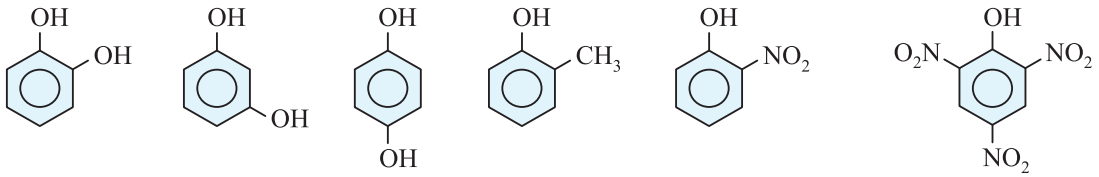
PHENOLS — Section - 2

Phenols are compounds containing a hydroxyl group : –OH group, attached directly to an aromatic ring. These generally are derivatives of main member phenol, C_6H_5OH(ph – OH). The compounds in which OH group is not attached directly to the ring such as benzyl alcohol, $C_6H_5CH_2OH$ are not phenols. These are called as side chain aromatic alcohols having properties similar to aliphatic alcohols.

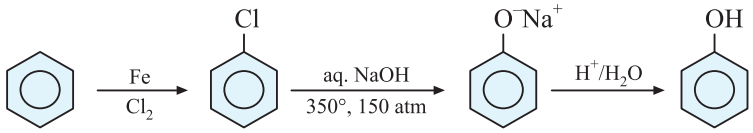
Some important phenols are :



Catechol | Rescorcinol | Hydroquinol | o - Cresol | o - Nitrophenol | 2, 4, 6-Trinitrophenol (Picric acid)

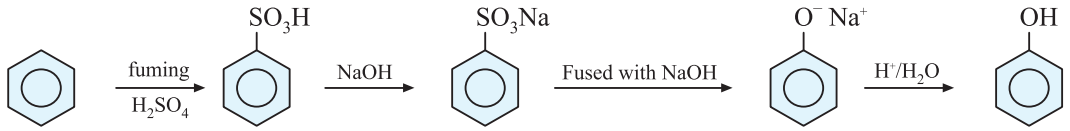
Preparation of Phenols

1. From Chlorobenzene :



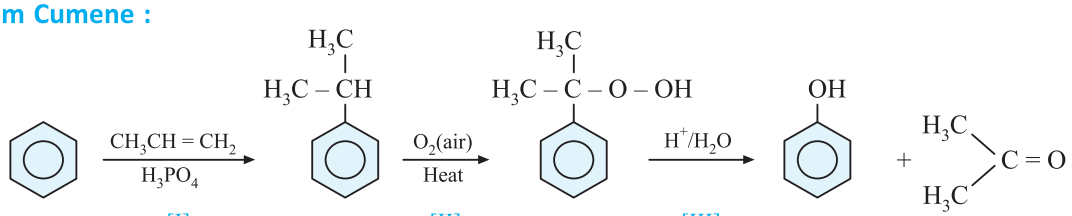
Sodium phenoxide

2. From Benzene sulphonic acid :



Benzene sulphonic acid | Sulphonate | Phenoxide

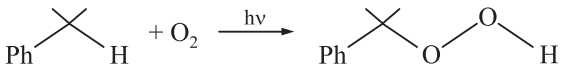
3. From Cumene :



