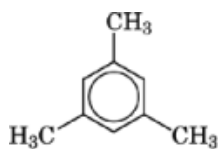


## POLYMETHYLBENZENES

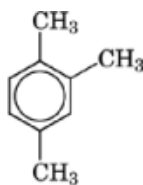
Polymethylbenzenes (PMBs) are aromatic compounds that contain a benzene ring and three to six methyl group substituents (for the lower homologues see Benzene; Toluene; Xylenes and ethylbenzene). Included are the trimethylbenzenes,  $C_9H_{12}$  (mesitylene **(1)**, pseudocumene **(2)**, and hemimellitene **(3)**), the tetramethylbenzenes,  $C_{10}H_{14}$  (durene **(4)**, isodurene **(5)**, and prehnitene **(6)**), pentamethylbenzene,  $C_{11}H_{16}$  **(7)**, and hexamethylbenzene,  $C_{12}H_{18}$  **(8)**. The PMBs are primarily basic building blocks for more complex chemical intermediates.

### 1. Physical Properties

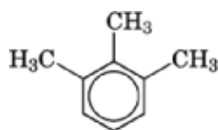
The structures of the eight PMBs are shown here and their physical and thermodynamic properties are given in Table 1.



**(1)**

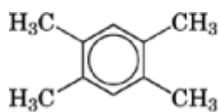


**(2)**

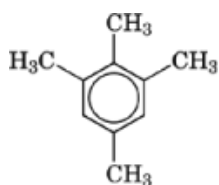


**(3)**

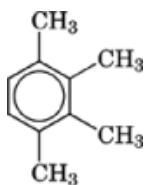
## 2 POLYMETHYLBENZENES



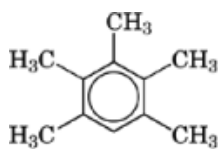
(4)



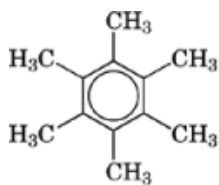
(5)



(6)



(7)



(8)

## 2. Chemical Properties

The PMBs, when treated with electrophilic reagents, show much higher reaction rates than the five lower molecular weight homologues (benzene, toluene, *o*-, *m*-, and *p*-xylene), because the benzene nucleus is highly activated by the attached methyl groups (Table 2). The PMBs have reaction rates for electrophilic substitution ranging from 7.6 times faster (sulfonylation of durene) to ca 607,000 times faster (nuclear chlorination

of durene) than benzene. With rare exception, the PMBs react faster than toluene and the three isomeric dimethylbenzenes (xylenes).

**Table 1. Physical and Thermodynamic Properties of Polymethylbenzenes<sup>a</sup>**

Property	Systematic (benzene) name							
	1,3,5-Tri-methyl-benzene	1,2,4-Tri-methyl-benzene	1,2,3-Tri-methyl-benzene	1,2,4,5-Tetra-methyl-benzene	1,2,3,5-Tetra-methyl-benzene	1,2,3,4-Tetra-methyl-benzene	Penta-methyl-benzene	Hexa-methyl-benzene
CAS Registry Number	[108-67-8]	[95-63-6]	[526-73-8]	[95-93-2]	[527-53-7]	[488-23-3]	[700-12-9]	[87-85-4]
mol wt	120.194	120.194	120.194	134.221	134.221	134.221	148.248	162.275
bp, °C	164.74	169.38	176.12	196.80	198.00	205.04	231.9	263.8
flash point, °C	43.0	46.0	51.0	67.0	68.0	73.0		
density, g/cm <sup>3</sup>								
at 20°C	0.8651	0.8758	0.8944	0.8875 <sup>b</sup>	0.8903	0.9052	0.917 <sup>c</sup>	solid
25°C	0.8611	0.8718	0.8905	0.8837 <sup>b</sup>	0.8865	0.9015	0.913 <sup>c</sup>	solid
freezing point, °C in air at 101.3 kPa <sup>c</sup>	-44.694	-43.881	-25.344	79.240	-23.689	-6.229	54.35	165.7
refractive index, $n_D$ at 25°C	1.49684	1.50237	1.51150	1.5093 <sup>b</sup>	1.5107	1.5181	1.525 <sup>b</sup>	solid
surface tension, mN/m (=dyn/cm), at 20°C	28.84	29.72	31.28	solid	33.51	35.81	solid	solid
critical temperature, °C	364.20	376.02	391.32	401.85	405.85	416.55		
critical pressure, kPa <sup>c</sup>	3127	3232	3454	2940	2860	2860		
critical volume, cm <sup>3</sup> /mol	427	427	427	482	482	482		
heat of vaporization at bp, kJ/mol <sup>d</sup>	39.0	39.2	40.0	45.52	43.81	45.02	45.1	48.2
heat of formation at 25°C, liquid, kJ/mol <sup>d</sup>	-63.4	-61.8	-58.5	-119.87 <sup>e</sup>	-96.35	-90.20	-135.1 <sup>e</sup>	-171.5 <sup>e</sup>
heat of combustion, kJ/mol <sup>d</sup> at 25°C	5193.1	5194.8	5198.0	5816.0 <sup>b</sup>	5839.6	5845.7	6490.8 <sup>b</sup>	
dielectric constant, at 20°C		2.383	2.636					
specific heat, $C_p$ , liquid, at 25°C, J/(mol·K) <sup>d</sup>	200.5	214.9	216.4		240.7	238.3		

<sup>a</sup>Refs. (1–3).

