

Year 2, Organic Chemistry, Chapter 09:

EAS Alkylation of Benzene

- I trust that you remember that “EAS” stand for Electrophilic Aromatic (or Arene) Substitution.
- The ‘A’ Level Syllabus requires that you know something about these EAS reactions

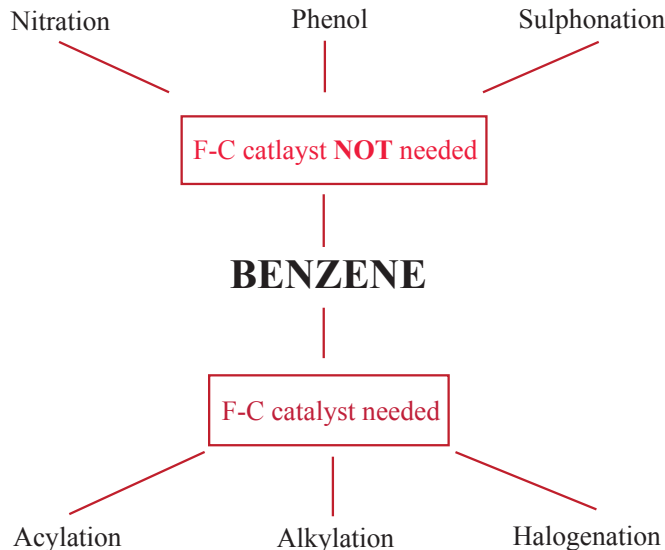
Those that need an FC catalyst

- | | | |
|----------------------------------|---------------------|--------------|
| - Alkylation of Benzene | with an FC catalyst | this Chapter |
| - Acylation of Benzene | with an FC catalyst | Chapter 10 |
| - Halogenation of Benzene | with an FC catalyst | Chapter 11 |

Those that do **NOT** need an FC catalyst

- | | | |
|---|-----------------------|------------|
| - Nitration of Benzene | no FC catalyst needed | Chapter 12 |
| - Sulphonation of Benzene | no FC catalyst needed | Chapter 13 |
| - The conversion of Benzene into Phenol | no FC catalyst needed | Chapter 13 |

EAS Reactions of Benzene



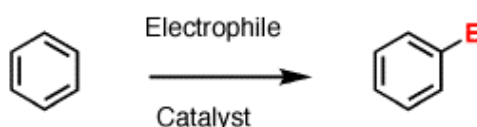
- | | |
|--|------------|
| - Addition Reactions of Benzene | Chapter 14 |
| - Phenol | Chapter 15 |
| - Azo Reactions ¹ | Chapter 16 |
| - Organic Synthesis | Chapter 26 |

so let us make sure that you do understand each one of these things.

¹ “Azote” is the French name for Nitrogen.

- Please remember that I want you to **understand** all these things so that it does not matter what they throw at you in the exams, you will still be able to answer the question in seconds because you *understand* what is going on. Learning something parrot-fashion can get you high marks – but it will not teach you how to deal with things about which you have **not** learnt.
- **Please keep in mind that I am not really trying to teach you Chemistry as such. I am teaching you how to cope with life so that you can lead happy and successful lives.**
- Chemistry as such is totally irrelevant. As far as I am concerned, Chemistry merely teaches you the ability to unravel complicated facts and then put together a solution to a problem. If I knew anything about Geology/or Biology/or Anthropology/or Archaeology/or Paleontology/or any other “-ology” for that matter – then I could do exactly the same thing for you with those subjects.
- Don’t worry about the Chemistry – **its your brains that I am trying to get you to use.** It does not matter about the girl/boy who sits next to you. **Before you leave here I want you to have fallen in love with your BRAINS.** This morning, whilst I was shaving, there was a Government Minister on the radio droning on about “Critical Thinking”, and the other morning there was someone going on about Edward de Bono’s “Lateral Thinking”. All that they were doing was saying what I am saying here viz. **learn to use your brain and learn to love it.**
- Three of the sources on the web that I have quoted to you are Jim Clark’s “chemguide” / Chemistry LibreTexts / Dr Ian Hunt’s Chemistry webbook, and now there is one more that I would like you to know about viz. “Master Organic Chemistry” at <http://www.masterorganicchemistry.com/reaction-guide/>. The following table is not in itself anything special (because I will be talking about all these points) but it is a little summary taken from Dr Ashenhurst’s website to introduce you to the existence of his website.