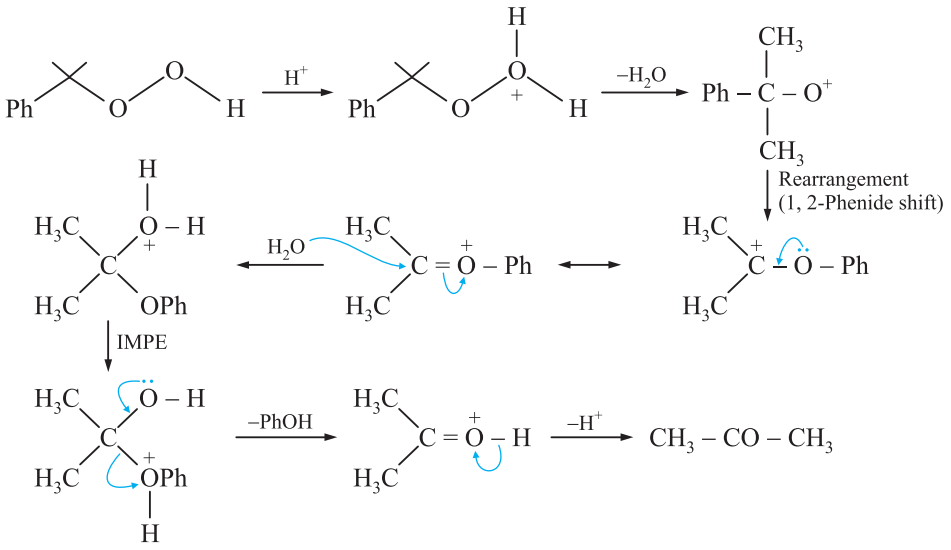
[I] | Cumene | [II] | Cumene hydroperoxide | [III] | Phenol

Reactions involved in above synthesis are as follows :

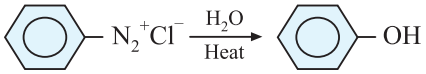
I. S_E reaction II. Free radical III. Acid catalysed hydrolytic rearrangement

II. 

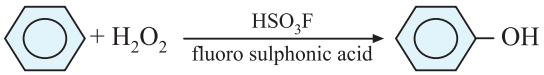
III.



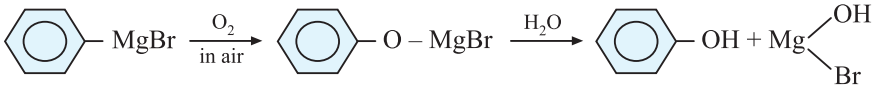
4. From Benzene Diazonium chloride :



5. From Benzene :



6. From Grignard Reagent :

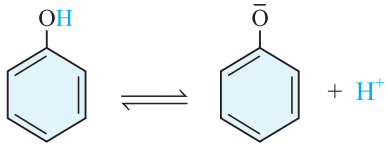


Reactions of Phenol

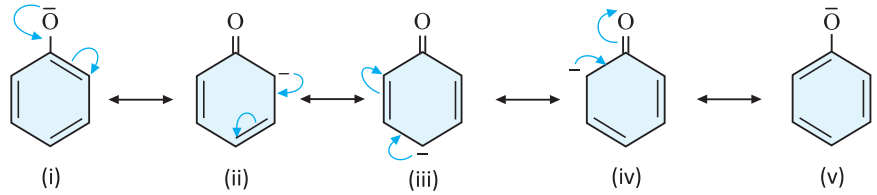
(A) Reactions of –OH group :

1. Salt Formation : Phenol is a weak acid and turns $FeCl_3$ solution violet, but fails to give litmus test. It reacts with sodium and NaOH to give phenoxides. Phenol however does not react with Na_2CO_3 and $NaHCO_3$.

The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water.

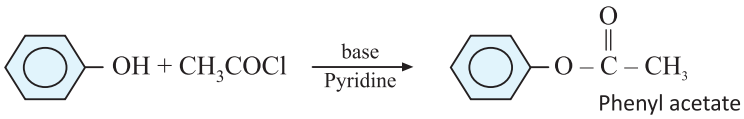


Due to the higher electronegativity of sp^2 hybridised carbon of phenol to which –OH is attached, electron density decreases on oxygen. This increases the polarity of O – H bond and results in an increase in ionisation of phenols than that of alcohols. Also phenoxide, the conjugate base of phenol is more stabilised than alkoxide, the conjugate base of alcohols. The delocalisation of negative charge (structures I-V) makes phenoxide ion more stable and favours ionisation of phenol.

