CHLOROTOLUENES, RING

1. Introduction

The ring-chlorinated derivatives of toluene form a group of stable, industrially important compounds. Many chlorotoluene isomers can be prepared by direct chlorination. Other chlorotoluenes are prepared by indirect routes involving the replacement of amino, hydroxyl, chlorosulfonyl, and nitro groups by chlorine and the use of substituents, such as nitro, amino, and sulfonic acid, to orient substitution followed by their removal from the ring.

The first systematic study of the reaction of chlorine with toluene was carried out in 1866 by Beilstein and Geitner. During the next 40 years, many studies were performed to isolate and identify the various chlorination products (1). During the early 1930s, Hooker Electrochemical Co. (Hooker Chemicals & Plastics Corp.) and the Heyden Chemical Corp. (Tenneco) began the manufacture of chlorotoluenes. Hooker Electrochemical Co. was later acquired by Occidental Petroleum Corp. and became the Occidental Chemical Corp. In the mid-1970s, Heyden exited chlorotoluenes production; Occidental exited the buisness in 2000. The current world producers are: Bayer (Germany), Tessenderlo (formerly Enichem in Italy), Ihara, Hodogaya (both in Japan), Zhuzhou, and Danyang (both in China).

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Mono- and dichlorotoluenes are used chiefly as chemical intermediates in the manufacture of pesticides, dyestuffs, pharmaceuticals, and peroxides, and as solvents. Total annual production was limited prior to 1960 but has expanded greatly since that time. Chlorinated toluenes are produced in Germany, Japan, Italy and China. Since the number of manufacturers is small and much of the production is utilized captively, statistics covering production quantities are not available. Worldwide annual production of *o*- and *p*-chlorotoluene is estimated at several tens of thousands of metric tons. Yearly productions of polychlorotoluene are in the range of 100–1000 tons.

2. Monochlorotoluenes

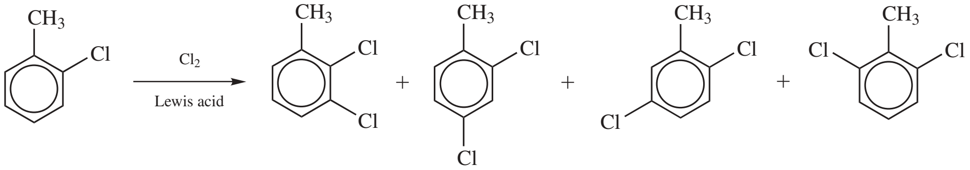
2.1. Physical Properties. *o*-Chlorotoluene [95-49-8] (1-chloro-2-methylbenzene, OCT) is a mobile, colorless liquid with a penetrating odor similar to chlorobenzene. It is miscible in all proportions with many organic liquids such as aliphatic and aromatic hydrocarbons, chlorinated solvents, lower alcohols, ketones, glacial acetic acid, and di-*n*-butylamine; it is insoluble in water, ethylene and diethylene glycols, and triethanolamine.

p-Chlorotoluene [106-43-4] (1-chloro-4-methylbenzene, PCT) and *m*-chlorotoluene [108-41-8] (1-chloro-3-methylbenzene, MCT) are mobile, colorless liquids with solvent properties similar to those of the ortho isomer.

Ortho and *p*-chlorotoluene form binary azeotropes with various organic compounds including alcohols, acids, and esters (2). Oxygen indexes, the minimum percentage of oxygen in an oxygen-nitrogen atmosphere required to sustain combustion after ignition, for the chlorotoluene isomers are ortho 19.2, meta 19.7, and para 19.1 (3). Ortho and *p*-chlorotoluene form stable ionic complexes with antimony pentachloride (4). They also form complexes with a number of organometallic derivatives, such as those of chromium (5), cobalt (6), iron (7), etc, many of which have synthetic utility. Physical properties of the monochlorotoluene isomers, mol wt 126.59, appear in Table 1 (8–13).

2.2. Chemical Properties. The monochlorotoluenes are stable to the action of steam, alkalies, amines, and hydrochloric and phosphoric acids at moderate temperatures and pressures. Three classes of reactions, those involving the aromatic ring, the methyl group, and the chlorine substituent, are known for monochlorotoluenes.