<sup>b</sup>Supercooled liquid.

<sup>c</sup>To convert kPa to atm, divide by 101.3.

<sup>d</sup>To convert J to cal, divide by 4.184.

<sup>e</sup>Crystal.

The methyl groups direct the entering group primarily to the ortho and para positions (Table 3). The preferred site of attack by an electrophile on pseudocumene and hemimellitene is shown as follows (13); however, steric hindrance can cause a shift such as a *tert*-butylation of hemimellitene predominantly at the 5-position. Mesitylene, all three tetramethylbenzenes, and pentamethylbenzene can only form one mono- and one disubstituted isomer (except pentamethylbenzene). Hence, high purity derivatives are possible.

## 4 POLYMETHYLBENZENES

**Table 2. Relative Reaction Rates for PMBs**

PMB	Sulfonylation <sup>a</sup>	Acylation <sup>b</sup>	Chloromethylation <sup>c</sup>	Ring chlorination <sup>d</sup>
reagent	benzenesulfonyl chloride	Reaction conditions benzoyl chloride	chloromethyl methyl ether <sup>e</sup>	chlorine
solvent	nitrobenzene	nitrobenzene	acetic acid	acetic acid
catalyst	AlCl <sub>3</sub>	AlCl <sub>3</sub>	none	none
temperature, °C	25	25	65	25
		Relative rate		
benzene	1.0	1.0	1.0	1.0
toluene	9	150		95
<i>o</i> -xylene	18	1,360		1,140
<i>m</i> -xylene	22	3,910	24	48,700
<i>p</i> -xylene	19	140		570
pseudocumene	31	7,600	46	
mesitylene	30	125,000	600	
hemimellitene	27	13,300		
durene	8	11,000		607,200
isodurene		212,000		
prehnitene		35,500	850	
pentamethyl-benzene	25	139,000		

<sup>a</sup>Ref. 4.

<sup>b</sup>Ref. 5.

<sup>c</sup>Refs. 6 and 7.

<sup>d</sup>Ref. 8.

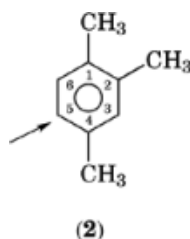
<sup>e</sup>Aqueous formaldehyde or paraformaldehyde in aqueous HCl is preferred.

**Table 3. PMB Reactions and Isomer Distribution for Monosubstitution, %<sup>a</sup>**

Reaction	Toluene		<i>o</i> -Xylene		<i>m</i> -Xylene		Pseudocumene		Hemimellitene	
orientation <sup>b</sup>	<b>1,4</b>	<b>1,2</b>	<b>1,2,4</b>	<b>1,2,3</b>	<b>1,3,4</b>	<b>1,2,3</b>	<b>1,2,4,5</b>	<b>1,2,3,4</b>	<b>1,2,3,4</b>	<b>1,2,3,5</b>
chloromethyl-ation	54	43	72	28	89	11	80	18	95	5
nitration	38	58					mainly			
chlorination	42	58			mainly					
sulfonation	62	32					mainly			
bromination	63	37			mainly					

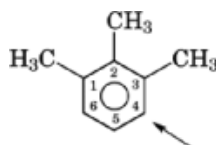
<sup>a</sup>Refs (9–12).

<sup>b</sup>The bold number shows the position on the parent (poly)methylbenzene where the incoming group will substitute.



**Table 4. Relative Basicity of the PMBs Toward HF–BF<sub>3</sub><sup>a</sup>**

Hydrocarbon	Positions of methyl group	Number of pairs in 1,3-positions	Basicity <sup>b</sup>
toluene	1-	0	ca0.01
<i>o</i> -xylene	1,2-	0	3
<i>p</i> -xylene	1,4-	0	1
<i>m</i> -xylene	1,3-	1	9
hemimellitene	1,2,3-	1	ca18
pseudocumene	1,2,4-	1	18
mesitylene	1,3,5-	3	1, 400
prehnitene	1,2,3,4-	2	85
durene	1,2,4,5-	2	60
isodurene	1,2,3,5-	3	2, 800
pentamethylbenzene	1,2,3,4,5-	4	4, 350
hexamethylbenzene	1,2,3,4,5,6-	6	44, 500

<sup>a</sup>Ref. 14.<sup>b</sup>Relative to *p*-xylene.**(3)**

The relative basicity of PMBs is summarized in Table 4, which shows that basicity increases with increasing number of methyl groups, and that methyl groups in the 1,3-position to one another greatly influence basicity.