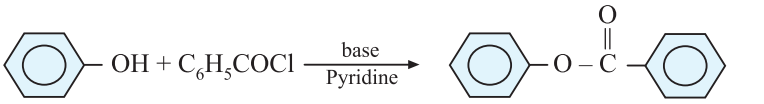


Resonating Structures of Phenoxide ion

2. Formation of Ester : The acetylation and benzoylation of phenols are called as Schotten-Baumann reactions.

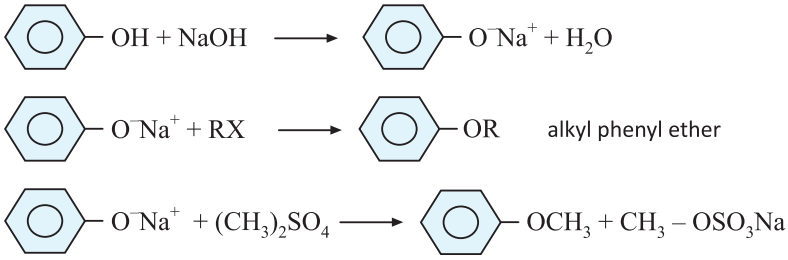


Phenyl acetate

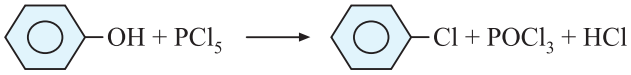


Phenyl benzoate

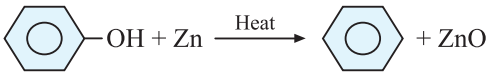
3. Formation of Ethers :



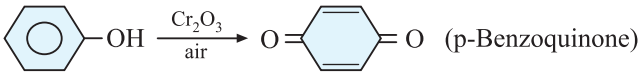
4. With PCl_5 : (Formation of Aryl halides)



5. With Zn-dust : (Reduction)

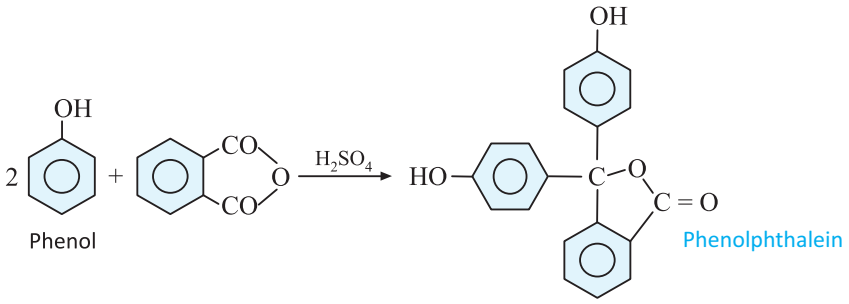


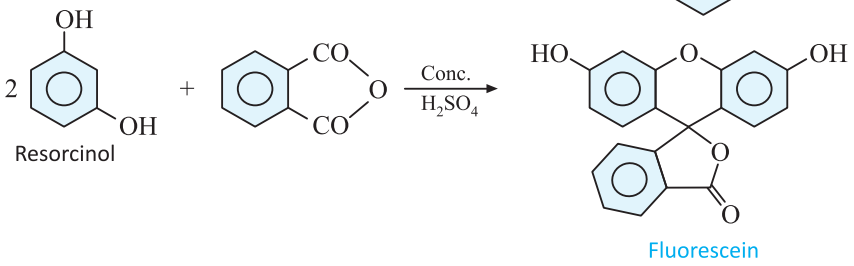
6. Oxidation :



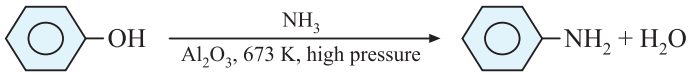
(p-Benzoquinone)

7. Condensation with Phthalic anhydride : Phenol undergoes a special Friedal Craft acylation with phthalic in presence of H_2SO_4 to form phenolphthalein (an acid-base neutralisation indicator).