6 Key Electrophilic Aromatic Substitution Reactions



Name	Electrophile	Catalyst	E
Chlorination	Cl ₂	FeCl ₃ or AlCl ₃	Cl
Bromination	Br ₂	FeBr ₃ or AlBr ₃	Br
Nitration	HNO ₃	H ₂ SO ₄	NO₂
Sulfonylation	SO ₃	H ₂ SO ₄	SO₃H
Friedel Crafts Alkylation	R-X	FeX ₃ or AlX ₃	R
Friedel Crafts Acylation	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{X}$	FeX ₃ or AlX ₃	$\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$

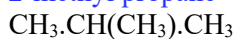
← SO₃H where H₂SO₄ has dissociated one proton.

- Any correctly constructed organic species can be designated as “R”, therefore we can designate any or all of the species on page 1 as “R” and we can use them in the Alkylation of a Benzene ring. Actually, we have no need to confine ourselves to Benzene. We can talk about any Arene, and we can use the designation “Ar” – and Alkylation will then give us “Ar-R”.

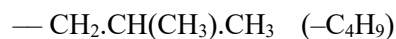
The Alkylation of Benzene

- The adjective “alkyl” is derived from the noun “Alkane”, and *technically* its use should be restricted to any Alkane species from which an H atom has been removed. Take any Alkane e.g. CH_4 / $\text{CH}_3\text{.CH}_3$ / $\text{CH}_3\text{.CH}_2\text{.CH}_3$ / $\text{CH}_3\text{.CH}_2\text{.CH}_2\text{.CH}_3$ / and so on, and remove a peripheral “H” atom and you will be left an “alkyl” species. For example the ones above would give $-\text{CH}_3$ / $-\text{CH}_2\text{.CH}_3$ / $-\text{CH}_2\text{.CH}_2\text{.CH}_3$ / $-\text{CH}_2\text{.CH}_2\text{.CH}_2\text{.CH}_3$ / and so on.
- I chose straight-chained alkanes in the above demonstration, but I could equally well have chosen branched alkanes to make my point. For example if we use

2-methyl propane



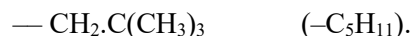
we would get



or 2,2-dimethyl propane



we would get



- Let me remind you of the Benzene info tree that I constructed for you – and please now concentrate only on the **Alkylation** bit of the tree.

The SUBSTITUTION reactions of Benzene

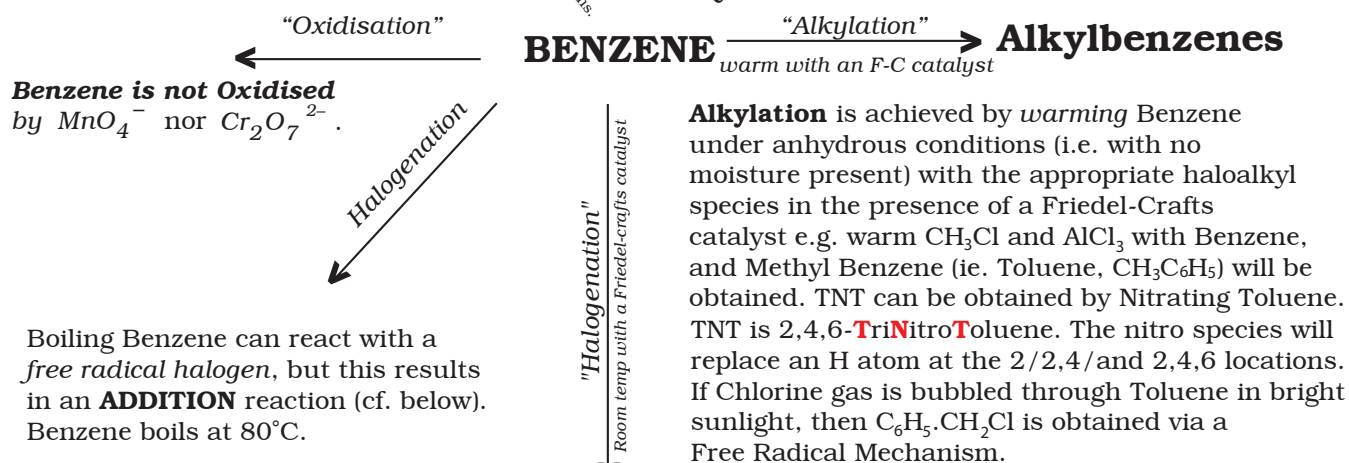
For 'A' Level purposes
Benzene can be obtained from the distillation of crude oil.
(In the olden days it was distilled from coal tar.)