### 3. Manufacture

High purity mesitylene, hemimellitene, and durene are often produced synthetically, whereas pseudocumene is obtained from extracted C<sub>9</sub> reformat by superfractionation. The composition of a typical extracted C<sub>9</sub> reformat and the boiling points of the nine C<sub>9</sub> isomers present are shown in Table 5. Pseudocumene is separated in high purity (>98%) by superfractionation alone, whereas mesitylene, hemimellitene, and durene cannot be cleanly separated because of the presence of close boiling compounds, eg, 2-ethyltoluene, indane, and isodurene, respectively.

Exploiting the relative basicity of the xylene isomers, commercial units employ superacids, typically HF–BF<sub>3</sub>, as the acid complexing agent for the separation of *m*-xylene (feedstock for isophthalic acid) (15). Amoco produces high purity *m*-xylene at its Texas City facility using the HF–BF<sub>3</sub> process (see Btx processing). Similar processes can be used for the separation of high purity mesitylene and isodurene from their C<sub>9</sub> and C<sub>10</sub> isomers, respectively.

Selective absorption of durene from heavy gasoline (bp 150–225°C) is possible using a version of UOP's Sorbex technology where the X zeolite is made selective for durene by replacing the exchangeable sodium cations with lithium ions (16).

## 6 POLYMETHYLBENZENES

**Table 5. Distribution of C<sub>9</sub> Aromatic Compounds in Reformate<sup>a</sup>**

Compound	CAS Registry Number	Boiling point, °C	Freezing point, °C	Wt % <sup>b</sup>	Wt % <sup>c</sup>
isopropylbenzene (cumene)	[98-82-8]	152	−96	0.6	2.2
<i>n</i> -propylbenzene	[103-65-1]	159	−99	5.2	6.2
3-ethyltoluene	[620-14-4]	161	−95	17.4	18.4
4-ethyltoluene	[622-96-8]	162	−62	8.6	7.9
1,3,5-trimethylbenzene (mesitylene)	[108-67-8]	165	−45	7.6	8.9
2-ethyltoluene	[611-14-3]	165	−81	9.1	7.5
1,2,4-trimethylbenzene (pseudocumene)	[95-63-6]	169	−44	41.3	38.1
1,2,3-trimethylbenzene (hemimellitene)	[526-73-8]	176	−25	8.2	8.8
indane	[496-11-7]	178	−51	2.0	2.0

<sup>a</sup>Based on the total C<sub>9</sub> aromatic compounds.

<sup>b</sup>Ref. 11. Solvent extracted to remove nonaromatics.

<sup>c</sup>Severe reforming (two refinery average, 1994).

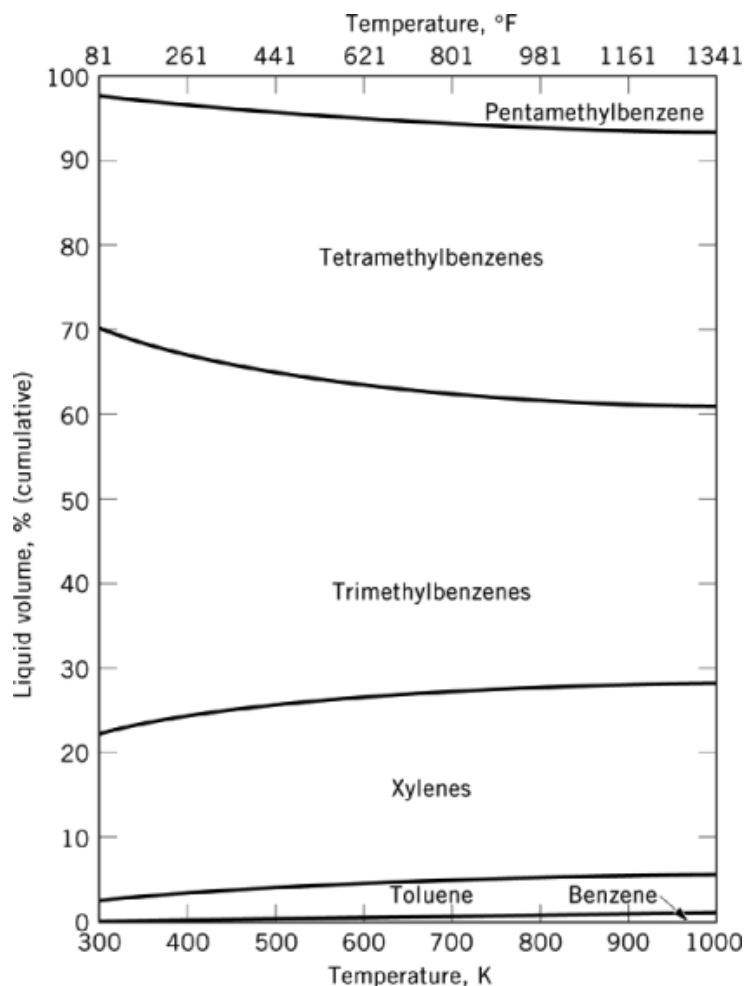
Mesitylene can be synthesized from acetone by catalytic dehydrocyclization (17). Similarly, cyclotrimerization of acetylenes has produced PMBs such as hexamethylbenzene (18). Durene has been recovered from Methanex's methanol-to-gasoline (MTG) plant in New Zealand (19).