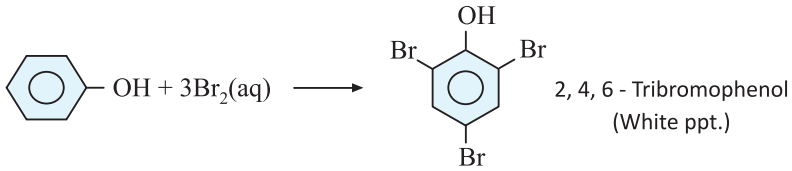
8. With NH_3 :

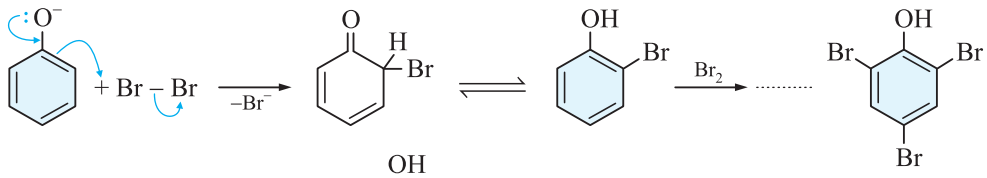


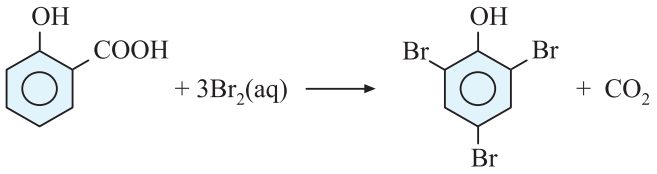
(B) Reactions of Benzene group :

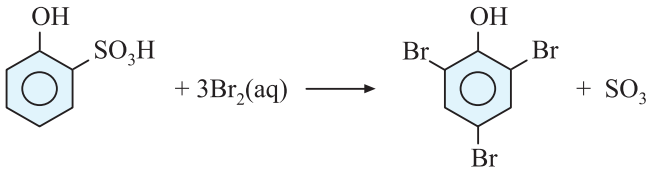
Phenol undergoes electrophillic substitution reactions much more readily as compared to benzene due to electron releasing ability of –OH group (activating agent). Also –OH group over benzene is strongly 'o' and 'p' directing due to +M effect of OH group.

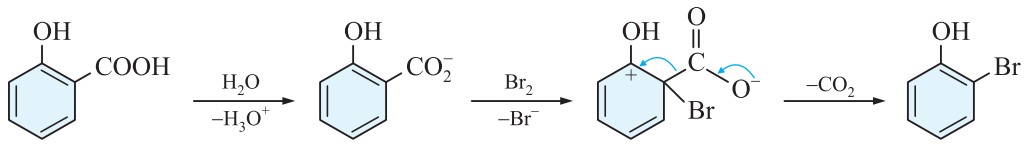
1. Halogenation :



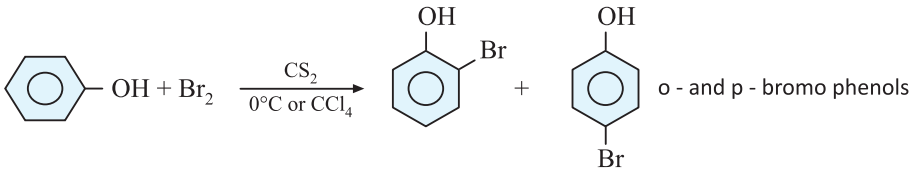






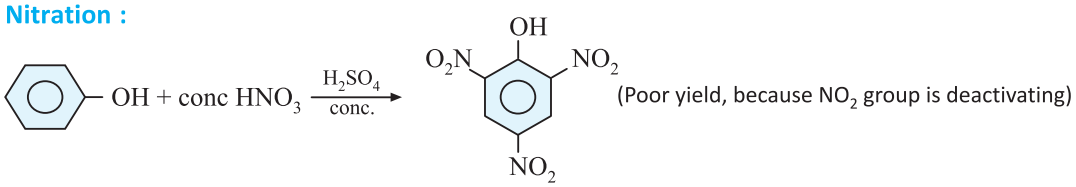


Note : Halogenation of phenol takes place even in absence of Lewis acid ($AlBr_3$, $FeBr_3$) due to the highly activating effect of –OH group.

