


Benzene Species in Crude Oil; Should We Analyse Them All?



AGAT Laboratories

SERVICE BEYOND ANALYSIS ▪
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Authors

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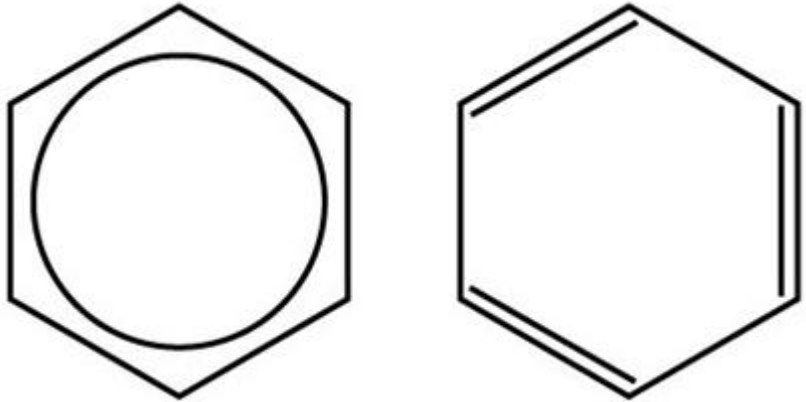
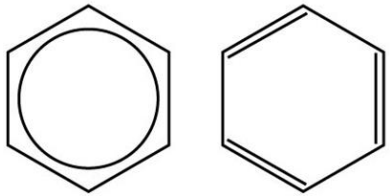
Benzene in the environment

- BTEX family
- Benzene CAS#: 71-43-2
- Colorless liquid
- Sweet odor, smell at 60 ppm
- Dissolves in water (limited)
- Evaporates easily
- Highly flammable
- Benzene comes from industries and nature
- It breaks slowly in water/soil



Reactions - Types of Substitutions

- Nitration: $C_6H_6 + HNO_3 \longrightarrow C_6H_6NO_2 + H_2O$



- Halogenation: Carbon Replaced by Halogen
- Sulfonation: Carbon Replaced by Sulfer
- Friedel-crafts: Acyl group (RCO-) Attaches to Ring to Make a Keytone

Physical Properties

	Formula	Molecular Weight (g/mol)	Vapor Pressure mm Hg at 25°C	Odor Threshold	Log K_{ow} (Octanol /Water)
Benzene	C_6H_6	78.11	95.1	1.5 ppm (5 mg/m3)	2.13

Sources of Benzene

- Origins
  - Old time: 1800s from coal tar
  - Modern: Petroleum (top 20 USA production)
- Industries: Styrofoam, resin, nylon, rubber, lubricant, dyes, detergent, drug & pesticides
- Nature: gas emission, volcano, forest fires

Health and Environmental Hazard

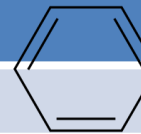
- Exposure by inhalation and skin
- Exposure from products (glue, tobacco, etc.)
- Emissions of car and industries: 20% total
- Permissible level in water 0-5 ppb
- 10ppb/water 0.4ppb/air, 1 extra cancer in 100,000

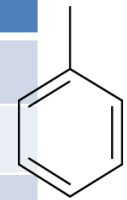
Legal Facts

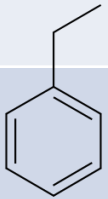
- July 1, 1999, Gasoline supply less than 1%
- Test Methods: D2163 - 14e1
- Benzene is classified as carcinogenic to humans *(i.e.,* as a non-threshold toxicant - a substance for which there is considered to be some probability of harm for the critical effect at any level of exposure)
- It is considered to be "toxic" as defined under Paragraph 11(*c*) of the *Canadian Environmental Protection Act.*
- On the basis of available data, benzene is not considered to be “toxic” as defined under Paragraphs 11(*a*) and 11(*b*) of CEPA (Canadian Council of Ministers of the Environment).