Koch Chemical Company is the only U.S. supplier of all PMBs (except hexamethylbenzene). Its process has the flexibility of producing isodurene, prehnitene, and pentamethylbenzene, should a market develop. Koch's primary process (20) is based on isomerization, alkylation, and disproportionation conducted in the presence of a Friedel-Crafts catalyst. For the synthesis of mesitylene and hemimellitene, pseudocumene is isomerized. If durene, isodurene, or prehnitene and pentamethylbenzene are desired, pseudocumene is alkylated with methyl chloride (see Alkylation; Friedel-Crafts reactions).

The thermodynamic equilibria are illustrated in Figures 1 and 2. Figure 1 shows the resulting composition after pure pseudocumene or a recycle mixture of C<sub>9</sub> PMBs is disproportionated with a strong Friedel-Crafts catalyst. At 127°C (400 K), the reactor effluent contains approximately 3% toluene, 21% xylenes, 44% C<sub>9</sub> PMBs, 29% C<sub>10</sub> PMBs, and 3% pentamethylbenzene. The equilibrium composition of the 44% C<sub>9</sub> PMB isomers is shown in Figure 2. Based on the values at 127°C, the distribution is 29.5% mesitylene, 66.0% pseudocumene, and 4.5% hemimellitene (Fig. 2). After separating mesitylene and hemimellitene by fractionation, toluene, xylenes, pseudocumene (recycle plus fresh), C<sub>10</sub> PMBs, and pentamethylbenzene are recycled to extinction.

If only durene is desired, pseudocumene is alkylated with methyl chloride to obtain a C<sub>10</sub> alkylate having a composition similar to that shown in Figure 3. The composition (at 127°C) is approximately 2% xylenes, 17% C<sub>9</sub> PMBs, 55% C<sub>10</sub> PMBs, 25.5% pentamethylbenzene, and 0.5% hexamethylbenzene. The isomer breakdown of the 55% C<sub>10</sub> PMBs is similar to the ratios shown in Figure 2 (37% durene, 52% isodurene, and 11% prehnitene). Because isodurene and durene boil very closely together, durene cannot be recovered in high purity by fractionation. However, the freezing points of durene and isodurene are 79 and −23.6°C, respectively. Consequently, the reactor effluent (C<sub>10</sub> PMBs alkylate) is distilled to give essentially a binary mixture of durene and isodurene which is fractionally crystallized to yield 96+% durene. The lighter and heavier PMBs present in the alkylate are separated by distillation (qv) and recycled to the reactor along with fresh pseudocumene and methyl chloride feed and the C<sub>10</sub> PMBs filtrate, which is rich in isodurene, from the crystallization unit.

Koch's process also permits recovery of prehnitene, isodurene, and pentamethylbenzene by fractionation. In the case of isodurene, only 85% purity is achieved when the filtrate from the durene crystallization unit is redistilled; durene is the principal impurity. Although hexamethylbenzene can be synthesized via the



**Fig. 1.** Disproportionation of trimethylbenzenes. Composition cited in text derived by differences between curves at given temperature.

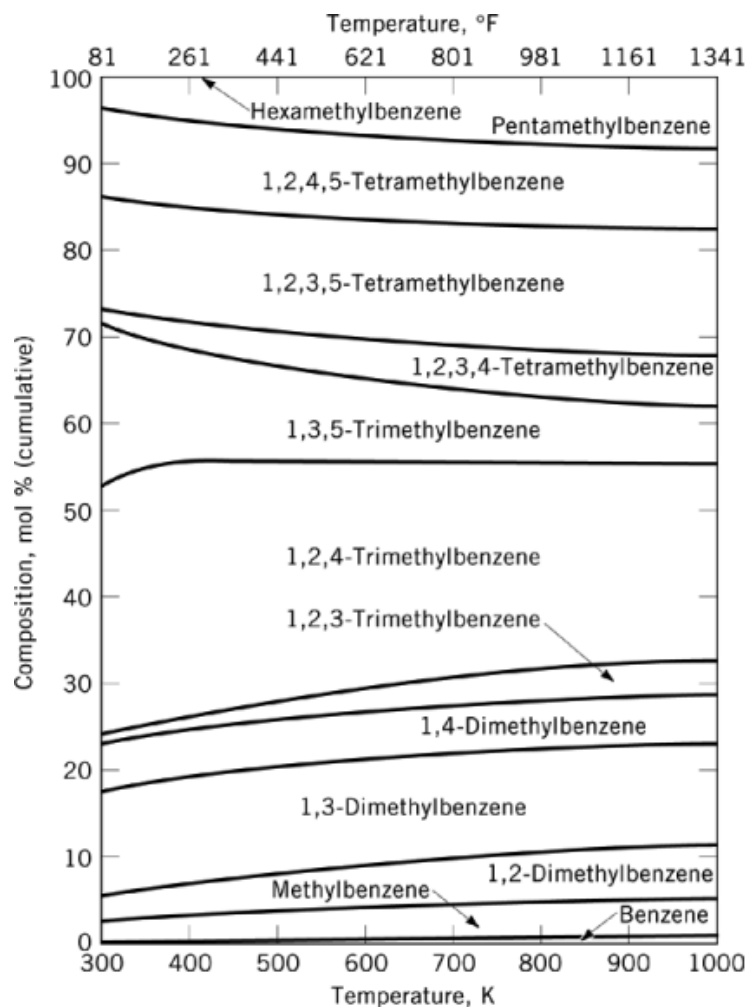
trimethylation of the readily available pseudocumene, its high melting point (105.5°C) presents more of a processing challenge.