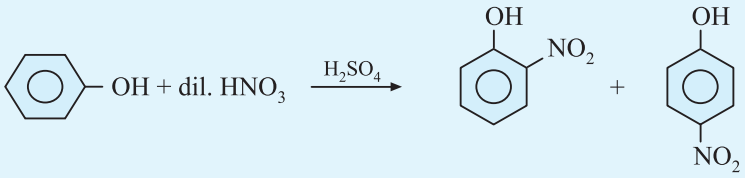


Note : –OH group is strongly activating, hence a tri-substituted product is formed. However, in CS_2 at 0°C, only Ortho (o) and Para (p) derivatives are formed.

2. Nitration :

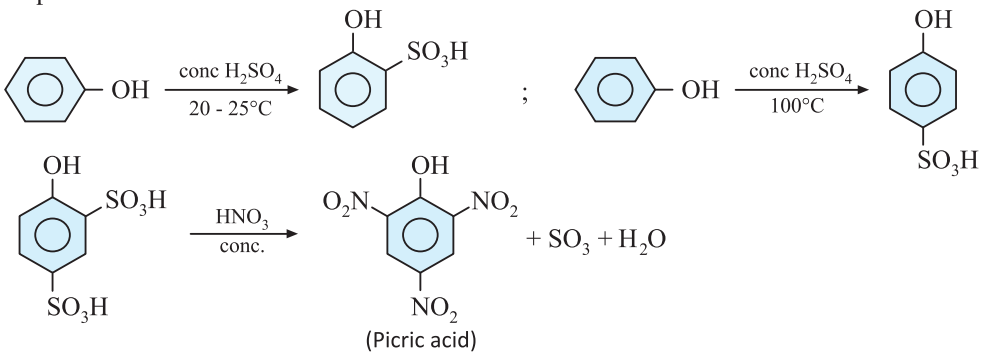


Note : With concentrated nitric acid, phenol forms 2, 4, 6-Trinitrophenol, commonly known as Picric acid. *With dilute acid, however, a mixture of o- and p- nitriphenol is formed*. This mixture can be separated by steam distillation.



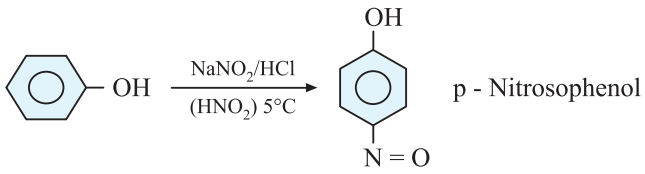
3. Sulphonation :

At 25°C, phenol gives only o-hydroxy benzene sulphonic acid, whereas at 100°C, it gives p-hydroxy benzene sulphonic acid.



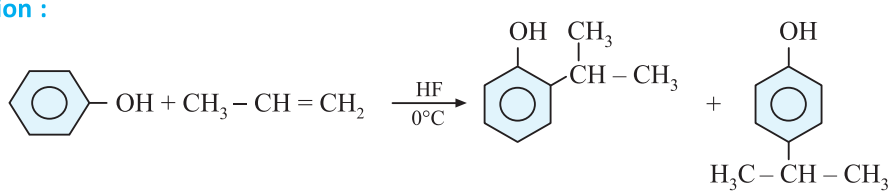
Picric acid is prepared in good yield by treating phenol first with concentrated H_2SO_4 which converts it to phenol-2, 4-disulphonic acid, then with concentrated HNO_3 to get 2, 4, 6-trinitrophenol.

4. Nitrosation :



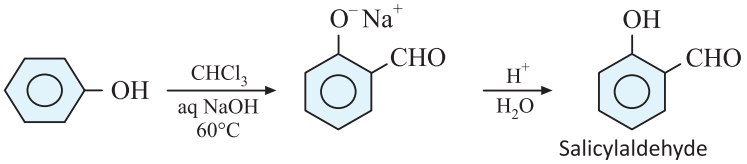
p - Nitrosophenol

5. Alkylation :



Phenols undergo Friedel Craft alkylation to give the product according to the most stable intermediate carbocation.