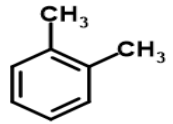
Benzene Derivatives (properties)

	Formula	Molecular Weight (g/mol)	Vapor Pressure mm Hg at 25°C	Odor Threshold	Log K_{ow} (Octanol /Water)
Benzene	C_6H_6	78.11	95.1	1.5 ppm (5 mg/m3)	2.13
Toluene	C_7H_8	92.15	28.4	2.9	2.69
Ethylbenzene	C_8H_{10}	106.16	9.53	2.3	3.13
Xylene	C_8H_{10}	106.16	6.728	1.1 (as per m-xylene)	3.12









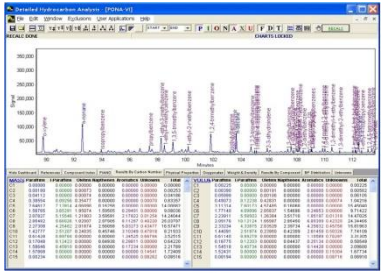
Toxicity of Toluene, Ethylbenzene & Xylenes

- Toxic to Vertebrate, Invertebrate, Plants, Earthworm, wheatgrass, etc.
- Toxic as low as 1 mg/L
- Cause acute and chronic effects (CNS)
- Acute: CNS dysfunction, fatigue, sleepiness, headaches, and nausea, swollen liver, congestion and hemorrhage of the lungs, tubular kidney necrosis, and impaired respiratory function.
- Chronic: drowsiness, ataxia, tremors, cerebral atrophy, nystagmus (involuntary eye movements), and impaired speech, hearing, and vision

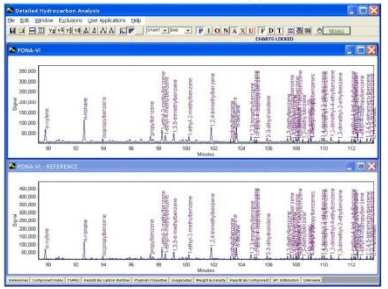
Research Question

- Are there more of similar benzene compounds in sources such as oil?

Methodology - Method



DRAGON DHA

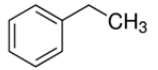
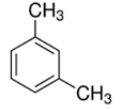
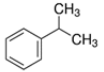
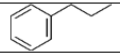
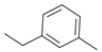


This is not a
Vacuum UltraViolet (VUV)

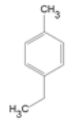
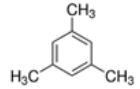
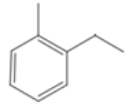
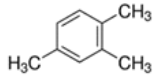
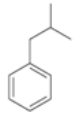
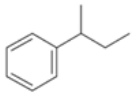
Results

- A total of 48 benzene compounds
- BTEX contain 6 in total
- There are 42 more benzene like compounds

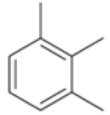
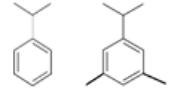
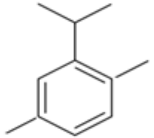
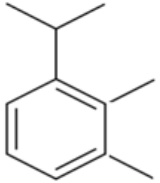
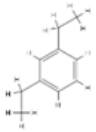
Identified Benzene Species (1)

	Component Name	Mol %	Molecular Weight	Density	Structure
1	benzene	0.3124	78.114	0.8789	
2	Ethylbenzene	0.4932	106.168	0.867	
3	1,3-dimethylbenzene (m-Xylene)	0.3615	106.168	0.8642	
4	1,4-dimethylbenzene (p-Xylene)	0.2728	106.168	0.861	
5	1,2-dimethylbenzene	0.2997	106.168	0.8802	
6	i-propylbenzene (Cumene)	0.0838	120.195	0.8618	
7	n-propylbenzene (phenylpropane)	0.1736	120.195	0.862	
8	1,3-methylethylbenzene	0.2783	120.195	0.8645	

