# CHLOROTOLUENES, BENZYL CHLORIDE, BENZAL CHLORIDE, AND BENZOTRICHLORIDE

## 1. Introduction

The chlorination of toluene in the absence of Lewis Acid catalysts occurs preferentially in the side chain. In the presence of Lewis Acid catalysts, ring chorination is the predominant pathway. Reaction on the side chain is promoted by free-radical initiators such as ultraviolet light, peroxides or Vazo® catalysts. Chlorination of the side chain takes place sequentially and can be controlled to give good yields of the intermediate chlorination products. Small amounts of metal sequestering agents are sometimes used to remove trace amounts of metal ions that promote ring chlorination.

Experimental data taken from the chlorination of toluene in an irradiated continuous stirred tank flow reactor at 111°C result in the product distribution shown in Table 1 (1).

Nearly all of the benzyl chloride [100-44-7], benzal chloride [98-87-3], and benzotrichloride [98-07-7] manufactured is converted to other chemical intermediates or products by reactions involving the chlorine substituents of the side chain. Each of the compounds has a single primary use that consumes the majority portion of the compound produced. Benzyl chloride is utilized in the manufacture of benzyl butyl phthalate, a vinyl resin plasticizer; benzal chloride is hydrolyzed to benzaldehyde; benzotrichloride is converted to benzoyl chloride. Benzyl chloride is also hydrolyzed to benzyl alcohol, which is used in the photographic industry, in perfumes (as esters), and in peptide synthesis by conversion to benzyl chloroformate [501-53-1] (see BENZYL ALCOHOL AND β-PHENETHYL ALCOHOL; CARBONIC AND CARBONOCHLORIDIC ESTERS).

Table 1. **Distributions of Reactor Products[a] from Batch Chlorination of Toluene**

| Mol $Cl_2$ / Mol reactant in product | Toluene | Benzyl chloride | Benzal chloride | Benzotrichloride |
|---|---|---|---|---|
| 0.30 | 0.717 | 0.271 | 0.012 | |
| 0.51 | 0.507 | 0.480 | 0.013 | |
| 0.82 | 0.250 | 0.685 | 0.065 | |
| 0.98 | 0.138 | 0.744 | 0.118 | |
| 1.19 | 0.040 | 0.729 | 0.231 | |
| 1.32 | 0.030 | 0.672 | 0.325 | |
| 1.53 | | 0.482 | 0.503 | 0.015 |
| 1.95 | | 0.105 | 0.842 | 0.053 |
| 2.18 | | 0.016 | 0.774 | 0.210 |

[a] Mole fractions.

Several related compounds, primarily ring-chlorinated derivatives, are also commercially significant. Compounds such as *p*-chlorobenzotrichloride, *o*-chlorobenzotrichloride, 3,4-dichlorobenzotrichloride, 2,4-dichlorobenzylchloride and others can be similarily prepared by the free radical chlorination of the parent ring chlorinated toluene. In the case of *p*-chlorobenzotrichloride this can be further converted to *p*-chlorobenzotrifluoride by reaction with HF. *p*-Chlorobenzotrifluoride is an important intermediate in the manufacture of dinitroaniline herbicides (Trifluralin). Additionally, *p*-chlorobenzalchloride or *o*-chlorobenzal chloride can be prepared by side-chain chlorination of *p*-chlorotoluene and *o*-chlorotoluene respectively. Para and ortho chlorinated benzal chlorides can in turn be hydrolyzed to *p*-chlorobenzaldehyde or *o*-chlorobenzaldehyde which find use as an agricultural intermediate (*p*-chlorobenzaldehyde) or as an intermediate in preparing optical brightners (*o*-chlorobenzaldehyde) (2).

## 2. Physical Properties

Benzyl chloride [(chloromethyl)benzene, α-chlorotoluene], $C_6H_5CH_2Cl$, is a colorless liquid with a very pungent odor. Benzyl chloride vapors are irritating to the eyes and mucous membranes, and it is classified as a powerful lacrimator. The physical properties of pure benzyl chloride are given in Table 2 (3–8). Benzyl chloride is insoluble in cold water, but decomposes slowly in hot water to benzyl alcohol. It is miscible in all proportions at room temperature with most organic solvents. The flash point of benzyl chloride is 67°C (closed cup); 74°C (open cup); autoignition temperature is 585°C; lower flammability limit: 1.1% by volume in air. Its volume coefficient of expansion is $9.72 \times 10^{-4}$.