#### 4. Production and Shipping

The only significant U.S. producer of PMBs is Koch Chemical Company. The only PMBs produced in any sizable quantity are pseudocumene, durene, mesitylene, and hemimellitene. Koch's production capability for pseudocumene is ca 35,000 t/yr; the combined production rate of the other PMBs is less than 5,000 t/yr.

Pseudocumene is shipped in barges, tank cars, tank trucks, isocontainers, and drums. Mesitylene is shipped in tank trucks, isocontainers, and drums, whereas durene is shipped molten in heated tank trucks, isocontainers, and occasionally as a cast solid in drums. Mesitylene, pseudocumene, and hemimellitene are classified as flammable liquids; the higher homologues are classified as combustible. The higher melting PMBs

## 8 POLYMETHYLBENZENES



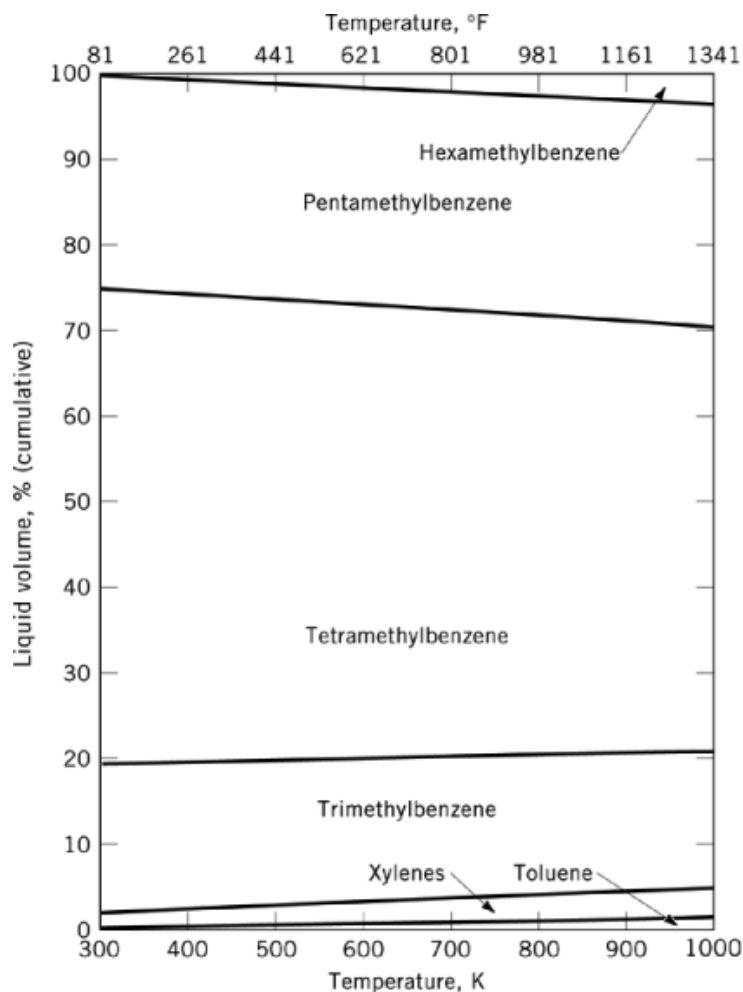
**Fig. 2.** Calculated equilibria among benzene and the C<sub>7</sub>–C<sub>12</sub> methylated benzenes. Composition cited in text derived by differences between curves at given temperature.

require additional precautions when handled in the molten state to avoid thermal burns. Detailed shipping and handling procedures are described in manufacturers' material safety data sheets (MSDS).

## 5. Specifications

The typical properties of commercial PMBs are shown in Table 6.





**Fig. 3.** Disproportionation of tetramethylbenzenes. Composition cited in text derived by differences between curves at given temperature.

## 6. Health and Safety Factors

The PMBs, as higher homologues of toluene and xylenes, are handled in a similar manner, even though their flash points are higher (see Table 1). Containers are tightly closed and use areas should be ventilated. Breathing vapors and contact with the skin should be avoided. Toxicity and primary irritation data are given in Table 7.