Reactions of the Aromatic Ring. Ring chlorination of *o*-chlorotoluene yields a mixture of all four possible dichlorotoluenes, the 2,3-, 2,4-, 2,5-, and 2,6-isomers as shown in equation 1 (14).



(1)

Table 1. **Physical Properties of the Monochlorotoluenes, C_7H_7Cl**

	Isomer		
Property	Ortho	Meta	Para
mp, °C	−35.6	−47.8	7.5
bp, °C	159.2	161.7	162.4
flash point, °C	47	47	49
density[a], kg/m^3			
20°C	1082.5	1072.2	1069.7
25°C	1077.6		$1065.1^{24.4}$
30°C	1072.7		
refractive index[a], n_D^t			
20°C	1.52680	1.5214^{19}	1.5211
25°C	1.52221		$1.5193^{24.4}$
surface tension[a], mN/m (= dyn/cm)	334.4^{20} 323.3^{30}		322.4^{25} 292.2^{30}
dielectric constant at 20°C	4.73	5.55	6.20
viscosity (dynamic), mPa·s (= cP)			0.09
dipole moment, C · m[b]	4.80×10^{-30}	5.97×10^{-30}	
heat of vaporization, kJ/mol[c]	43.01	42.18	42.475
vapor density (air = 1)			4.37
vapor pressure, °C at kPa[d]			
0.13	5.4	4.8	5.5
1.3	43.2	43.2	43.8
5.3	72.0	73.0	73.5
13.3	94.7	96.3	96.6
53.3	137.1	139.7	139.8

[a] Superscript indicates temperature.

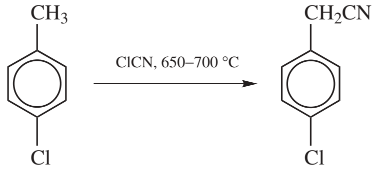
[b] To convert C·m to debye, divide by 3.336×10^{-30}.

[c] To convert kJ to kcal, divide by 4.184.

[d] To convert kPa to mm Hg, multiply by 7.5.

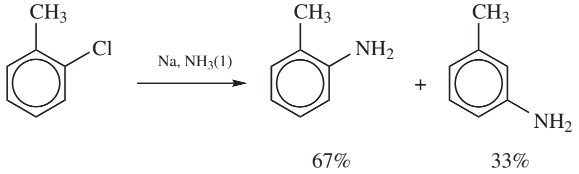
The principal isomer, 2,5-dichlorotoluene, constitutes up to 60% of the product mixture (15,16). Similarly, nitration of *o*-chlorotoluene produces a mixture of the four corresponding nitrochlorotoluene isomers. Nitration of *p*-chlorotoluene gives a mixture of 66% 4-chloro-2-nitrotoluene [89-59-8] and 34% of 4-chloro-3-nitrotoluene [89-60-1], $C_7H_6ClNO_2$, (17). Chlorosulfonation of *o*-chlorotoluene produces 2-chloro-5-chlorosulfonyltoluene [6291-02-7], (4-chloro-3-methylbenzene-sulfonyl chloride), $C_7H_6Cl_2O_2S$, as the principal product (18). Sulfonation of *p*-chlorotoluene with 20% oleum gives the 2-sulfonic acid derivative in 68% yield (19). Trifluoromethylation of monochlorotoluenes has been achieved by reaction with carbon tetrachloride and hydrogen fluoride (20). Chloromethylation of *o*-chlorotoluene gives 2-chloro-4-chloromethyltoluene [2719-40-6] as the sole product. With *p*-chlorotoluene, a mixture of 4-chloro-2-chloromethyltoluene [34060-72-5] and 4-chloro-3-chloromethyltoluene [34896-68-9], $C_8H_8Cl_2$, is formed in a 63:37 ratio, respectively (21).