Benzal chloride (MW = 161.03) [(dichloromethyl)benzene, α,α-dichlorotoluene, benzylidene chloride], $C_6H_5CHCl_2$, is a colorless liquid with a pungent, aromatic odor. Benzal chloride is insoluble in water at room temperature but is miscible with most organic solvents.

Benzotrichloride (MW = 195.47) [(trichloromethyl)benzene, α,α,α-trichlorotoluene, phenylchloroform], $C_6H_5CCl_3$, is a colorless, oily liquid with a pungent odor. It is soluble in most organic solvents, but it reacts with water and alcohol.

Table 2. **Physical Properties of Benzyl Chloride, Benzal Chloride, and Benzotrichloride**

| Property | Benzyl chloride | Benzal chloride | Benzotrichloride |
|---|---|---|---|
| mol wt | 126.58 | 161.03 | 195.48 |
| freezing point, °C | −39.2 | −16.4 | −4.75 |
| boiling point, °C | 179.4 | 205.2 | 220.6 |
| density, kg/m$^3$ | $1113.5_4^4$ | $1256_{14}^{14}$ | $1374_4^{20}$ |
|  | $1104_{15}^{15}$ |  |  |
|  | $1100_{20}^{15}$ |  |  |
| refractive index, $n_\mathrm{D}^t$ | $1.54124^{15}$ |  |  |
|  | $1.5392^{20}$ | $1.5502^{20}$ | $1.55789^{20}$ |
| surface tension, | $19.50^{179.5}$ | $20.20^{203.5}$ | $38.03^{20}$ |
| mN/m(= dyn/cm) | $0.03765^{20}$ |  |  |
| dipole moment[a], C · m | $6.24 \times 10^{-30}$ | $6.9 \times 10^{-30}$ | $7.24 \times 10^{-30}$ |
| diffusion of vapor in air, $D_o$, cm$^2$/s | 0.066 |  |  |
| vapor density (air = 1) | 4.34 |  | 6.77 |
| heat of combustion, kJ/mol[b] | 3708[c] | 3852[d] | 3684[d] |
| specific heat at 25°C, ($J$/kg · K)[b] | 1444 | 1377 | 1206 |
| heat of vaporization, kJ/mol[b] | 50.1[e] | 50.4[f] | 52[g] |
| vapor pressure, °C at kPa[h] |  |  |  |
| 0.13 | 22.0 | 35.4 | 45.8 |
| 0.67 | 47.8 | 64.0 | 73.7 |
| 1.33 | 60.8 | 78.7 | 87.6 |
| 5.33 | 90.7 | 112.1 | 119.8 |
| 8.00 | 100.5 | 123.6 | 130.0 |
| 13.3 | 114.2 | 138.3 | 144.3 |
| 26.7 | 134.0 | 160.7 | 165.6 |
| 53.3 | 155.8 | 187.0 | 189.2 |

[a] In dilute benzene solution. To convert C · m to debye, divide by $3.336 \times 10^{-30}$.

[b] To convert J to cal, divide by 4.184.

[c] At constant volume.

[d] At constant pressure.

[e] At 25°C.

[f] At 72°C.

[g] At 80°C.

[h] To convert kPa to mm Hg, multiply by 7.50.

For benzotrichloride the flash point is 127°C (Cleveland open cup) and the autoignition temperature is 211°C (9).

Binary azeotropic systems are reported for all three derivatives (10). The solubilities of benzyl chloride, benzal chloride, and benzotrichloride in water have been calculated by a method devised for compounds with significant hydrolysis rates (11).

## 3. Chemical Properties

The reactions of benzyl chloride, benzal chloride, and benzotrichloride may be divided into two classes: (*1*) reactions taking place on the side chain containing the halogen; and (*2*) reactions taking place on the aromatic ring.

**3.1. Reactions of the Side Chain.** Benzyl chloride is hydrolyzed slowly by boiling water and more rapidly at elevated temperature and pressure in the presence of alkalies (12). Reaction with aqueous sodium cyanide, preferably in the presence of a quaternary ammonium chloride, produces phenylacetonitrile [140-29-4] in high yield (13). The presence of a lower molecular-weight alcohol gives faster rates and higher yields. In the presence of suitable catalysts benzyl chloride reacts with carbon monoxide to produce phenylacetic acid [103-82-2] (14−16). Different catalysts in the presence of calcium hydroxide afford double carbonylation to phenylpyruvic acid [156-06-9] (17). Benzyl esters are formed by heating benzyl chloride with the sodium salts of acids, likewise benzyl ethers can be formed by reaction with sodium alkoxides. The ease of ether formation is improved by the use of phase-transfer catalysts (18) (see CATALYSIS, PHASE-TRANSFER).