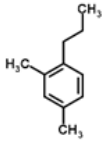
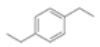
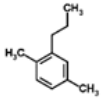
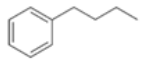
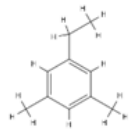
Identified Benzene Species (2)

	Component Name	Mol %	Molecular Weight	Density	Structure
9	1,4-methylethylbenzene	0.1407	120.195	0.8612	
10	1,3,5-trimethylbenzene	0.1128	120.195	0.8652	
11	1,2-methylethylbenzene	0.2246	120.195	0.8807	
12	1,2,4-trimethylbenzene	0.2884	120.195	0.8758	
13	i-butylbenzene	0.0129	134.222	0.8532	
14	sec-butylbenzene	0.0917	134.222	0.862	

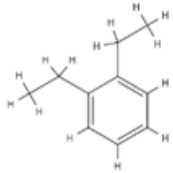
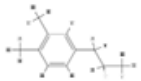
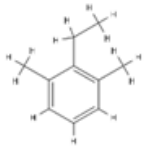
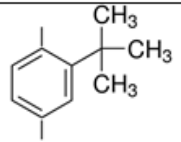
Identified Benzene Species (3)

	Component Name	Mol %	Molecular Weight	Density	Structure
15	1,2,3-trimethylbenzene	0.12	120.195	0.8944	
16	1,3-methyl-i-propylbenzene	0.0703	134.222	0.861	
17	1,4-methyl-i-propylbenzene	0.0669	134.222	0.8573	
18	1,2-methyl-i-propylbenzene	0.2116	134.222	0.8766	
19	1,3-diethylbenzene	0.0832	134.222	0.8639	

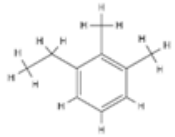
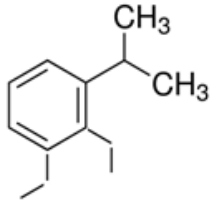
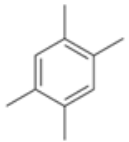
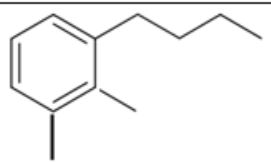
Identified Benzene Species (4)

	Component Name	Mol %	Molecular Weight	Density	Structure
20	1,3-methyl-n-propylbenzene	0.1035	134.222	0.8609	
21	1,4-diethylbenzene	0.0366	134.222	0.862	
22	1,4-methyl-n-propylbenzene	0.0559	134.222	0.8584	
23	n-butylbenzene	0.0582	134.222	0.861	
24	1,3-dimethyl-5-ethylbenzene	0.0613	134.222	0.88	

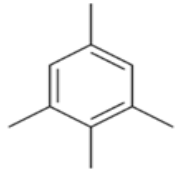
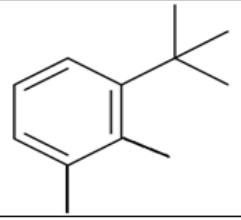
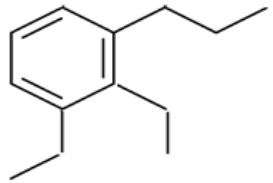
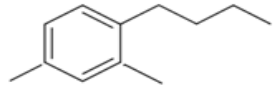
Identified Benzene Species (5)

	Component Name	Mol %	Molecular Weight	Density	Structure
25	1,2-diethylbenzene	0.0846	134.222	0.8799	
26	1,2-methyl-n-propylbenzene	0.2263	134.222	0.8736	
27	1,3-dimethyl-2-ethylbenzene	0.024	134.222	0.8904	
28	1,4-methyl-t-butylbenzene	0.0435	148.24	0.85	

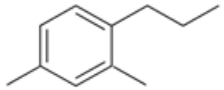
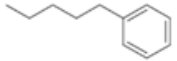
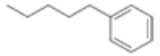
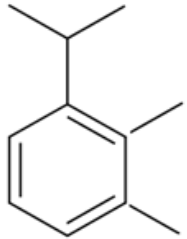
Identified Benzene Species (6)