Reactions of the Methyl Group. Monochlorotoluenes are widely used to synthesize compounds derived from reactions of the methyl group. Chlorination under free-radical conditions leads successively to the chlorinated benzyl, benzal, and benzotrichloride derivatives (see CHLOROCARBONS AND CHLOROHYDROCARBONS—BENZYL CHLORIDE, BENZAL CHLORIDE, AND BENZOTRICHLORIDE). Oxidation to form chlorinated benzaldehydes and benzoic acids can be performed under both liquid- and vapor-phase conditions (22,23). Catalytic ammoxidation under vapor-phase conditions with oxygen and ammonia produces chlorobenzonitriles (24). Reaction of *p*-chlorotoluene with cyanogen chloride at 650–700°C gives *p*-chlorophenylacetonitrile [140-53-4], C_8H_6ClN, as shown in equation 2 (25). Side-chain bromination of *p*-chlorotoluene by bromine catalyzed by lanthanum triacetate is a facile process (26).



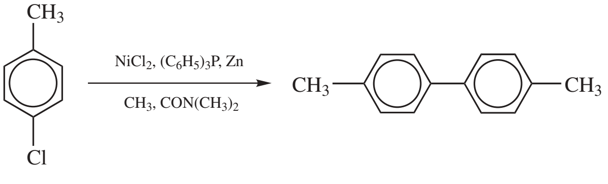
(2)

Halogen Reactions. Hydrolysis of chlorotoluenes to cresols has been effected by aqueous sodium hydroxide. Both displacement and benzyne formation are involved (27,28). *o*-Chlorotoluene reacts with sodium in liquid ammonia to afford a mixture of 67% of *o*-toluidine [95-53-4] and 33% of *m*-toluidine [108-44-1], C_7H_9ClN, as shown in equation 3 (29).



(3)

With hydrogen sulfide at 500–600°C, monochlorotoluenes form the corresponding thiophenol derivatives (30). In the presence of palladium catalysts and carbon monoxide, monochlorotoluenes undergo carbonylation at 150–300°C and 0.1–20 MPa (1–200 atm) to give carboxylic acids (31). Oxidative coupling of *p*-chlorotoluene to form 4,4′-dimethylbiphenyl can be achieved in the presence of an organonickel catalyst, generated *in situ*, and zinc in dipolar aprotic solvents such as dimethylacetamide (32,33). An example is shown in equation 4.



(4)

Dehalogenation of monochlorotoluenes can be readily effected with hydrogen and noble metal catalysts (34). Conversion of *p*-chlorotoluene to *p*-cyanotoluene is accomplished by reaction with tetraethylammonium cyanide and zero-valent Group (VIII) metal complexes, such as those of nickel or palladium (35). The reaction proceeds by initial oxidative addition of the aryl halide to the zerovalent metal complex, followed by attack of cyanide ion on the metal and reductive elimination of the aryl cyanide. *p*-Methylstyrene is prepared from *p*-chlorotoluene by a vinylation reaction using ethylene as the reagent and a catalyst derived from zinc, a triarylphosphine, and a nickel salt (36).

2.3. Preparation. Monochlorotoluenes have been prepared by chlorinating toluene with a wide variety of chlorinating agents, catalysts, and reaction conditions. The ratio of ortho and para isomers formed can vary over a wide range. Particular attention has been given to studies aimed at increasing the para isomer content owing to its greater commercial significance. The meta isomer can be prepared by either indirect means since only a small amount, <1%, is formed by direct chlorination or by isomerization of the ortho isomer (97). Isolation may then be achieved by selective absorption/desorbtion with various zeolites. (98)

Chlorinations with Elemental Chlorine. Reaction of toluene with chlorine in the presence of certain Lewis acid catalysts including the chlorides of aluminum, tin, titanium, and zirconium give monochlorotoluene mixtures that contain more than 70% of the ortho isomer (37,38). A number of catalyst systems have been developed to enhance the formation of *p*-chlorotoluene in toluene chlorination. Monochlorotoluenes containing 45–55% of the *p*-isomer are obtained through the use of certain specific metal sulfides or cocatalyst systems consisting of specific metal salts and sulfur, inorganic sulfides, or divalent sulfur compounds with or without other functional groups (39–45). A growing number of heterogeneous processes that employ zeolite-type catalysts for chlorination of aromatics have been discovered (see CATALYSIS). The majority of these catalysts are synthetic zeolites, specifically the L-type zeolites (46). It is sometimes possible to achieve highly regioselective chlorination of arenes, such as toluene, by the use of certain specific types of zeolites. A catalyst system comprised of TSZ-506, which is a synthetic zeolite, and monochloroacetic acid affords *p*-chlorotoluene with a selectivity of 75% relative to the ortho isomer at an operating temperature of 70°C (47). One common problem during zeolite-catalyzed chlorination is the structural breakdown of the zeolite lattice because of reaction with hydrogen chloride liberated in the reaction. However, modifications in the synthetic procedure have enabled the preparation of newer types of zeolites that are more resistant to structural deterioration (48).