The benzylation of a wide variety of aliphatic, aromatic, and heterocyclic amines has been reported. Benzyl chloride is converted into a mixture of mono-, di-, and tribenzylamines by reaction with ammonia. N-Phenylbenzylamine [103-32-2] results from the reaction of benzyl chloride with aniline. Reaction of benzyl chloride with tertiary amines yields quaternary ammonium salts; with trialkylphosphines, quaternary phosphonium salts; and with sulfides, sulfonium salts are formed.

Benzyl chloride readily forms a Grignard compound by reaction with magnesium in ether with the concomitant formation of substantial coupling product, 1,2-diphenylethane [103-29-7]. Benzyl chloride is oxidized first to benzaldehyde [100-52-7] and then to benzoic acid. Nitric acid oxidizes directly to benzoic acid [65-85-0]. Reaction with ethylene oxide produces the benzyl chlorohydrin ether, $C_6H_5CH_2OCH_2CH_2Cl$ (19). Benzylphosphonic acid [10542-07-1] is formed from the reaction of benzyl chloride and triethyl phosphite followed by hydrolysis (20).

Benzyl chloride reacts with alkali hydrogen sulfides, sulfides, and polysulfides to yield benzenethiol, dibenzyl sulfide, and dibenzyl polysulfide, respectively. With sodium cyanate it forms benzyl isocyanate (21).

Benzyl chloride reacts with benzene in the presence of a Lewis acid catalyst to give diphenylmethane [101-81-5]. It undergoes self-condensation to form polymeric oils and solids (22). With phenol, benzyl chloride produces a mixture of *o*- and *p*-benzylphenol.

Benzal chloride is hydrolyzed to benzaldehyde under both acid and alkaline conditions. Typical conditions include reaction with steam in the presence of ferric chloride or a zinc phosphate catalyst (23) and reaction at 100°C with water containing an organic amine (24). Cinnamic acid in low yield is formed by heating benzal chloride and potassium acetate with an amine as catalyst (25).

Benzotrichloride is hydrolyzed to benzoic acid by hot water, concentrated sulfuric acid, or dilute aqueous alkali. Benzoyl chloride [98-88-4] is produced by the reaction of benzotrichloride with an equimolar amount of water or an equivalent of benzoic acid. The reactions are catalyzed by Lewis acids such as ferric chloride and zinc chloride (26). Reaction of benzotrichloride with other organic acids or with anhydrides yields mixtures of benzoyl chloride and the acid chloride derived from the acid or anhydride (27). Benzotrifluoride [98-08-8] is formed by the reaction of benzotrichloride with anhydrous hydrogen fluoride under both liquid- and vapor-phase reaction conditions.

**3.2. Aromatic Ring Reactions.** In the presence of an iodine catalyst chlorination of benzyl chloride yields a mixture consisting mostly of the *ortho* and *para* compounds. More recently, use of catalytic amounts of zeolites as chlorination catalysts yielded *ortho* and *para* chlorination of benzyl cloride (28). With strong Lewis acid catalysts such as ferric chloride, chlorination is accompanied by self-condensation. Nitration of benzyl chloride with nitric acid in acetic anhydride gives an isomeric mixture containing about 33% *ortho*, 15% *meta*, and 52% *para* isomers (29); with benzal chloride, a mixture containing 23% *ortho*, 34% *meta*, and 43% *para* nitrobenzal chlorides is obtained.

Chlorosulfonation of benzotrichloride with chlorosulfonic acid (30) or with sulfur trioxide (29) gives *m*-chlorosulfonyl benzoyl chloride [4052-92-0] in high yield. Under more driving conditions the 3,5 disulfonic acid adduct can be formed which upon reaction with 2 equivalents of benzotrichloride forms the 3,5 bis-sulfonylchloride adduct of benzoyl chloride [37828-01-6]. This bis-sulfonyl chloride can then be chlorodesulfonated form 3,5-dichlorobenzoyl chloride [2905-62-6], an important agricultural chemical intermediate (32). Nitration with nitronium fluoroborate in sulfolane gives 68% *m*-nitro-benzotrichloride [709-58-0] along with 13% of the *ortho* and 19% of the *para* isomers (33).

