sulfonation is carried out at 60–80°C using oleum at 15–20%. The subsequent desulfonation usually calls on aqueous alkali solutions at 15–20% at temperatures between 170 and 230°C.

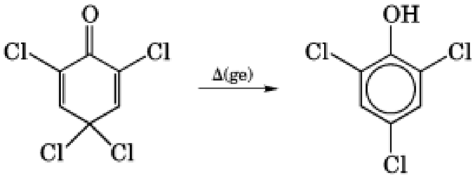
3. Analysis and Specifications

The light chlorophenols, normally have a purity greater than 98.5%, but they often reach over 99%, or even 99.5% with direct phenol chlorination. The APHA color test is always below 100. For 2,4,6-trichlorophenol, the 2,4,5-trichlorophenol content constitutes an essential quality index and should be under 20 mg/kg. None of the light chlorophenols contain any polychlorodibenzoparadioxins or polychlorodibenzofurans.

Polychlorophenoxyphenols are the principal impurity in mixtures of tetrachlorophenols and pentachlorophenols. Traces of polychlorodibenzoparadioxins and polychlorodibenzofurans can also be present if the chlorination is not conducted correctly. 2,3,7,8-Tetrachlorodibenzoparadioxin [1746-01-6], which is highly toxic, has never been detected in any products derived by chlorination.

3.1. Chlorophenol Analysis

The chlorophenols can be analyzed by acidimetric titration of the hydroxyl function (50). This overall method yields only an approximate evaluation for mixtures. To analyze chlorophenol mixtures, gas chromatography has been the reference method used, as it made it possible to separate and quantify the various chlorophenols (51), but this technique can be a source of errors: **the gem-chlorinated cyclohexadienones that may be present along with the chlorophenols are broken back down into lighter chlorophenols** under the analysis conditions usually employed.



Therefore, hplc methods seem more effective. By using a combined uv and electrochemical detection technique (52), the gem-chlorinated cyclohexadienones, the chlorophenols, and the phenoxyphenols present in the chlorination mixtures can be determined with great accuracy.

All the chlorophenols can be separated using C_{18}-grafted silica columns. In NH_2-grafted columns, the elution depends on the pK_a. An electrochemical detector in oxidation mode, more sensitive than uv detectors, is generally used to detect very low quantities, especially in analyzing 2,4,5-trichlorophenol.

Table 2. Worldwide Chlorophenol Production in 1989[a], t / yr

Region	Mono (para + ortho)	Di 2,4	Tri	Penta
Western Europe	8,000	14,000	2,500	4,000
United States, Canada, Brazil		19,000		15,000
Asia	2000–3000	11,000[b]	1,000	6,000[c]
Total	*10,000–11,000*	*44,000*	*3,500*	*25,000*

[a] Excluding China, India, and Russia.
[b] Asia and other miscellaneous countries.
[c] Southeast Asia, South America, and Africa.

Polychlorodibenzodioxins, polychlorodibenzofurans, and polychlorophenoxyphenols formed during thermal or chemical breakdown of chlorophenols can be analyzed by hplc (with uv detection in concentrations as low as ~1 mg/kg) (53). To increase sensitivity and to lower detection thresholds, samples are placed in an alkaline medium, extracted with hexane, and separated in a liquid chromatography column to bunch the products in homogeneous groups. Final detection is effected after gpc separation by electron capture or by mass spectrometry. The detection limit for 2,3,7,8-tetrachlorodibenzodioxin is less than 1 μg/kg.

4. Health and Safety

4.1. Effects in Animals

The LD in rats for all light chlorophenols, irrespective of the administration route, lies between 130 and 4000 mg/kg body weight. The toxicity of these compounds in order of increasing strength is: tetrachlorophenols $>$ monochlorophenols $>$ dichlorophenols $>$ trichlorophenols when the chlorophenol is administered either orally or by subcutaneous injection.

The principal symptoms of chlorophenols at lethal doses are general effects on the central nervous system. Chlorophenols are of medium irritation to the skin and eyes. The effect increases with the number of chlorine atoms in the phenol nucleus. No sensitizing effect has been observed in chlorophenols. Long-term studies have demonstrated effects on the liver and kidneys which accumulate high concentrations of chlorophenols. A carcinogenicity study of 2,4-dichlorophenol run for two years in rats and mice proved negative. The toxicology of chlorophenols is made more complicated by the presence of microcontaminants such as polychlorophenoxyphenols and polychlorodibenzofurans in the technical products.

4.2. Effects in Humans

In chlorophenol production, irritation symptoms of the nose, eyes, respiratory tract, and skin resulting in chloroacne have been observed. The results of epidemiology studies on the long-term effects of chlorophenols are quite contradictory and have not allowed the experts to reach any firm conclusions (54).