	Component Name	Mol %	Molecular Weight	Density	Structure
29	1,2-dimethyl-3-ethylbenzene	0.1057	134.222	0.8921	
30	1,2-ethyl-i-propylbenzene	0.0161	148.24	0.89	
31	1,2,4,5-tetramethylbenzene	0.0614	134.222	0.8875	
32	1,2-methyl-n-butylbenzene	0.0163	148.24	0.89	

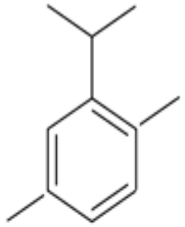
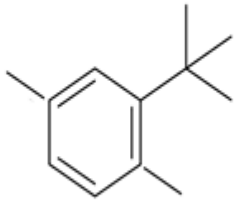
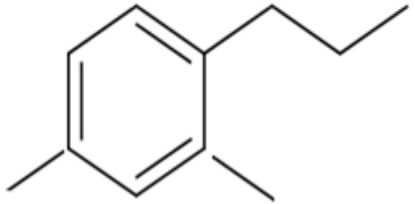
Identified Benzene Species (7)

	Component Name	Mol %	Molecular Weight	Density	Structure
33	1,2,3,5-tetramethylbenzene	0.0961	134.222	0.8903	
34	1,2-methyl-t-butylbenzene	0.0054	148.24	0.89	
35	1,2-ethyl-n-propylbenzene	0.1794	148.24	0.89	
36	1,3-methyl-n-butylbenzene	0.0584	148.24	0.89	

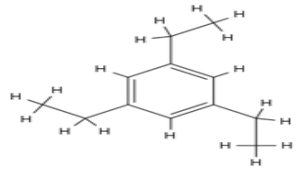
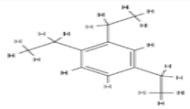
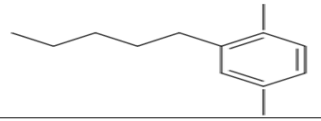
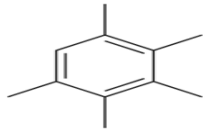
Identified Benzene Species (8)

	Component Name	Mol %	Molecular Weight	Density	Structure
37	1,3-di-i-propylbenzene	0.0616	162.272	0.89	
38	s-pentylbenzene	0.0516	148.24	0.89	
39	n-pentylbenzene	0.1	148.24	0.89	
40	1,2-di-i-propylbenzene	0.0857	162.272	0.89	

Identified Benzene Species (9)

	Component Name	Mol %	Molecular Weight	Density	Structure
41	1,4-di-i-propylbenzene	0.2529	162.272	0.89	
42	1,4-ethyl-t-butylbenzene	0.1247	162.272	0.89	
43	1,3-di-n-propylbenzene	0.0519	162.272	0.89	