Nitrobenzotrichloride is also obtained in high yield with no significant hydrolysis when nitration with a mixture of nitric and sulfuric acids is carried out below 30°C (34). 2,4-Dihydroxybenzophenone [131-56-6], an important component in many uv stabilizers is formed in 90% yield by the uncatalyzed reaction of benzotrichloride with resorcinol in hydroxylic solvents (35) or in benzene containing methanol or ethanol (36). Benzophenone derivatives are formed from a variety of aromatic compounds by reaction with benzotrichloride in aqueous or alcoholic hydrofluoric acid (37).

Benzotrichloride with zinc chloride as catalyst reacts with ethylene glycol to form 2-chloroethyl benzoate [7335-25-3] (38). Perchlorotoluene is formed by chlorination with a solution of sulfur monochloride and aluminum chloride in sulfuryl chloride (39).

## 4. Manufacture

Benzyl chloride is manufactured by the thermal or photochemical chlorination of toluene at 65–100°C (40). At lower temperatures the amount of ring-chlorinated by-products is increased. The chlorination is usually carried to no more than about 50% toluene conversion in order to minimize the amount of benzal chloride formed (see Table 1). Once toluene is recycled and the overchlorinated products are removed by distillation, overall yield based on toluene is more than 90%. Various materials, including phosphorus pentachloride, have been reported to catalyze the side-chain chlorination. These compounds and others such as amides also reduce ring chlorination by complexing metallic impurities (41).

Liquid-phase batch photochlorination of toluene to benzylchloride reaches a maximum conversion of about 70% after 1.1 moles of chlorine per mole of toluene have been consumed (42). Higher yields of benzyl chloride have been claimed: 80% for low temperature chlorination (43); 80–85% for light-catalyzed chlorination in the vapor phase (44), and 93.6% for continuous chlorination above 125°C in a column packed with glass rings (45).

In commercial practice, chlorination may be carried out either batchwise or continuously. Glass-lined or nickel reactors may be used. Because certain metallic impurities such as iron catalyze ring chlorination and self-condensation, their presence must be avoided. The crude product is purged of dissolved hydrogen chloride, neutralized with alkali, and distilled. Chlorine efficiency is high; muriatic acid made by absorbing the by-product hydrogen chloride in water is usually free of significant amounts of dissolved chlorine.

An 80% yield of benzyl chloride is obtained with sulfuryl chloride as chlorinating agent. Use of NaX-type zeolites are an effective means of directing chlorination to the side chain using sulfuryl chloride as the chlorinating agent (46) Yields of >70% of benzyl chloride are obtained by the zinc chloride-catalyzed chloromethylation of benzene, but formation of bis-chloromethyl ether presents a health hazard for this reaction pathway.

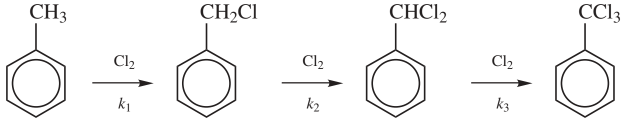
Benzyl chloride undergoes self-condensation relatively easily at high temperatures or in the presence of trace metallic impurities. The risk of decomposition during distillation is reduced by the use of various additives including lactams (47) and amines (48,49). Soluble organic compounds that are reported to function as stabilizers in low concentration include propylene oxide, DMF (50), arylamines (51), and triphenylphosphine (52).

Benzal chloride can be manufactured in 70% yield by chlorination with 2.0–2.2 moles of chlorine per mole of toluene. The benzal chloride is purified by distillation. Benzal chloride is also formed by the reaction of dichlorocarbene ($:CCl_2$) with benzene (53).

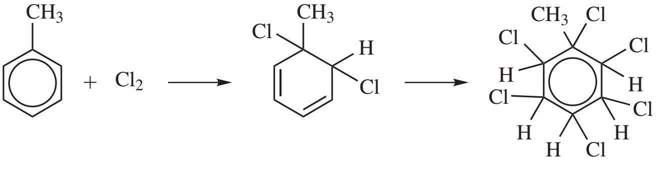
Further chlorination at a temperature of 100–140°C with ultraviolet light yields benzotrichloride. The chlorination is normally carried to a benzotrichloride content of greater than 95% with a low benzal chloride content. After purging with inert gas to remove hydrogen chloride, the crude product is utilized directly or purified by distillation. Under batch conditions chlorine efficiency during the latter stages of the chlorination is low. Product quality and chlorine efficiency can be improved by carrying out the chlorination continuously in a multistage system (54). Additives such as phosphorus trichloride are used to complex metallic impurities. Contaminants or reaction conditions that cause darkening and thereby reduce light penetration must be avoided if the chlorination is to be efficient (55). The radiation-initiated chlorination of toluene has also been investigated (56–60).