## 7. Environmental Considerations

All the PMBs are listed on the U.S. EPA's Toxic Substances Control Act NonConfidential Chemical Substances Inventory (Table 8). In the early to mid-1980s, pseudocumene, mesitylene, hemimellitene, and trimethylbenzene were covered by TSCA Section 8(a) Preliminary Assessment Information Rule (PAIR) reporting

## 10 POLYMETHYLBENZENES

**Table 6. Typical Properties of Commercial PMBs<sup>a</sup>**

	(1)	(2)	(3)	(4)	(5)	(6)
		Composition, wt %				
mesitylene	98.5	0.5				
pseudocumene	1.0	97.7	4.0			
hemimellitene	nil	0.5	90.5			
durene				96.3	16.5	0.5
isodurene				3.0	82.5	1.5
prehnitene						90.5
other aromatics	0.5	1.2	5.5	1.5	1.0	2.5
		Distillation, °C				
initial boiling point, °C	164.5	168.9	175.0	194.0	197.0	203.0
dry point	166.5	170.6	176.8	197.5	200	206
freezing point, °C				77.0		
color, Saybolt	+30	+30	+30	snow white	+30	+30
sp gr 15/15°C	0.8690	0.8800	0.8950		0.8956	0.9042

<sup>a</sup>The composition of pentamethylbenzene is 95.5 wt % **(7)** and 4.5% other aromatics; its fp is 51°C and its color is snow white.

**Table 7. Toxicological Properties<sup>a</sup>**

Compound	Structure number	ACGIH TLV–TWA, <sup>b</sup> ppm	LD <sub>50</sub> <sup>c</sup> , mg/kg	Skin irritation, mg/24 h	Eye irritation, mg/24 h
mesitylene	<b>(1)</b>	25		20, moderate	500, mild
pseudocumene	<b>(2)</b>	25	5000		
hemimellitene	<b>(3)</b>	25			
trimethylbenzene <sup>d</sup>		25	8970	500, mild	500, mild
durene	<b>(4)</b>	NE	6989		
isodurene	<b>(5)</b>	NE	5157		
prehnitene	<b>(6)</b>	NE	6408	100, mild	
pentamethylbenzene	<b>(7)</b>	NE			
hexamethylbenzene	<b>(8)</b>	NE			

<sup>a</sup>Ref. 21.

<sup>b</sup>NE = none established.

<sup>c</sup>Oral (rat).

<sup>d</sup>Trimethylbenzene is a generic listing, ie, mixed isomers.

requirements (22) and by TSCA Section 8(d) for health and safety data (23). Mesitylene is the subject of a test rule; subacute oral toxicity and subchronic oral toxicity in rats were underway in 1994 (24). The Safe Drinking Water Act (SDWA) allows monitoring for pseudocumene and mesitylene at the discretion of the State (25). Of the PMBs, only pseudocumene is subject to SARA Title III section 313 annual release reporting (26).

Other evaluations (27, 28) of environmental considerations report vapor pressure, water solubility, and the octanol/water partition coefficient for trimethylbenzenes.

## 8. Uses

Pseudocumene is used as a component in liquid scintillation cocktails for clinical analyses. Prehnitene, isodurene, pentamethylbenzene, and hexamethylbenzene have no significant commercial uses, however, there is a great deal of intriguing patent activity. The higher polymethylbenzenes show potential as highly regiospecific

Table 8. PMB Regulatory Status<sup>a</sup>

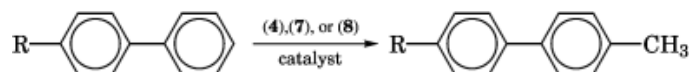
PMB	CAS Registry Number	TSCA <sup>a</sup> listed	EINECS <sup>a, b</sup> number	Canadian status <sup>b</sup>
mesitylene	[108 – 67 – 8]	yes	202-604-4	DSL
pseudocumene	[95 – 63 – 6]	yes	202-436-9	DSL
hemimellitene	[526 – 73 – 8]	yes	208-394-8	DSL
trimethylbenzene <sup>c</sup>	[25551 – 13 – 7]	yes	247-099-9	DSL
durene	[95 – 93 – 2]	yes	202-465-7	DSL
isodurene	[527 – 53 – 7]	yes	208-417-1	DSL
prehnitene	[488 – 23 – 3]	yes	207-673-1	DSL
pentamethylbenzene	[700 – 12 – 9]	yes	211-837-8	NDSL
hexamethylbenzene	[87 – 85 – 4]	yes	201-777-0	DSL

<sup>a</sup>All eight PMBs are listed on the U.S. EPA's TSCA Inventory (May 1, 1994 ed.) and on the European Communities' EINECS inventory (June 15, 1990).

<sup>b</sup>All but pentamethylbenzene are listed on the Canadian Domestic Substances List (DSL) (Apr. 6, 1994). Pentamethylbenzene is listed on the Canadian Nondomestic Substances List (NDSL) (Apr. 6, 1994) and as of July 1, 1994 was subject to New Substance Notification if manufactured in or imported into Canada.

<sup>c</sup>Trimethylbenzene is a generic listing, ie, mixed isomers.

methylation agents for methylation of 4-alkylbiphenyls to form 4,4'-alkylmethylbiphenyls (29, 30) which can be oxidized to the monomer 4,4'-biphenyldicarboxylic acid [787-70-2] (see Liquid crystalline materials).