Noncatalytic ring chlorination of toluene in a variety of solvents has been reported. Isomer distributions vary from approximately 60% ortho in hydroxylic solvents, eg, acetic acid, to 60% para in solvents, eg, nitromethane, acetonitrile, and ethylene dichloride (49,50). Reaction rates are relatively slow and these systems are particularly appropriate for kinetic studies.

Chlorination with Other Reagents. Chlorotoluenes can also be obtained in good yields by the reaction of toluene with stoichiometric proportions of certain Lewis acid chlorides such as iron(III) chloride, as the chlorinating agent (51). Generally, the product mixture contains *p*-chlorotoluene as the principal component. Several modifications have been proposed to improve product yields (52,53).

Toluene chlorination has also been effected with hydrogen chloride as the chlorinating agent. The reaction is catalyzed by nitric acid under aqueous conditions to give a good conversion and yield on monochlorotoluenes (54). Oxychlorination of toluene with oxygen and hydrogen chloride in the vapor phase over supported copper and palladium catalysts yields chlorotoluene mixtures containing up to 60% of *p*-chlorotoluene along with varying amounts of side-chain chlorinated products (55,56).

Other methods for preparing *p*-chlorotoluene include α-elimination from an organotellurium(IV) halide (57), palladium-catalyzed decarbonylation of 4-methylbenzoyl chloride (58), and desulfonylation of *p*-toluenesulfonyl chloride catalyzed by chlorine (59) or chlorotris(triphenylphosphine)rhodium (60).

Pure monochlorotoluene isomers are prepared by diazotization of the corresponding toluidine isomers followed by reaction with copper(I) chloride (Sandmeyer reaction). This is the preferred method of obtaining *m*-chlorotoluene.

Significant yields of *m*-chlorotoluene have been reported by reacting 3-methyl-phenol with phenylphosphorous pentachloride at 160°C (99). Also, *m*-chlorotoluene as a co-product has been reported by reacting trifluoromethyl benzene in a reagent system of nitryl chloride and titanium tetrachloride (100).

The rate of chlorination of toluene relative to that of benzene is about 345 (61). Usually, chlorination is carried out at temperatures below 70°C with the reaction proceeding at a profitable rate even at 0°C. The reaction is exothermic with ca 139 kJ (33 kcal) of heat produced per mole of monochlorotoluene formed. Chlorine efficiency is high, and toluene conversion to monochlorotoluene can be carried to about 90% with the formation of only a few percent of dichlorotoluenes. In most catalyst systems, decreasing temperatures favor formation of increasing amounts of *p*-chlorotoluene. Concentrations of required catalysts are low, generally on the order of several tenths of a percent or less.

Only trace amounts of side-chain chlorinated products are formed with suitably active catalysts. It is usually desirable to remove reactive chlorides prior to fractionation in order to minimize the risk of equipment corrosion. The separation of *o*- and *p*-chlorotoluenes by fractionation requires a high efficiency, isomer-separation column. The small amount of *m*-chlorotoluene formed in the chlorination cannot be separated by fractionation and remains in the *p*-isomer fraction. The toluene feed should be essentially free of paraffinic impurities that may produce high boiling residues that foul heat-transfer surfaces. Trace water contamination has no effect on product composition. Steel can be used as construction material for catalyst systems containing iron. However, glass-lined equipment is usually preferred and must be used with other catalyst systems.

Both batch and continuous processes are suitable for commercial chlorination. The progress of the chlorination is conveniently followed by specific gravity measurements.

2.4. Handling and Shipment. Monochlorotoluenes are shipped in bulk in steel tank cars and tank trucks. Drum shipments are made using lined or unlined steel drums. Aluminum tanks can be used to store only acid-free material. Under DOT regulations, for transport of over 415 L (110 gal) of monochlorotoluenes, freight classification is combustible liquid NOS, and for truck transport, chemical NOI. The storage vessels are vented to a safe atmosphere and should be protected with suitable diking. Protection against static charge is essential when transferring material. Suitable ventilation should be provided and sources of ignition avoided as the vapor forms flammable mixtures with air.