An understanding of competing reactions in the manufacturing process is important if by-products are to be minimized. Three competing reactions are possible under conditions of the reaction.

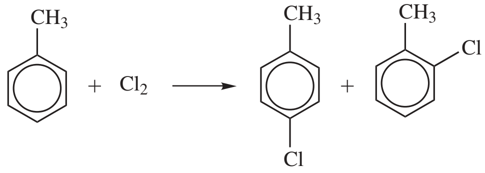
### 4.1. Free-radical Substitution of the Side Chain of Toluene



### 4.2. Addition to the Aromatic Ring



### 4.3. Electrophilic Substitution on the Aromatic Ring



An extensive kinetic study of the photochlorination of toluene in a continuous annular reactor has investigated the parameters that effect the product distribution from these reactions (42). Chlorination on the aromatic ring can occur by either addition followed by elimination of HCl or electrophilic aromatic substitution. Both reactions occur at low (40°C) temperature and are promoted by high concentration of chlorine. Electrophilic substitution is catalyzed by traces of metals like iron and aluminum. Formation of ring-chlorinated compounds is markedly increased by lowering the temperature to 40°C and chlorinating in the dark. These products contribute to a high boiling fraction that reduces the yield of side-chain chlorination products.

Free-radical chlorine substitution of the methyl group hydrogens is promoted by elevated temperature (80–130°C), a radical producing light source, and free-radical catalysts like peroxides. Oxygen inhibits the reaction. The ratio of benzyl to benzal to benzotrichloride depends on the ratio of chlorine to toluene in the reaction. From analyses of the product distribution for the free-radical chlorination at 100°C and irradiation with blue light, the relative rates are $k_1/k_2 = 5.9$ and $k_2/k_3 = 5.2$. Blue light (energy maximum at about 425 nm) gives a higher rate of chlorination than ultraviolet (about 370 nm) because it more effectively penetrates a solution containing free chlorine.

## 5. Handling and Shipment

As is the case during manufacture, contact with those metallic impurities that catalyze Friedel-Crafts condensation reactions must be avoided. The self-condensation reaction is exothermic and the reaction can accelerate producing a rapid buildup of hydrogen chloride pressure in closed systems.

Benzyl chloride is available in both anhydrous and stabilized forms. Both forms can be shipped in glass carboys, nickel and lined-steel drums, and nickel tank trucks and tank cars. Stabilized benzyl chloride can be shipped in unlined and lacquer-lined drums, and tank trucks or cars of construction other than nickel. Glass-lined tanks are the first choice for bulk storage of anhydrous benzyl chloride; lead-lined, nickel, or ceramic tanks can also be used.

Benzyl chloride is classified by DOT as chemicals NO1BN, poisonous, corrosive and a hazardous substance (100 lbs = 45.45 kg). Benzal chloride is classified as poisonous and a hazardous substance (5000 lbs = 2270 kg). Benzotrichloride is classified under DOT regulation as a corrosive liquid NOS and a hazardous substance (10 lbs = 4.5 kg). The Freight Classification Chemical NOI applies. It is shipped in lacquer-lined steel drums and nickel-lined tank trailers. Benzal chloride is handled in a similar fashion.

## 6. Economic Aspects

Plant capacities for the production of benzyl chloride in the United States is estimated to be 100 million lbs. per year in 1990; in Europe about 108 million lbs per year is produced. Solutia, with plants in Belgium (23,000 t/yr) and Bridgeport, New Jersey (40,000 t/yr), is the world's largest producer. Bayer in West Germany (20,000 t/yr) and Tessenderlo Chemie in Belgium (18,000 t/yr) are also principal producers. Japan does not have significant production of benzyl chloride. Total Western world production in 1990 was approximately 180 million lbs. The list price for benzyl chloride as of June 2000 was $0.69/lb.

Benzotrichloride is produced from total side-chain chlorination of toluene or of residual products from benzyl chloride production. In Western Europe, Bayer has the largest capacity (14,000 t/yr), and there are only two significant producers in the United States: Occidental Chemical in Niagara Falls, New York (20,000 t/yr), and Velsicol Chemical (11,000 t/yr). Total capacity in the Western world is 68,000 t/yr and production of benzotrichloride in 1988 was estimated at 31,500 t. The list price for benzotrichloride is $0.90/lb.