Similar regiospecific syntheses employing PMBs and dialkylnaphthalene have been used to prepare 2,6-dimethylnaphthalene [581-42-0] which is oxidized to the corresponding 2,6-naphthalenedicarboxylic acid [1141-38-4], also used as a monomer for liquid crystal polymers.

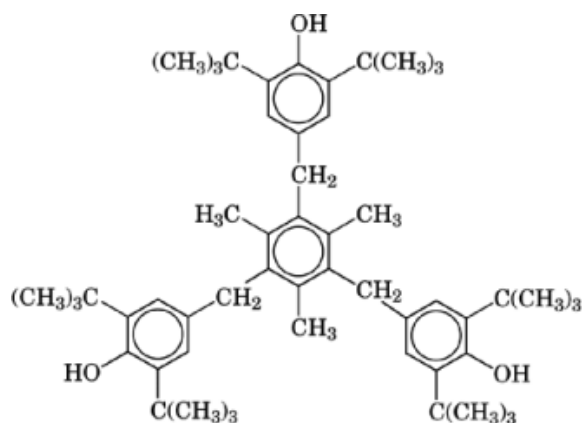
## 9. Derivatives

Little interest has been shown in prehnitene and pentamethylbenzene, even though dozens of derivatives have been prepared from each (13).

### 9.1. Mesitylene

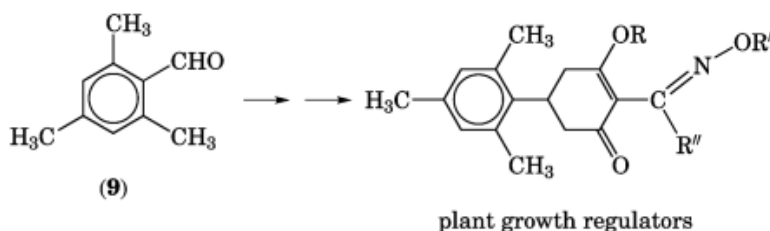
One of the principal derivatives of mesitylene is the sterically hindered phenol of the structure shown in Figure 4. Its trade name is Ethanox 330 and it is produced by Albemarle Corporation (formerly Ethyl Corporation) (31). Ethanox 330 is an important noncoloring antioxidant and thermal stabilizer for plastics, adhesives, rubber, and waxes (qv) (32, 33) (see Antioxidants). The oral toxicity of Antioxidant 330 is extremely low (oral LD<sub>50</sub> in rats >15 g/kg) since its large size, C<sub>54</sub>H<sub>78</sub>O<sub>3</sub>, effectively eliminates absorption from the gastrointestinal tract.

Another significant use for mesitylene is in the production of mesitaldehyde, [487-68-3], 2,4,6-trimethylbenzaldehyde (**9**) (AlliedSignal Inc.), an early intermediate in Zeneca's commercial synthesis of certain 5-(2,4,6-trimethylphenyl)cyclohexane-1,3-dione derivatives used as plant growth regulators (34) (see Growth regulators, plant). The Gattermann-Koch formylation reaction of mesitylene with carbon monoxide yields mesitaldehyde when carried out in the presence of a superacid catalyst typically derived from

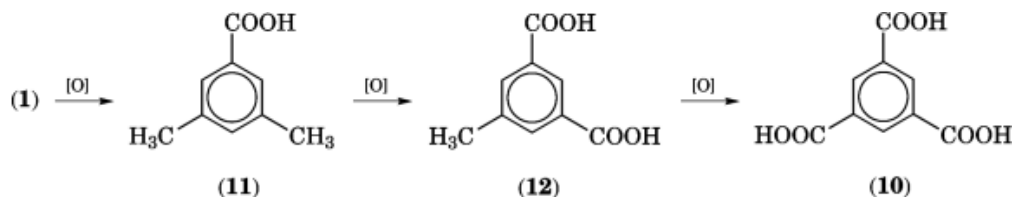


**Fig. 4.** 1,3,5-Trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene [1709-70-2] derived from mesitylene.

combination of a Brønsted acid and a Lewis acid, eg,  $\text{HF}-\text{BF}_3$ ,  $\text{HCl}-\text{AlCl}_3$  (35), or  $\text{HF}-\text{SbF}_5$ , although certain Brønsted acids such as trifluoromethanesulfonic acid [1493-13-6] (triflic acid) alone are strong enough to catalyze the formylation of mesitylene (36) (see Friedel-Crafts reactions). Mesitaldehyde can also be prepared from mesitylene by chloromethylation to  $\alpha^2$ -chloroisodurene [1585-16-6] followed by oxidation.



Liquid-phase air oxidation of mesitylene with Co, Mn, and Br catalysis produces 1,3,5-benzenetricarboxylic acid [554-95-0] (trimesic acid) (10) (37) as does the oxidation with dilute nitric acid (qv). Amoco has oxidized mesitylene to trimesic acid on a small scale (see Phthalic acid and other benzenecarboxylic acids). Less vigorous stepwise oxidation of mesitylene can yield 3,5-dimethylbenzoic acid [499-06-9] (11) and 5-methylisophthalic acid [499-49-0] (12).