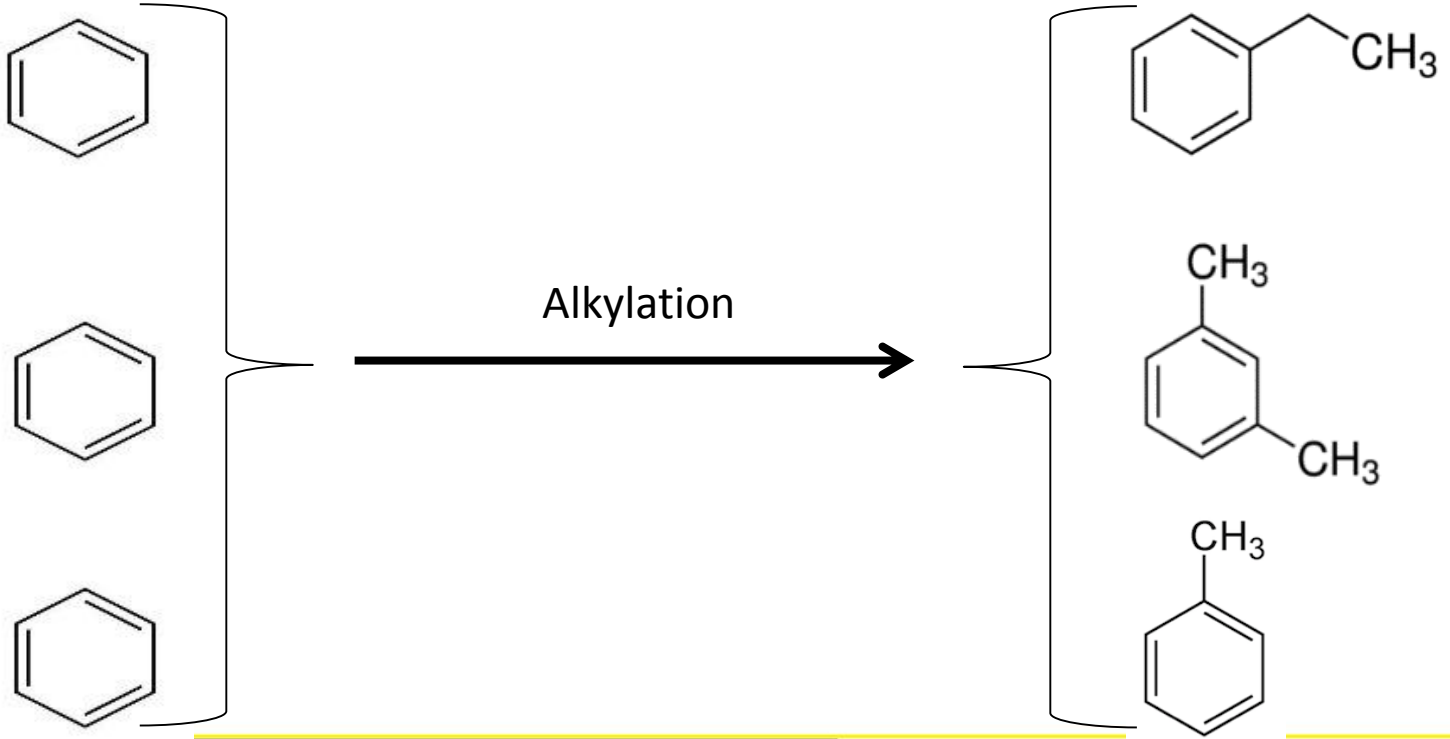
Identified Benzene Species (10)

	Component Name	Mol %	Molecular Weight	Density	Structure
44	1,3,5-triethylbenzene	0.0354	162.272	0.8897	
45	1,2,4-triethylbenzene	0.0771	162.272	0.8897	
46	1,4-methyl-n-pentylbenzene	0.0688	162.272	0.8897	
47	n-hexylbenzene	0.1058	162.272	0.8897	
48	1,2,3,4,5-pentamethylbenzene	0.1097	148.24	1	