SULPHONATION

An H atom is replaced by an SO_3H species from H_2SO_4 to give $\text{C}_6\text{H}_5\cdot\text{SO}_3\text{H}$ (i.e. Benzenesulphonic Acid) which is used in the manufacture of drugs/detergents/and dyes. In a laboratory it can be hydrolysed (with NaOH) to make Phenol.

NITRATION

One H atom can be replaced by an electrophilic NO_2^+ species by refluxing Benzene at 60°C with HNO_3 and $2\text{H}_2\text{SO}_4$. 1,3-**d**initrobenzene is obtained by refluxing at 95°C with conc HNO_3 and $2\text{H}_2\text{SO}_4$



HALOGENATION

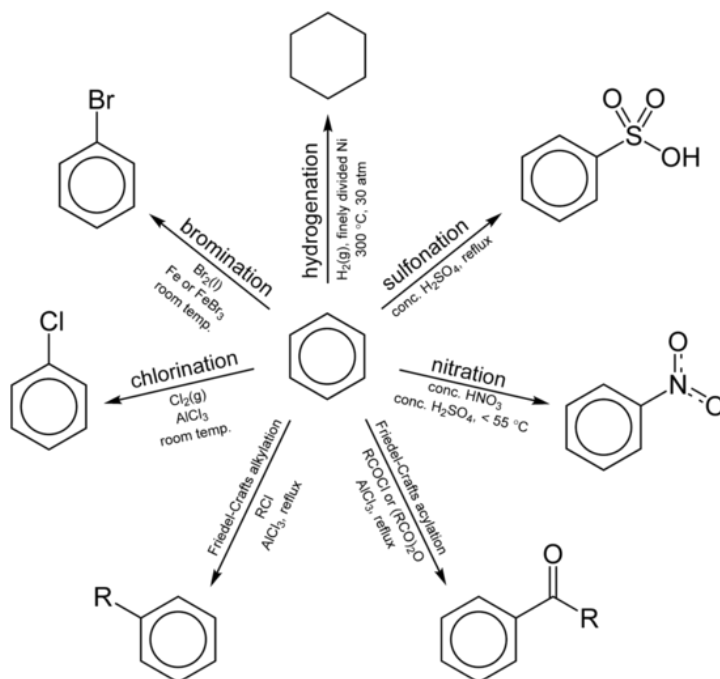
Benzene is much more stable than an Alkene therefore it does not react with a Halogen **by itself**, but it will react with a Halogen that is attached to a Friedel-Crafts' catalyst (i.e. a Halogen carrier). Br_2 and FeBr_3 will react with Benzene to replace an H in C_6H_6 with a Br. (HBr is also produced.) Cl_2 and AlCl_3 will react with Benzene to replace an H in C_6H_6 with a Cl. (HCl is also produced.) It is more difficult to react Iodine with Benzene, but Iodine will react with Benzenediazonium Chloride. The Halogen molecule forms a dative bond with the Friedel-Crafts' catalyst and this creates a separation of charge in the Halogen molecule, and it is the "+" part of the Halogen molecule (i.e. the *electrophilic* part of the polarised molecule) that now attacks the Benzene ring.

ADDITION REACTIONS

- Benzene will react with **Hydrogen** gas at 150°C in the presence of finely powdered Nickel to give C_6H_{12} .
- Benzene will react with a **Halogen** gas via a Free Radical Mechanism to give 1,2,3,4,5,6-hexachlorocyclohexane (with an H and a Halogen at each of the six apices).

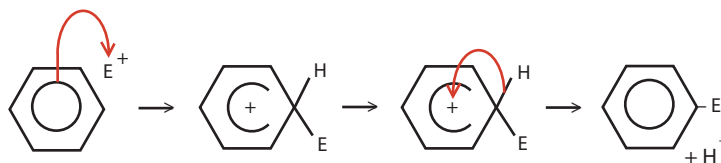
NB Benzene is not oxidised by Potassium Permanganate nor by Potassium Dichromate, but the $-\text{CH}_3$ group in Toluene will be oxidised by an alkaline manganate ion to give Benzoic Acid ($\text{C}_6\text{H}_5\cdot\text{COOH}$).