2.5. Identification and Analysis. A number of analytical methods have been developed for the determination of chlorotoluene mixtures by gas chromatography. These are used for determinations in environments such as air near

Table 2. **Toxicity Parameters for Monochlorotoluenes**

Parameter	Ortho	Para
LD_{50} (rat), mg/kg	2350[a]	2100[b]
TLV[c], ppm	50	
PEL[d], ppm	50	

[a] Ref. 69.
[b] Ref. 70.
[c] ACGIH, 259 mg/m^3, 8 h TWA (71).
[d] OSHA, 250 mg/m^3, 8 h TWA.

industry (62) and soil (63). Liquid crystal stationary columns are more effective in separating *m*- and *p*-chlorotoluene than conventional columns (64). Prepacked columns are commercially available. Zeolites have been examined extensively as a means to separate chlorotoluene mixtures (see MOLECULAR SIEVES). For example, a Y-type zeolite containing sodium and copper has been used to separate *m*-chlorotoluene from its isomers by selective absorption (65). The presence of benzylic impurities in chlorotoluenes is determined by standard methods for hydrolyzable chlorine. Proton (66) and carbon-13 chemical shifts, characteristic IR absorption bands, and principal mass spectral peaks are available along with sources of reference spectra (67).

2.6. Health and Safety Factors. Inhalation of high concentrations of monochlorotoluenes will cause symptoms of central nervous system depression. Inhalation studies produced an LC_{50} (rat, 4 h) of 7119 ppm for *o*-chlorotoluene (68). *o*- and *p*-Chlorotoluene are both considered moderately toxic by ingestion (Table 2). A study of the relationship between the electronic structure and toxicity parameters for a series of mono-, di-, and tri-chlorotoluenes has been reviewed (72). A thin-layer chromatographic method has been developed to assess the degree of occupational exposure of workers to chlorotoluenes by determining *p*-chlorohippuric acid [13450-77-6], $C_9H_8ClNO_3$, (*N*-(4-chlorobenzoyl)glycine) in urine samples (73). Health and environmental issues related to chlorinated toluenes are included in the Hazardous Substances Data Bank (101).

A study to isolate and examine the genetic characteristics of bacteria that metabolize chlorotoluenes, such as OCT, PCT, and 2,6-dichlorotoluene, has been reported (74). Two products were isolated from a study of the metabolism of PCT by *Pseudomonas putida*: (+)-*cis*-4-chloro-2,3-dihydroxy-1-methylcyclohex-4,6-diene and 4-chloro-2,3-dihydroxy-1-methylbenzene (75). Enzymatic dehydrogenation of the former compound to the latter was also demonstrated.

3. Higher Chlorotoluenes

3.1. Dichlorotoluenes. There are six possible dichlorotoluene isomers, $C_7H_6Cl_2$, (mol wt 161.03) all of which are known. Physical properties of the dichloro- and other higher chlorotoluenes are given in Table 3.

2,4-Dichlorotoluene (2,4-dichloro-1-methylbenzene) constitutes 80–85% of the dichlorotoluene fraction obtained in the chlorination of PCT with antimony trichloride (76) or zirconium tetrachloride (77) catalysts. It is separated from

Table 3. **Physical Properties of the Higher Chlorotoluenes**

Toluene	CAS Registry number	Mp, °C	Bp, °C	n_D^t	Density at 20°C, kg/m^3
2,3-dichloro	[32768-54-0]	5	208.3	1.5511^{20}	
2,4-dichloro	[95-73-8]	−13.5	201.1	1.5480^{22}	1249.8
2,5-dichloro	[19398-61-9]	5	201.8	1.5449^{20}	1253.5
2,6-dichloro	[118-69-4]		200.6	1.5507^{20}	1268.6
3,4-dichloro	[95-75-0]	−15.3	208.9	1.5471^{20}	1256.4
3,5-dichloro	[25186-47-4]	26	201.2	1.5438^{20}	
2,3,4-trichloro	[7359-72-0]	43–44	244		
2,3,5-trichloro	[56961-86-5]	45–46	229–231		
2,3,6-trichloro	[2077-46-5]	45–46	118[a]		
2,4,5-trichloro	[6639-30-1]	82.4	229–230[b]		
2,4,6-trichloro	[23749-65-7]	38			
3,4,5-trichloro	[21472-86-6]	45–45.5	246–247[c]		
2,3,4,5-tetrachloro	[1006-32-2]	98.1			
2,3,4,6-tetrachloro	[875-40-1]	92	266–276		
2,3,5,6-tetrachloro	[1006-31-1]	93–94			
pentachloro	[877-11-2]	224.5–225.5	301		