Benzyl chloride and butyl alcohol react with phthalic anhydride in one step to yield benzyl butyl phthalate [85-68-7], a plasticizer made by Monsanto and known by its trade name Santicizer 160.

## 7. Identification and Analysis

The side-chain chlorine contents of benzyl chloride, benzal chloride, and benzotrichlorides are determined by hydrolysis with methanolic sodium hydroxide followed by titration with silver nitrate. Total chlorine determination, including ring chlorine, is made by standard combustion methods (59). Several procedures for the gas chromatographic analysis of chlorotoluene mixtures have been described (60,61). Proton and $^{13}C$ nuclear magnetic resonance shifts, characteristic infrared absorption bands, and principal mass spectral peaks have been summarized including sources of reference spectra (62). Procedures for measuring trace benzyl chloride in air (63) and in water (64) have been described.

A gas chromatographic determination of benzotrichloride and related compounds in the work environment, after adsorption on a polymeric adsorbant and desorption with $CCl_4$ has been reported (65). Trace amounts of benzyl chloride, benzal chloride, and benzotrichloride in environmental samples can be analyzed by Method 8120 of *EPA Manual SW-846* with modifications (66).

## 8. Health and Safety Factors

Benzyl chloride is a severely irritating liquid and causes damage to the eyes, skin, and respiratory tract including pulmonary edema. Other possible effects of overexposure to benzyl chloride are CNS depression, liver, and heart damage. Table 3 lists some exposure limits.

Benzyl chloride induced a positive mutagenic response in the Ames Assay in strain TA 100 with and without rat liver S-9 metabolic activation. Benzyl

Table 3. **Toxicology of Side-Chain Chlorinated Toluenes**

| | Benzyl chloride | Benzal chloride | Benzotrichloride |
|---|---|---|---|
| $LD_{50}$ (rat), mg/kg | $1000^{a,b}$ | | $6000^{b,c}$ |
| $LD_{50}$ (mice), mg/kg | | $467^{d,e}$ | |
| $LC_{50}$ (mice, inhalation 2 h), ppm | $80^{f}$ | | |
| $LC_{50}$ (rat, inhalation), ppm | $150^{f}$ | $82^{g}$ | $30^{f}$ |

[a] Administered subcutaneously in oil.
[b] Slightly toxic.
[c] Ref. 63.
[d] Moderately toxic.
[e] Ref. 64.
[f] Ref. 65.
[g] Ref. 66.

chloride also induced *in vitro* cellular transformation in Syrian hamster embryo cultures and DNA alkylation in several organs of the male mouse following iv administration. In summary, IARC states there is limited evidence that benzyl chloride is carcinogenic in experimental animals; epidemiological data were inadequate to evaluate carcinogenicity to humans (74).

Other toxicological effects that may be associated with exposure to benzyl chloride based on animal studies are skin sensitization and developmental embryo and/or fetal toxicity. A 1988 OSHA regulation has established a national occupational exposure limit for benzyl chloride of 5 mg/m$^3$ (1 ppm). Concentrations of 160 mg/m$^3$ (32 ppm) in air cause severe irritation of the eyes and respiratory tract (72). The recommended exposure limit is 1 ppm (15 min). Exposure monitoring protocols are described in OSHA documents.

Vapors of both benzal chloride and benzotrichloride are strongly irritating and lacrimatory. Reported toxicities appear in Table 3. Also, for benzotrichloride, the lowest published lethal dose (frog) is 2150 mg/kg (73), and the toxic dose level (inhalation rats) is 125 ppm/4 h (73).

For all three compounds, biological data relevant to the evaluation of carcinogenic risk to humans are summarized in the World Health Organization International Agency for Research on Cancer monograph which was updated in 1987 (75).

## 9. Uses

Nearly all uses and applications of benzyl chloride are related to reactions of the active halide substituent. More than two-thirds of benzyl chloride produced is used in the manufacture of benzyl butyl-phthalate, a plasticizer used extensively in vinyl flooring and other flexible poly(vinyl chloride) uses such as food packaging. Other significant uses are the manufacture of benzyl alcohol [100-51-6] and of benzyl chloride-derived quaternary ammonium compounds, each of which consumes more than 10% of the benzyl chloride produced. Smaller volume uses include the manufacture of benzyl cyanide [140-29-4], benzyl esters such as benzyl acetate [140-11-4], butyrate, cinnamate, and salicylate, benzylamine [100-46-9], and benzyldimethylamine [103-83-8], and *p*-benzylphenol [101-53-1].