- However, you may prefer Wikipedia's info tree to mine.



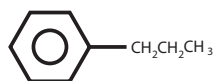
Alkylation of a Benzene ring

- At this point, please could you go back and read Chapter 7 again. I told you about Friedel-Crafts' (FC) catalysts, because for Alkylation (and also for Acylation and Halogenation) you will need an FC catalyst to enable you to create an **Electrophilic Aromatic Substitution reaction** of the electrophile "R" ("E⁺" or "C_nH_{2n+1}⁺") onto the Benzene (or any Arene) ring.
- In the diagram overleaf (where I am substituting/replacing an H atom on the Benzene ring with the alkyl species "–CH₂CH₂CH₃") I have heated/refluxed² Benzene (C₆H₆) with 1-chloropropane (Cl.C₃H₇) and an FC catalyst (AlCl₃) and this will cause the Cl to bond with the AlCl₃ and thereby create an electrophile of the "–C₃H₇⁺" species and thus allow the 1° (primary) carbo-cation to replace one of the H atoms on the C₆H₆ in an electrophilic substitution reaction.
- As described in Chapters 6 and 7, the AlCl₃ will take on the Cl from the 1-chloropropane to leave the positively charged "R⁺" electrophile (–C⁺H₂.CH₂.CH₃). The electrophile (E⁺) will be attracted to the electron cloud surrounding the Benzene ring and perform the EAS reaction below

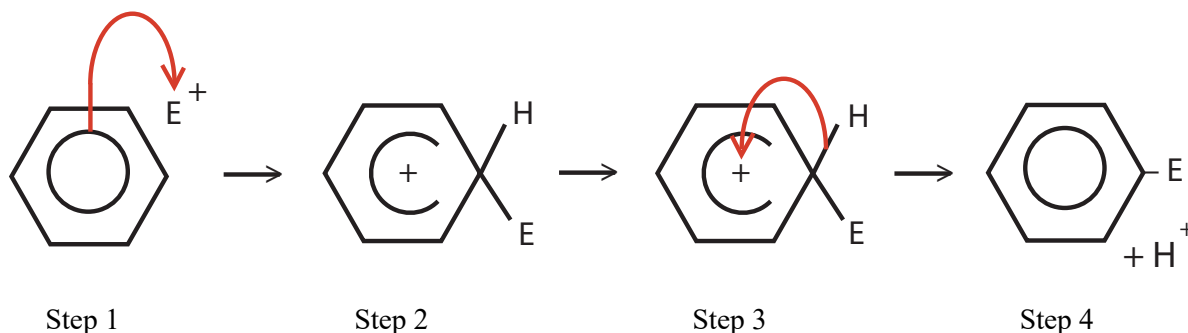


and the result is

² This speeds up the reaction. Heat confers greater energy on reacting molecules therefore they move faster therefore they collide more frequently therefore they react more quickly.



- The “R⁺” / “E⁺” electrophile (you can tie whichever label you want to onto it) has no way of choosing which of the six C atoms to marry/to bond with (and it just chooses one of the sextuplets) and lives ‘happily ever after’ with her after that. (*I have deliberately used silly 12-year old Mills & Boon terminology to underline the fact that all the 6 C atoms are equally attractive to the “R⁺” electrophile.*) The above reaction is an electrophilic aromatic substitution (EAS) reaction.
- I would like you to draw all EAS reactions as follows (and I explain each step below)



Step 1

The electrophile E⁺ attached to the FC catalyst is attracted to the area of high electron density surrounding the Benzene ring, and Benzene then forms a dative bond with E⁺ and Benzene thus “loses” one electron in doing so.

Step 2

E⁺ is now no longer short of an electron – but the **Benzene ring** has lost an electron and the ring has been broken³ and it must therefore be shown as incomplete and with a positive sign in it. The C atom where substitution will occur is now temporarily bonded to both an H and the Electrophile.

Step 3

The Hydrogen atom that is bonded to the C atom to which the electrophile is attached breaks away (as a proton) leaving behind its electron – and this now recreates the Benzene π ring!