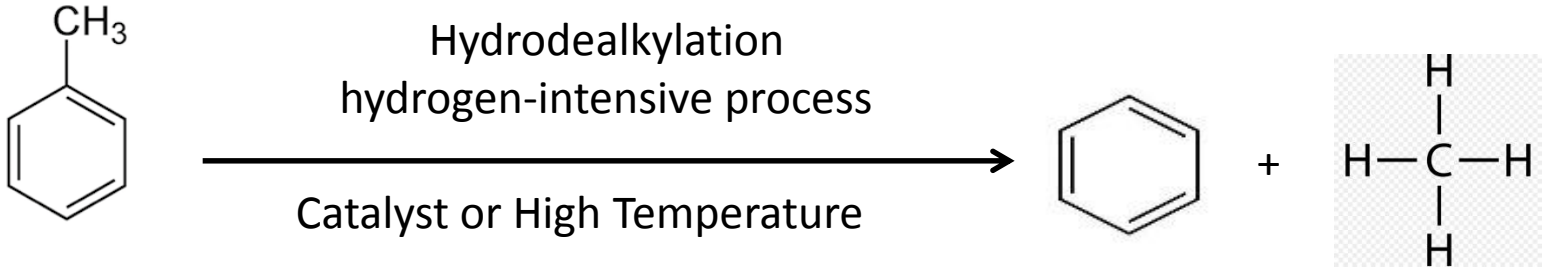
Concentrations

- BTEX: 1.7396 Mol%
- Other Alkylated Benzenes: 4.3167 Mol%

Alkylation of Benzene



Hydrodealkylation

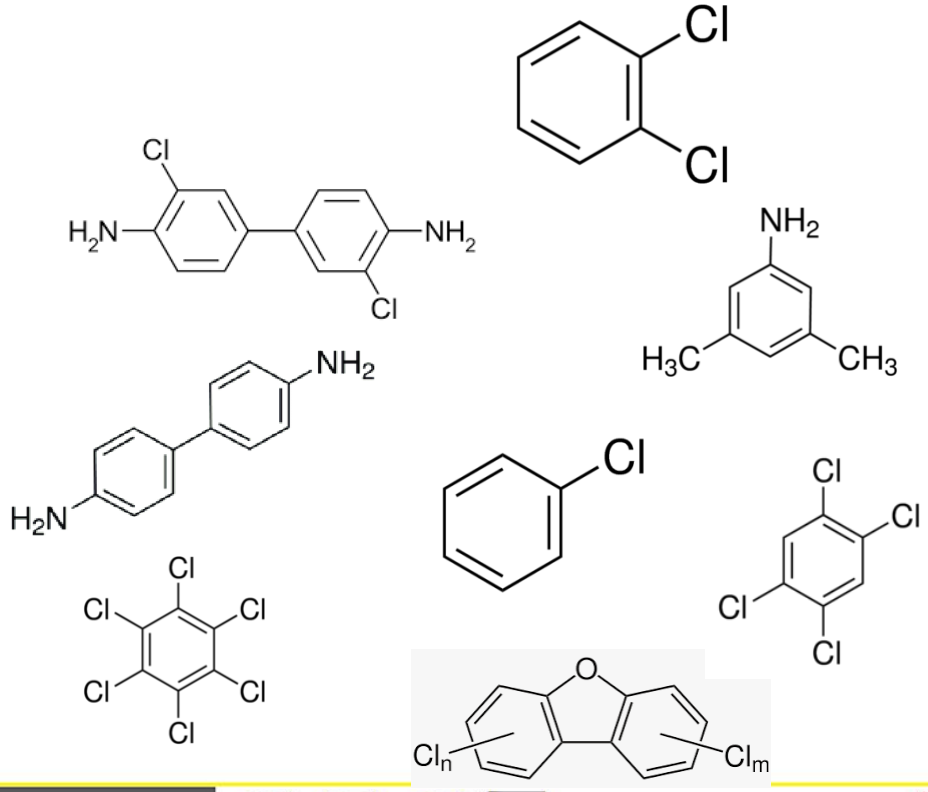


Schedule 1 (July 11, 2018)

- Benzene
- Hexachlorobenzene
- Tetrachlorobenzenes
- Pentachlorobenzene
- 1,2-Benzenediol
- 1,4-Benzenediol
- Benzene, (chloromethyl)-,
- Benzene, 1-methyl-2-nitro-
- Benzene, 1,2-dimethoxy-4-(2-propenyl)-

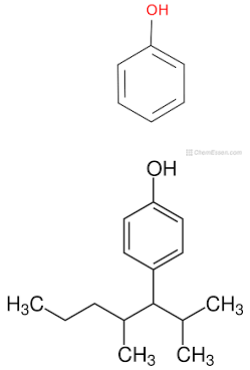
Priority Substances List 1 (PSL1), 1989

- 1,2-Dichlorobenzene
- 1,4-Dichlorobenzene
- 3,5-Dimethylaniline
- Benzidine
- Chlorobenzene
- Hexachlorobenzene
- Polychlorinated Dibenzofurans
- Tetra/Trichlorobenzenes
- PAHs, Toluene, Benzene, Xylenes