In the dye industry benzyl chloride is used as an intermediate in the manufacture of triphenylmethane dyes (qv). First-generation derivatives of benzyl chloride are processed further to pharmaceutical, perfume, and flavor products.

Nearly all of the benzal chloride produced is consumed in the manufacture of benzaldehyde. Benzaldehyde (qv) is used in the manufacture of perfume and flavor chemicals, dyes, and pharmaceuticals. The principal part of benzotrichloride production is used in the manufacture of benzoyl chloride (see BENZOIC ACID). Lesser amounts are consumed in the manufacture ofbenzotrifluoride, as a dyestuff intermediate, and in producing hydroxybenzophenone ultraviolet light stabilizers. Benzotrifluoride is an important intermediate in the manufacture of herbicides, pharmaceuticals, antimicrobial agents, and the lampreycide, 4-nitro-3-(trifluoromethyl)phenol [88-30-2].

Benzyl-derived quaternary ammonium compounds are used widely as cationic surface-active agents and as germicides, fungicides, and sanitizers. Benzyl alcohol is used in a wide spectrum of applications including pharmaceuticals and perfumes, as a solvent, and as a textile dye assistant.

## 10. Derivatives

**10.1. Ring-Substituted Derivatives.** The ring-chlorinated derivatives of benzyl chloride, benzal chloride, and benzotrichloride are produced by the direct side-chain chlorination of the corresponding chlorinated toluenes or by one of several indirect routes if the required chlorotoluene is not readily available. Physical constants of the main ring-chlorinated derivatives of benzyl chloride, benzal chloride, and benzotrichloride are given in Table 4.

The 2- and 4-monochloro- and 2,4- and 3,4-dichlorobenzyl chloride, benzal chloride, and benzotrichlorides are manufactured by side-chain chlorination of the appropriate chlorotoluene. *p*-Chlorobenzotrichloride (1-chloro-4-trichloromethylbenzene) can be prepared by peroxide-catalyzed chlorination of *p*-toluenesulfonyl chloride or di-*p*-toluylsulfone (76). 2,4-Dichlorobenzotrichloride (1,3-dichloro-4-trichloromethylbenzene) is obtained by the chlorination of 2-chloro-4-chlorosulfonyltoluene (77).

3,4-Dichlorobenzyl chloride (1,2-dichloro-4-chloromethylbenzene) containing some 2,3-dichlorobenzyl chloride is produced by the chloromethylation of *o*-dichlorobenzene in oleum solution (78). Chlorination of 2-chloro-6-nitrotoluene at 160–185°C gives a mixture of 2,6-disubstituted benzal chloride and 2,6-dichlorobenzyl chloride (79).

The ring-chlorinated benzyl chlorides are used in the preparation of quaternary ammonium salts and as intermediates for pharmaceuticals and pesticides. *p*-Chlorobenzyl chloride is an intermediate in the manufacture of the rice herbicide, Saturn ((S-4-chlorobenzyl)-*N*,*N*-diethylthiolcarbamate [28249-77-6] (80). The *o*- and *p*-chlorobenzal chlorides (1-chloro-2-and 4-dichloromethylbenzenes) are starting materials for the manufacture of *o*- and *p*-chlorobenzaldehydes.

The *o*- and *p*-monochloro- and 2,4- and 3,4-dichlorobenzotrichlorides are intermediates in the manufacture of the corresponding chlorinated benzoic acids and benzoyl chlorides. Fluorination of the chlorinated benzotrichlorides

Table 4. **Physical Constants of the Main Ring-Chlorinated Derivatives of Benzyl Chloride, Benzal Chloride, and Benzotrichloride**