Step 4

The reaction is now complete and the substitution reaction is finished. The proton that broke away will bond with the other “half” of the electrophile which at that stage is still attached to the FC catalyst. In this case, the H⁺ that breaks away bonds with the Cl that is attached to the FC catalyst (here AlCl₃) and forms HCl.

- The FC catalyst has now turned back into AlCl₃ as indeed it must in order to return to its original form otherwise **it would not be a catalyst** and would be a **reactant** in the EAS reaction.

³ If the ring were not broken, then the C atom which now has the electrophile attached to it would have 5 bonds – and this it cannot have.

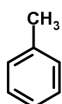
- The stability of a carbocation will increase according to the number of alkyl groups that are attached to it

the ability to donate electron density increases from Right to Left

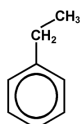
INCREASING Stability of the carbocation < 3° alkyl > 2° alkyl > 1° alkyl > methyl

< $\text{C}(\text{CH}_3)_3$ < $\text{CH}(\text{CH}_3)_2$ < $\text{CH}_2(\text{CH}_3)$ < CH_3

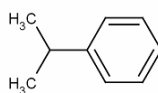
1°
Methyl Benzene
 $\text{C}_6\text{H}_5.\text{CH}_3$



1°
Ethyl Benzene
 $\text{C}_6\text{H}_5.\text{CH}_2\text{CH}_3$

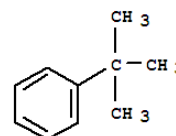


2°
Isopropyl Benzene⁴
 $\text{C}_6\text{H}_5.\text{CH}(\text{CH}_3)_2$



Cumene

3°
tert-butyl Benzene⁵
 $\text{C}_6\text{H}_5.\text{C}(\text{CH}_3)_3$

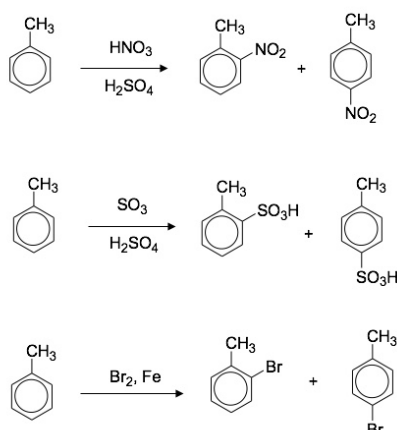


because Alkyl groups push electron density – and here they are pushing electron density along the σ bond that connects “R” to C_6H_5 .

NB Please remember that the convention in Organic skeletal diagrams is that the C and H atoms/and the bond lines to H atoms are **not** shown.

- A 3° alkyl electrophile will push a bit more electron density onto a Benzene ring than a 2° , and it in turn will push a bit more than a 1° , and so on – and this will make the reactions of an alkylated Benzene **faster** than ordinary Benzene. The following table comes from California State University, Dominguez Hills

toluene



faster than the same reactions with benzene

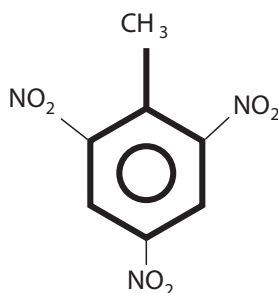
- Through a +I effect, the alkyl group ($-\text{CH}_3$) has increased the electron density on the π ring by a small amount and this speeds up the above reactions by activating the Benzene ring at 2 and 4 (and please remember that 2 is the same as 6).

⁴ Isopropyl Benzene, $\text{C}_6\text{H}_5.\text{CH}(\text{CH}_3)_2$, is also known as “Cumene”.

⁵ (1,1-dimethylethyl) Benzene, 2-methyl-2-phenyl propane, but most often called “tert-butyl Benzene” (“tert” being short for ‘tertiary’).