[a] At 2.4 kPa (18 mm Hg).
[b] At 95.4 kPa (716 mm Hg).
[c] At 102.4 kPa (768 mm Hg).

3,4-dichlorotoluene (1,2-dichloro-4-methylbenzene), the principal contaminant, by distillation. Chlorination of OCT with sulfuryl chloride gives mainly 2,4-dichlorotoluene and small amounts of the 2,3 isomer (78). 2,5-Dichlorotoluene (1,3-dichloro-2-methylbenzene) is formed in up to 60% yield in the sulfide-cocatalyzed chlorination of OCT. Purification by recrystallization gives 99% pure product (15,16).

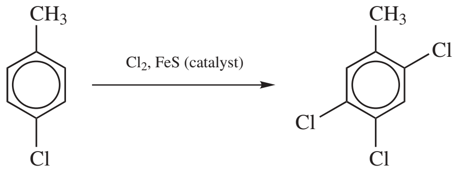
Chlorination of OCT with chlorine at 90°C in the presence of L-type zeolites as catalyst reportedly gives a 56% yield of 2,5-dichlorotoluene (79). Pure 2,5-dichlorotoluene is also available from the Sandmeyer reaction on 2-amino-5-chlorotoluene. 3,4-Dichlorotoluene (1,2-dichloro-4-methylbenzene) is formed in up to 40% yield in the chlorination of PCT catalyzed by metal sulfides or metal halide–sulfur compound cocatalyst systems (80).

2,3-Dichlorotoluene (1,2-dichloro-3-methylbenzene) is present in about 10% concentration in reaction mixtures resulting from chlorination of OCT. It is best prepared by the Sandmeyer reaction on 3-amino-2-chlorotoluene.

2,6-Dichlorotoluene (1,3-dichloro-2-methylbenzene) is prepared from the Sandmeyer reaction on 2-amino-6-chlorotoluene. Other methods include ring chlorination of *p*-toluenesulfonyl chloride followed by desulfonylation (81), and chlorination and dealkylation of 4-*tert*-butyltoluene (82) or 3,5-di-*tert*-butyltoluene (83,84). Isomerization (102) and purification (103) of 2,6-DCT, prepared as a mixture with 2,3-,2,4-, and 2,5-DCT from the $FeCl_3$ catalyzed chlorination of OCT, can be achieved by the use of zeolites, in a fashion similar to MCT, above.

3.2. Trichlorotoluenes. The chlorination of toluene and *o*- and *p*-chlorotoluenes produces a mixture of trichlorotoluenes, ($C_7H_5Cl_3$, (mol wt 195.48): the 2,3,6-isomer (1,2,4-trichloro-3-methylbenzene) and 2,4,5-trichlorotoluene (1,2,4-trichloro-5-methylbenzene) containing small amounts of 2,3,4-trichlorotoluene

(1,2,3-trichloro-4-methylbenzene) and 2,4,6-trichlorotoluene (1,3,5-trichloro-2-methylbenzene). When toluene is chlorinated in the presence of iron(III) chloride catalyst, a mixture containing nearly equal amounts of 2,4,5- and 2,3,6-trichlorotoluenes is produced (38,85). Chlorination of OCT yields a mixture containing $>60\%$ of 2,3,6-trichlorotoluene (86). Reaction of *p*-toluenesulfonic acid with chlorine and antimony trichloride in chloroform and then sulfuric acid at reflux affords 2,3,6-trichlorotoluene in 89% yield (87). Metal sulfide-catalyzed chlorination of PCT gives trichlorotoluene fractions containing more than 75% of the 2,4,5-isomer (eq. 5) (88). The other chlorotoluenes are available from the Sandmeyer reaction on the corresponding amines. A gas chromatographic study has been conducted to determine the isomer selectivity of stationary phases of different polarity with respect to various chlorotoluenes including the trichlorotoluene isomers (89).