5. Economic Aspects

Overall, the chlorophenol market is in decline. Table 2 gives worldwide production figures for 1989, excluding China, India, and Russia. Part of Western Europe's production is exported to Russia for reasons of quality. The main producers are brought together in Table 3 according to the nature of their chlorophenol production.

Table 3. Producers of Light Chlorophenols

Chlorophenol	Producers	Country
o-chlorophenol	Rhône-Poulenc	France
p-chlorophenol	Rhône-Poulenc	France
	Coalite	UK
	Inui	Japan
2,4-dichlorophenol	Dow[a]	United States, Brazil
	Rhône-Poulenc	France
	Coalite	UK
2,4,6-trichlorophenol	Coalite	UK
	Rhône-Poulenc	France
	Inui	Japan

[a] Dow produces 2,4-dichlorophenol chiefly for a captive market in the United States and Brazil.

Table 4. Pentachlorophenol Producers

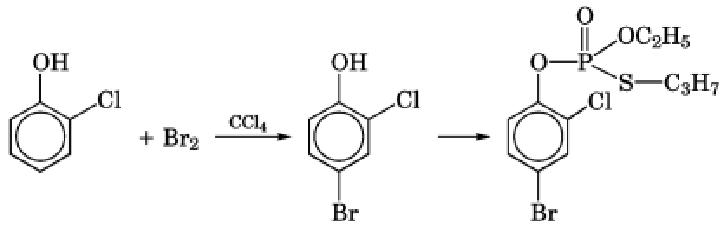
Producer	Production, t/yr	Product
Vulcan (USA)	12,000	pentachlorophenol
Idacon (USA)	8,000	pentachlorophenol
Rhône-Poulenc	4,000	pentachlorophenol, Na pentachlorophenate
Chapman	1,500	Na pentachlorophenate

Rhône-Poulenc, with a capacity of around 20,000 t/yr, is the world's leading producer of light chlorophenols. Excluding the unknown factors for which no statistics are available (China, Russia), the market for pentachlorophenol can be estimated at $\sim 25,000$ t/yr. The principal producers of pentachlorophenol are given in Table 4.

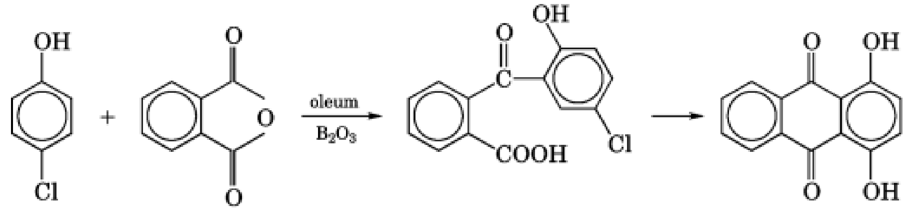
6. Applications

The main applications of mono-, di-, or trichlorophenols are in agrochemicals and for pentachlorophenol in wood protection.

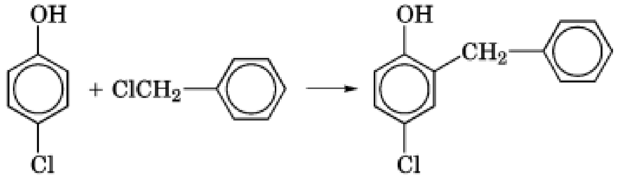
2-Chlorophenol is used chiefly in the **manufacture of an insecticide** [41198-08-7] (55, 56)



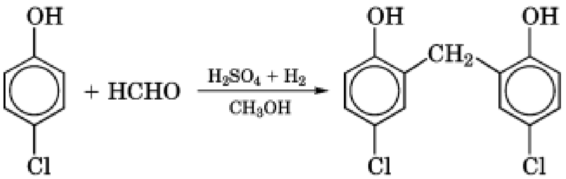
One of the most important applications of 4-chlorophenol is **in the synthesis of derivatives of** quinizarin [81-64-1], anthraquinone dyes (see Dyes, anthraquinone).