Alkylation using an Alkene

- Instead of using an **Alkane** and an FC catalyst, it is possible to use an **Alkene** together with HCl and an FC catalyst to alkylate an Arene. What happens is that (as we learnt last year in Chapter 5), the Alkene (e.g. C_2H_4) will react with the HCl in an electrophilic addition reaction to form an intermediate $(CH_3CH_2)^+$ carbo-cation (E^+) and a Cl^- anion. The anion will bond with the FC catalyst while the E^+ cation will perform an EAS reaction with Benzene to form $C_6H_5.C_2H_5$ while the replaced H atom from the Benzene ring will bond the Cl^- on the FC catalyst (halogen carrier) to reform HCl.
- That's it. That is how **Alkylation** takes place – but let me now combine what I have told you about Alkylation with what I told you about **Activation** (at 2/4/6) and **Deactivation** (at 2/4/6, but with Activation at 3/5).
- Any/every Alkyl species will push electron density along the sigma bond by which it is attached to a Benzene ring, and this will Activate the Benzene ring at 2/4/and 6. This means that where there was an enormous electron cloud of 6 delocalised electrons above and below the Benzene ring, there is now even more electron density – and it is concentrated more at 2/4/6 than it is at 3/5.
- Increasing the amount of delocalised electron density increases the ‘nucleophilicity’ of the Ar-R species and it also increases its stability – and this makes alkylated benzenes a useful precursor in the manufacture of many compounds. One of these is the explosive TNT (or 2,4,6-TriNitroToluene or 2,4,6-trinitro methylbenzene) $CH_3.C_6H_2.(NO_2)_3$.
- An explosion is what happens when a solid substance turns into a gaseous substance very quickly – and any substance that contains elements of the Periodic Table that will oxidise rapidly into gaseous molecules will thus be highly explosive. Here you have Carbon, Nitrogen, Hydrogen and Oxygen all packed together just waiting to ‘blow up’.⁶



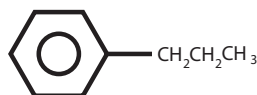
- I hope that you can now see that once you understand how things work, then instead of ‘compartmentalising’ your knowledge, you can put it to (good or bad) use.
- One of the UK Exam Boards (either OCR or Edexcel) in a recent exam paper asked a question about the reaction of Potassium Permanganate with an Alkene. In certain circumstances Benzene can be regarded as a substance with alternating double and single bonds, therefore the examiners could ask about the reactions between **Benzene** and Potassium Permanganate.
- As far as I am aware, under normal conditions, Benzene by itself will not react with any of the common oxidising agents such as the Dichromate(VI) ion/the Manganate(VII) ion, etc. **The delocalisation of the Benzene ring gives too much stability to the species for it to happen.** For oxidation to take place, the Benzene ring must first be activated (cf. Chapter 8).

⁶ Apart from the fact that Benzene is carcinogenic, can you now see why we do not allow Benzene into schools in England.

The oxidation of an Alkyl Benzene into a Carboxylic Acid

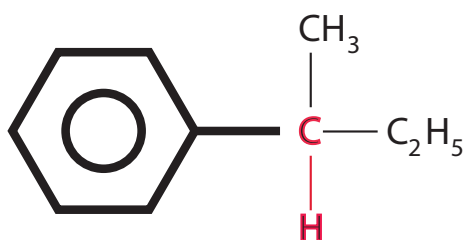
NB The Alkylation of an Alkyl Benzene will convert it into a Carboxylic Acid.

- Alkanes and Alkyl groups are not easily oxidised (other than by combustion); but, an Alkyl-Benzene ($C_6H_5.C_nH_{2n+1}$) such as $C_6H_5.CH_3$ / $C_6H_5.C_2H_5$ / $C_6H_5.C_3H_7$ (below)



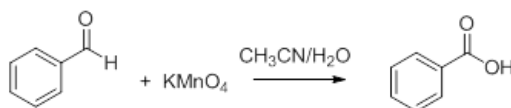
will react with an oxidising agent, and **the reaction occurs through the oxidation of the Alkyl Group.**

- What is happening is that the electron in the unhybridised 'p' orbital of the C atom that is attached to the Benzene ring has (by virtue of a positive Mesomeric effect) become a part of the delocalised Benzene ' π ' ring, and this causes electron density between the C atom and the H atoms to be diminished (it is pulled towards the Benzene ring), and thus the C-H bonds have become 'weakened' and are now easily 'breakable'.
- However, because the oxidation of the Alkyl Benzene takes place through the weakened "C-H" bond, the oxidation of an Alkyl Benzene **cannot take place unless there is at least one H species attached to the C atom that has bonded onto the Benzene ring.** Thus, for example, if that C atom is a 3° C atom (i.e. it has three C based groups attached to it), **then the Alkyl Benzene will not be oxidised.**
- Please note that there are six "C-H" bonds in Benzene, but **none of them will break in an oxidation reaction** (unless the Benzene ring has been activated by something like an "O-H" species or an "N-H₂" species). Here it is not the "C-H" bond on the Benzene ring that is breaking, **but it is the "C-H" bond on the Alkyl species that is undergoing the oxidation reaction. A tertiary Alkane attached to "-C₆H₅" will therefore not be oxidised.**