(5)

Gas-phase ammoxidation of trichlorotoluenes in the presence of catalyst affords the corresponding benzonitrile derivatives (90). In a 28-day feeding study, 2,3,6-trichlorotoluene showed only mild toxicological changes when administered to rats (91).

3.3. Tetra- and Pentachlorotoluenes. 2,3,4,6-Tetrachlorotoluene, $C_7H_4Cl_4$ (mol wt 229.93) (1,2,3,5-tetrachloro-4-methylbenzene), is prepared from the Sandmeyer reaction on 3-amino-2,4,6-trichlorotoluene. 2,3,4,5-Tetrachlorotoluene (1,2,3,4-tetrachloro-5-methylbenzene) is the principal isomer in the further chlorination of 2,4,5-trichlorotoluene. Exhaustive chlorination of *p*-toluenesulfonyl chloride, followed by hydrolysis to remove the sulfonic acid group yields 2,3,5,6-tetrachlorotoluene (1,2,4,5-tetrachloro-3-methylbenzene) in good yield (92). Pentachlorotoluene (pentachloromethylbenzene), $C_7H_3Cl_5$ (mol wt 264.37), is formed in 90% yield by the ferric chloride-catalyzed chlorination of toluene in carbon tetrachloride or hexachlorobutadiene solution (93). Oxidation of pentachlorotoluene with excess sulfur trioxide, followed by hydrolysis of the intermediate pentachlorobenzyl disulfooxonium hydroxide inner salt produces pentachlorobenzyl alcohol in 91% yield (94). Gas chromatographic separation selectivities of stationary phases of different polarities toward tetrachlorotoluene isomers and pentachlorotoluene have been examined (89).

4. Uses

Chlorotoluenes are used as intermediates in the pesticide, pharmaceutical, peroxide, dye, and other industries. Many side chain-chlorinated derivatives are converted to end products. *p*-Chlorotoluene is used primarily in the manufacture of *p*-chlorobenzotrifluoride [98-56-6], a key intermediate in dinitroaniline and diphenyl ether herbicides (95). Other applications include manufacture of *p*-chlorobenzyl chloride, *p*-chlorobenzaldehyde, *p*-chlorobenzoyl chloride, *p*-chlorobenzoic acid, and 2,4- and 3,4-dichlorotoluenes. *p*-Chlorotoluene is an intermediate for a novel class of polyketone polymers (96).

Mono and di-chlorotoluenes have been used as a solvent/desorbent to separate dichlorobenzenes using zeolites (104–107). Separation of 3,5-Dichlorocumene from its isomeric mixture in pure form was achieved by using zeolites and subsequent desorption from the zeolites was effected by using mono or dichlorotouene(108), *o*-Chlorotoluene use as a solvent was identified in the preparation of hydroxynaphthoic acid arylides (109).

Chlorotoluene isomer mixtures, especially those containing a relatively high amount of *o*-chlorotoluene, are widely used as solvents in industry for such purposes as metal-cleaning formulations, railroad industrial cleaners, diesel fuel additives, carbon removal procedures, paint thinners, and agricultural chemicals. Halso 99 and Halso 125 are examples of such solvents. Separation of methanol and methylcarbonate by distillation was effected by *o*-Chlorotoluene as an extractant(110)

2,4-Dichlorotoluene is an intermediate for manufacture of herbicides. It is also used to obtain 2,4-dichlorobenzyl chloride and 2,4-dichlorobenzoyl chloride. 2,4-Dichlorotoluene has been used as a solvent in the preparation of trifluoromethylpyridine derivatives(111). 2,6-Dichlorotoluene is applied as a herbicide and dyestuff intermediate. 2,6-Dichlorotoluene has been used as an entrainer to separate ethanol from isopropanol by extractive distillation(112). 2,3,6-Trichlorotoluene is used as a herbicide intermediate. The other polychlorotoluenes have limited industrial application.

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