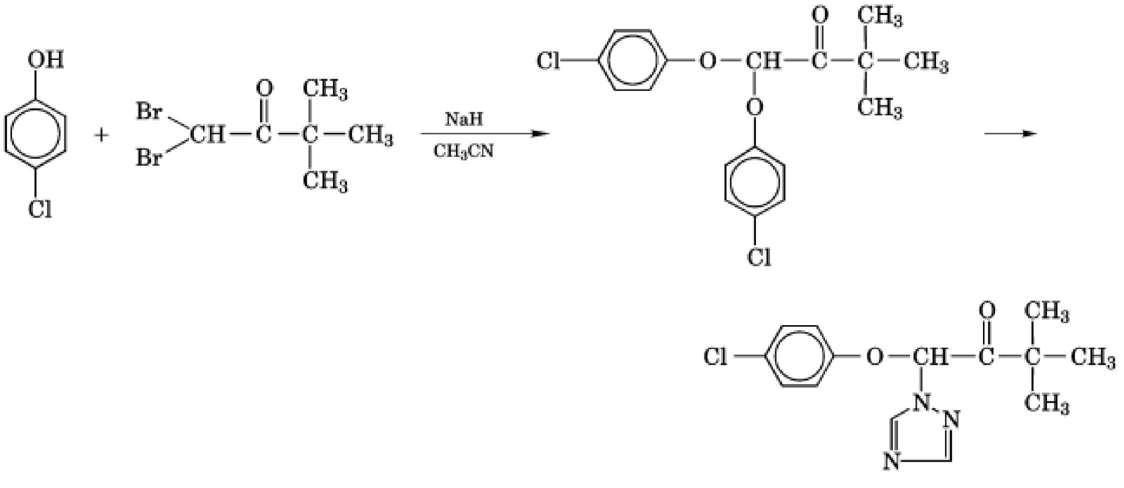
4-Chlorophenol also enters into **the synthesis of a biocide** (57), 2-benzyl-4-chlorophenol [120-32-1].



4-Chlorophenol is one of the raw materials used for **the synthesis of two fungicides**, dichlorophen [97-23-4] and triadimefon [43121-43-3] (58, 59).

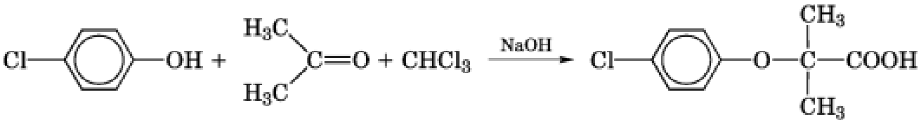


dichlorophen

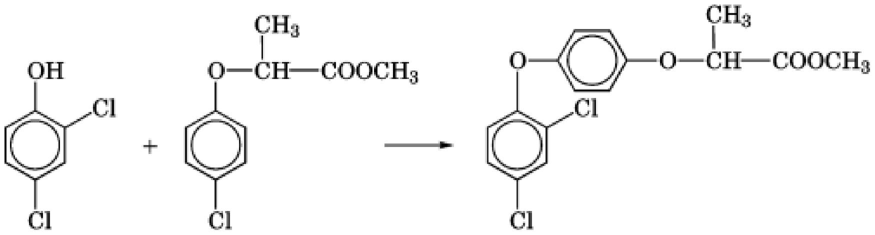


triadimefon

Another application of 4-chlorophenol is in **the synthesis of a drug**, ethyl α, α-dimethyl-4-chlorophenoxy acetate [637-07-0] (60), used as a cholesterol-reducing agent. This synthesis involves reaction with acetone and chloroform, followed by ethanol esterification.

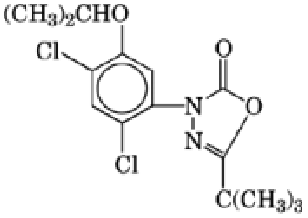


In addition to the use of 2,4-dichlorophenol in the synthesis of 2,4-D herbicides (acid 2,4-D, acid 2,4-DP, acid 2,4-DB), it is also found in **the selective post-emergence herbicide**, diclofop-methyl [51338-27-3] (61) and as **a selective pre-emergence herbicide**, oxadiazon [19666-30-9] (62). A postemergence herbicide is applied between the emergence of a seedling and the maturity of a crop plant.



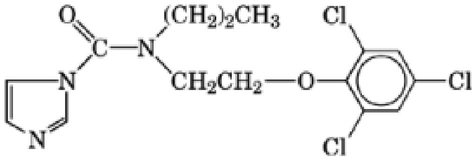
diclofop-methyl

A preemergence herbicide is used before emergence of seedlings above ground.



oxadiazon

2,4,6-Trichlorophenol has had two main applications. It is still widely used in **the synthesis of a fungicide**, prochloraz [67747-09-5] (63).



It is also used to manufacture chloranile, [118-75-2], a coloring agent, but a new process to synthesize this product has greatly reduced this market. This new process, with hydroquinone as raw material (64–67), has the advantage of giving a product of much higher quality than can be obtained with 2,4,6-trichlorophenol.

Pentachlorophenol is used in three types of products for treating and preserving wood. One is the provisional protection of freshly cut wood from blue rot by soaking it in an aqueous solution containing 3–5% sodium pentachlorophenate. The protection lasts 6–11 months. Sodium pentachlorophenate [131-52-2] is formed by the reaction of pentachlorophenol with NaOH. The second use is the long-term protection of wood from fungi by soaking it or permeating it in an autoclave with solvents containing pentachlorophenol at 3–5% concentration. Protection lasts 25–40 years. This is the only use of pentachlorophenol in the United States. Last is the treatment of heavy-duty textiles used in manufacturing cables, rigging, and tarpaulins. The treatment is based on the lauric ester of pentachlorophenol. This market is not large and no longer exists in the United States.

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