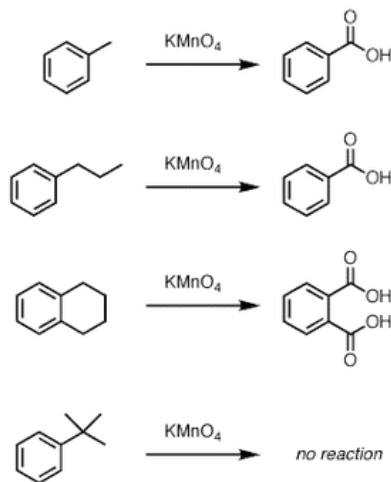


There must be at least **ONE "C-H"** bond attached to the "-C₆H₅" for oxidation to take place

- Equally, the C atom that is attached to the Benzene ring could be a '-C=O(HO)' Aldehyde species in which case it will be oxidised (just as will any Aldehyde) into a Carboxylic Acid e.g.



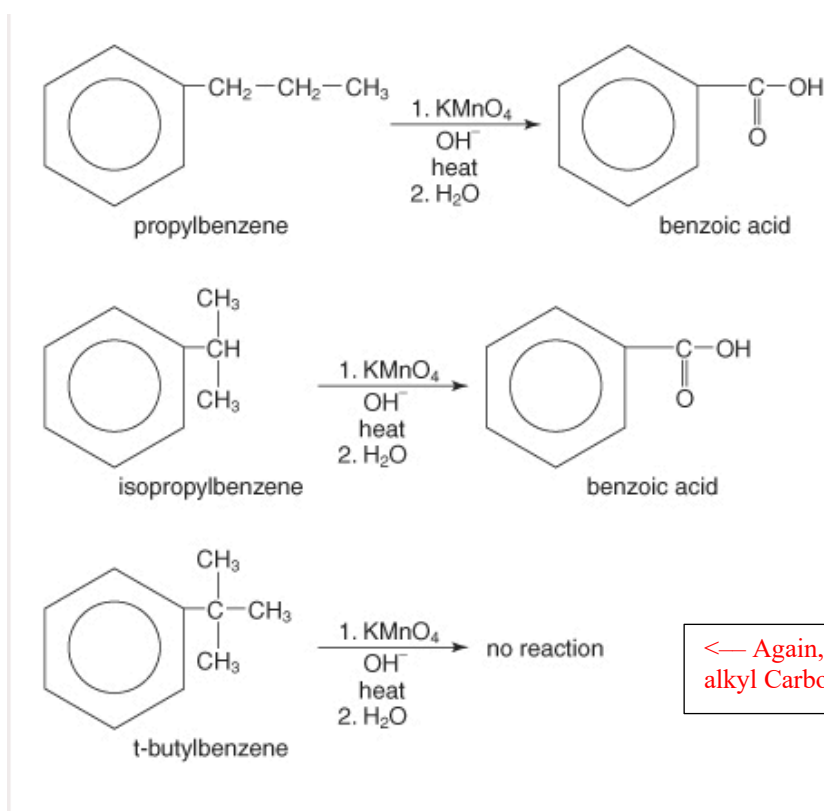
- The oxidation of an Alkyl Benzene (by e.g. $\text{Cr}_2\text{O}_7^{2-}$ or MnO_4^-) usually takes place in alkaline conditions wherein a Benzoate (a '-C₆H₅' Ester) is formed, and then conc. Sulphuric Acid is added to convert the Ester into a Carboxylic Acid.
- Dr James Ashenhurst of MasterOrganicChemistry shows this nicely below



<— NO REACTION because the alkyl Carbon is a 3° Carbon.

and “CliffsNotes” (another extremely good website) at <https://www.cliffsnotes.com/study-guides/chemistry/organic-chemistry-ii/carboxylic-acids-and-their-derivatives/preparation-of-carboxylic-acids>

shows a slightly different procedure to convert an alkyl Benzene into a Carboxylic Acid.



<— Again, NO REACTION because the alkyl Carbon is a 3° Carbon.

Where “t” stands for “tertiary”.