| Benzene derivative | CAS Registry number | Common name | Mp,°C | Bp,°C | $n_{\mathrm{D}}^{20}$ | Density, kg/m$^3$ |
|---|---|---|---|---|---|---|
| 1-chloro-2-(chloromethyl) | [611-19-8] | *o*-chlorobenzyl chloride | −17 | 217 | 1.5330 | 1270 |
| 1-chloro-3-(chloromethyl) | [620-20-2] | *m*-chlorobenzyl chloride |  | 215–216[a] |  | 1269.5 |
| 1-chloro-4-(chloromethyl) | [104-83-6] | *p*-chlorobenzyl chloride | 31 | 222 | 1.5554 |  |
| 1-chloro-2-(dichloromethyl) | [88-66-4] | *o*-chlorobenzyl chloride |  | 228.5 | 1.5670[b] | 1399 |
| 1-chloro-3-(dichloromethyl) | [15145-69-4] | *m*-chlorobenzal chloride |  | 235–237 |  |  |
| 1-chloro-4-(dichloromethyl) | [13940-94-8] | *p*-chlorobenzal chloride |  | 236[c] |  |  |
| 2,4-dichloro-1-(chloromethyl) | [94-99-5] | 2,4-dichlorobenzyl chloride | −2.6 | 248 | 1.5761 | 1407 |
| 1,3-dichloro-2-(chloromethyl) | [2014-83-7] | 2,6-dichlorobenzyl chloride | 39–40 | 117–119[d] |  |  |
| 1,2-dichloro-4-(chloromethyl) | [102-47-6] | 3,4-dichlorobenzyl chloride | 37–37.5 | 241 |  | 1412 |
| 1-chloro-2-(trichloromethyl) | [2136-89-2] | *o*-chlorobenzotrichloride | 29.4 | 264.3 | 1.5836 | 1519 |
| 1-chloro-3-(trichloromethyl) | [2136-81-4] | *m*-chlorobenzotrichloride |  | 255 | 1.4461 | 1495 |
| 1-chloro-4-(trichloromethyl) | [5216-25-1] | *p*-chlorobenzotrichloride |  | 245 | 1.4463 | 1495 |
| 1,3-dichloro-2-(dichloromethyl) | [81-19-6] | 2,6-dichlorobenzal chloride |  | 250 |  |  |
| 1,2-dichloro-4-(dichloromethyl) | [56961-84-3] | 3,4-dichlorobenzal chloride |  | 257 |  | 1518 |
| 2,4-dichloro-1-(dichloromethyl) | [134-25-8] | 2,4-dichlorobenzal chloride | 47–48 | 155–159[e] |  |  |
| 1,2-dichloro-4-(trichloromethyl) | [13014-24-9] | 3,4-dichlorobenzotrichloride | 25.8 | 283.1 | 1.5886 | 1591 |

[a] At 100.4 kPa (753 mm Hg).

[b] At 16°C.

[c] At 100.7 kPa (755 mm Hg).

[d] At 1.87 kPa (14 mm Hg).

[e] At 2.67 kPa (20 mm Hg).

produces the chlorinated benzotrifluorides, intermediates in the manufacture of dinitroaniline and diphenyl ether herbicides (81).

2,6-Dichlorobenzal chloride is used in the manufacture of 2,6-dichlorobenzaldehyde and 2,6-dichlorobenzonitrile (82). With the exception of certain products used in the manufacture of herbicides, the volume of individual compounds produced is small, amounting to no more than several hundred tons annually for any individual compound.

**10.2. Side-Chain Chlorinated Xylene Derivatives.** Only a few of the nine side-chain chlorinated derivatives of each of the xylenes are available from direct chlorination. All three of the monochlorinated compounds, α-chloro-*o*-xylene [1-(chloromethyl)-2-methylbenzene [552-45-4], α-chloro-*m*-xylene (1-(chloromethyl)-3-methylbenzene [620-19-9]], and α-chloro-*p*-xylene [1-(chloromethyl)-4-methylbenzene [104-82-5]] are obtained in high yield from partial chlorination of the xylenes. 1,3-bis(Chloromethyl)benzene [626-16-4] can be isolated in moderate yield from chlorination mixtures (84,84).

The fully side-chain chlorinated products, 1,3-bis(trichloromethyl)benzene [881-99-1] and 1,4-bis(trichloromethyl)benzene [68-36-0], are manufactured by exhaustive chlorination of *meta* and *para* xylenes. For the *meta* compounds, ring chlorination cannot be completely eliminated in the early stages of the reaction. The xylene hexachlorides are intermediates in the manufacture of the xylene hexafluorides and of iso- and terephthaloyl chloride [100-20-9] (see PHTHALIC ACIDS).

1-(Dichloromethyl)-2-(trichloromethyl)benzene [2741-57-3], the end product of exhaustive side-chain chlorination of *o*-xylene (85) is an intermediate in the manufacture of phthalaldehydic acid [119-67-5].

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