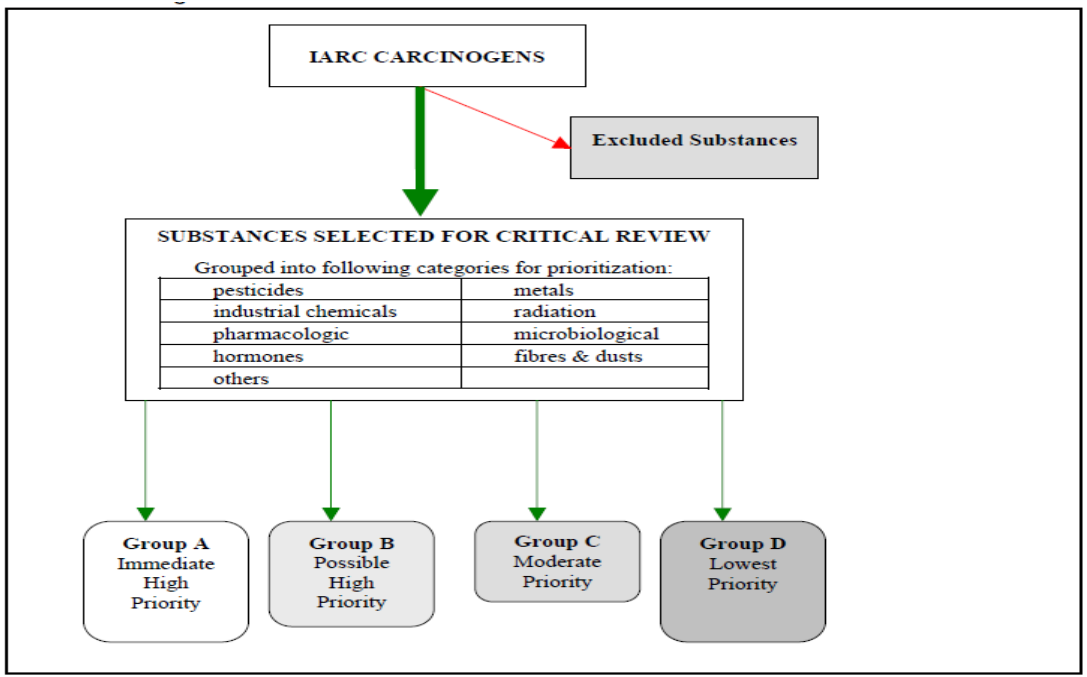


Priority Substances List 2 (PSL2) (CEPA) December, 1995

- Phenol
- Nonylphenol

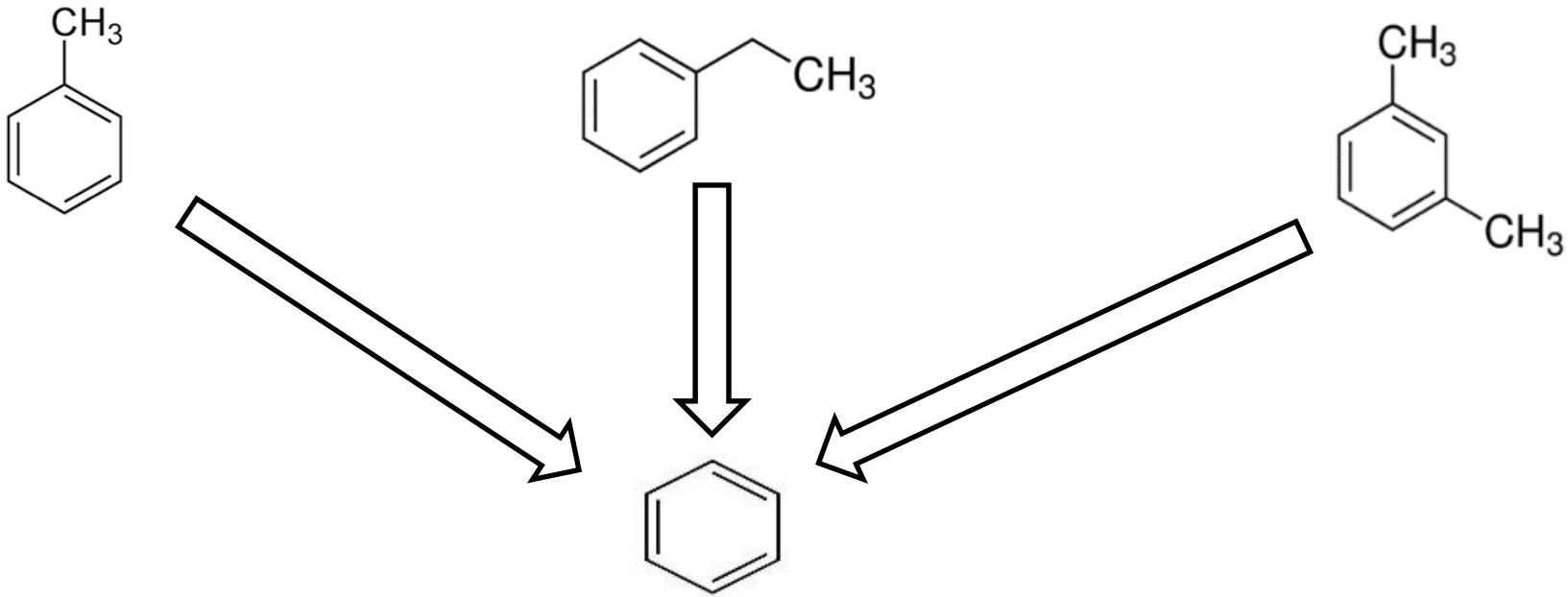


CAREX Canada – Prioritization Process Occupational

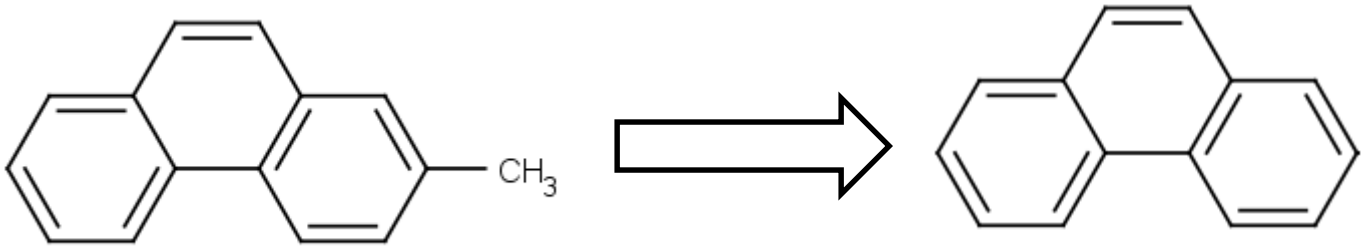


CAREX Canada is a national surveillance project that estimates the number of Canadians exposed to substances associated with cancer in workplace and community environments.

Does A Reverse Process Exist?



An Example of Dealkylation



Remember…

- BTEX: 1.7396 Mol%
- Other Alkylated Benzenes: 4.3167 Mol%

Conclusion and Suggestions

- Alkylated benzene compounds deemed to be toxic due to their structural similarity with BTEX compounds.
- Toxicity and carcinogenicity of all benzene compounds need to be assessed.
- Any petroleum product must be assessed for new benzene compounds.
- Pyrolysis derivatives of benzene contain products can be measured for potential hazard.
- PIONA GC-FID is an easy to operate instrument and cost effective for alkylated benzene content analysis.

Laboratory solutions

Environmental,

Energy, Mining,

Agri-food, Industrial

Transportation

Life Sciences

Thank You

Questions and Discussion