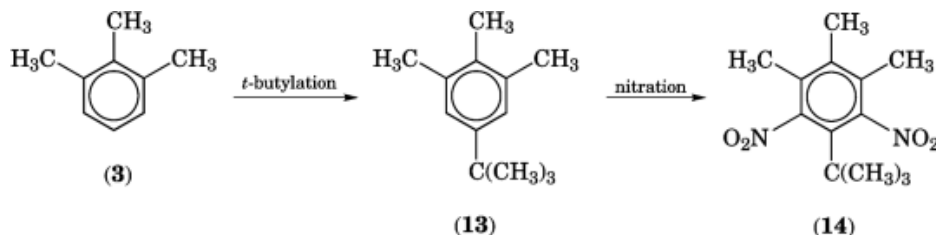


Mesitylene is converted to a dye intermediate, 2,4,6-trimethylaniline [88-05-1] (mesidine), via nitration to 1,3,5-trimethyl-2-nitrobenzene [603-71-4] followed by reduction, eg, catalytic hydrogenation (38). Trinitromesitylene has been prepared for use in high temperature tolerant explosives (39). The use of mesitylene to scavenge contaminant NO from an effluent gas stream has been patented (40).

Mesitylene continues to be of considerable interest as a research chemical. Its trilateral structure, extremely high reactivity for electrophilic reactions, and the fact that large supplies are available point to good growth potential.

### 9.2. Hemimellitene

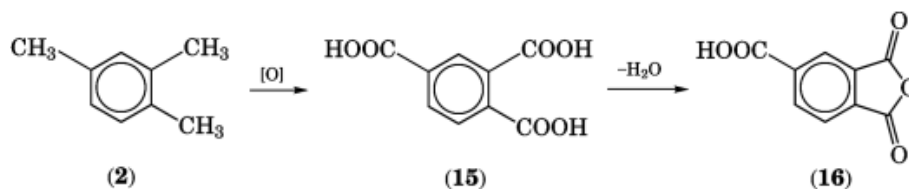
In addition to some specialized solvent applications, hemimellitene can be converted to musk Tibetine [145-39-1], 1-*tert*-butyl-3,4,5-trimethyl-2,6-dinitrobenzene (**14**) via 5-*tert*-butyl-1,2,3-trimethylbenzene [98-23-7] (**13**).



Important derivatives are obtained from PMBs by oxidation (see Phthalic acid and other benzenecarboxylic acids). For example, hemimellitene is oxidized to hemimellitic acid dihydrate [36362-97-7] or hemimellitic acid [569-51-7] which can be dehydrated to hemimellitic anhydride [3786-39-8].

### 9.3. Pseudocumene

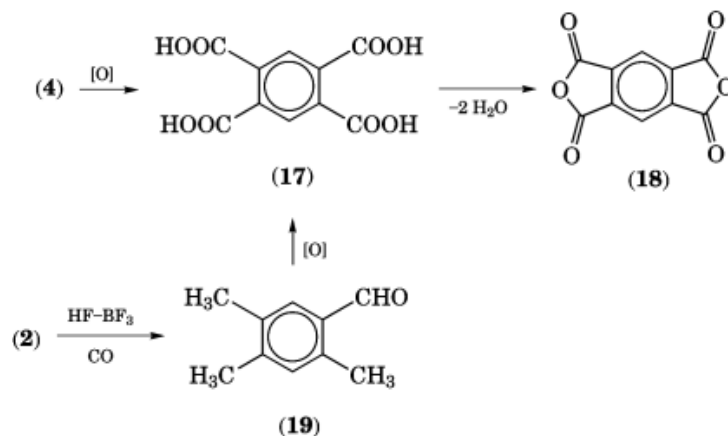
The liquid-phase air oxidation of pseudocumene yields trimellitic acid [528-44-9] (**15**) which is dehydrated to trimellitic anhydride [552-30-7] (TMA) (**16**). Amoco Chemical is the sole U.S. producer with a plant at Joliet, Illinois, having a capacity of ca 47,000 t/yr. Lonza in Italy is the sole European TMA producer.



Trimellitic anhydride is converted to PVC plasticizers, polyesters, water-soluble alkyd coatings, and polyamide-imide resins. The trimellitate plasticizers have a lower volatility than those derived from phthalic anhydride (see Plasticizers).

### 9.4. Durene

The oxidation of durene (**4**) yields pyromellitic acid [89-05-4] (**17**) or pyromellitic dianhydride [89-32-7] (**18**) directly. The oxidation can be carried out with dilute nitric acid in solution, with air and catalyst either in the vapor phase over a solid vanadium pentoxide-based catalyst or in the liquid phase with a soluble catalyst system based on Co, Mn, and Br. PMDA (**18**) is also made from pseudocumene (**2**) by carbonylation to 2,4,5-trimethylbenzaldehyde [5779-72-6] (**19**) using  $\text{HF-BF}_3$  followed by oxidation to pyromellitic acid. PMDA can also be converted to plasticizers; however, the main application is for the production of polyimides resistant to high temperature (see Polyimides).



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## Related Articles

Benzene; Toluene; Xylene and ethylbenzene; Alkylation; Friedel Crafts reactions