6. Reimer - Tiemann Reaction :

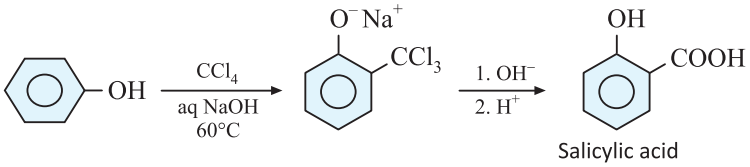


Salicylaldehyde

Ortho product is formed as major because :

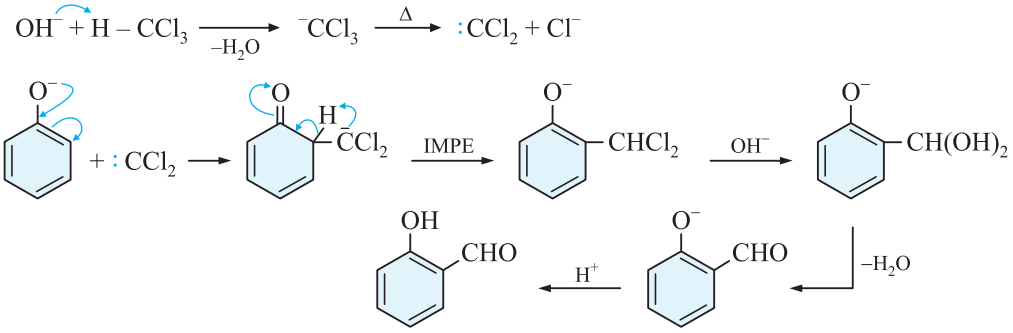
(i) Ortho position is more activated

(ii) Stabilization by chelation

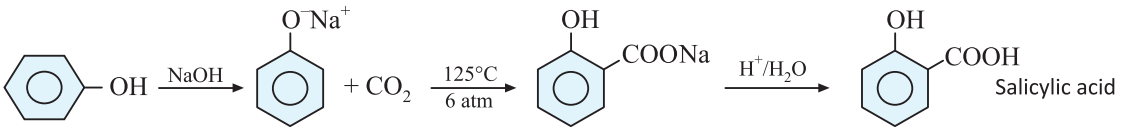


Salicylic acid

Mechanism of Reimer – Tiemann Reaction: The reaction involves electrophillic substitution on the highly reactive phenoxide ring. Here the electrophile is dichlorocarbene : CCl_2, generated from $CHCl_3$ by the action of a base.

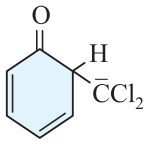
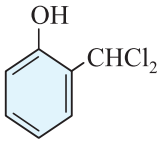
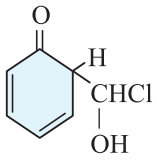
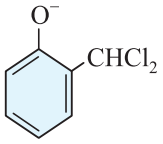


7. Kolbe's Reaction :



Salicylic acid

*5. *When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediate ?*

(A)  (B)  (C)  (D) 

6. *Phenol is also called* :

(A) *salicylic acid* (B) *benzyl alcohol* (C) *carbolic acid* (D) *salol*

7. *Phenols do not react with* :

(A) *sodium bicarbonate* (B) *sodium hydroxide*
(C) *potassium hydroxide* (D) *ferric chloride*

8. *Phenol on treatment with diethyl sulphate in presence of NaOH gives* :

(A) *Anisole* (B) *Ethyl phenyl ether (phenetole)*
(C) *Diethyl ether* (D) *No Reaction*

*9. *Benzyl alcohol and phenol can be distinguished by the use of* :

(A) $FeCl_3$ (B) *Na* (C) *Lucas reagent* (D) *None of these*

*10. $C_6H_5OH \xrightarrow[NaOH\,(aq.)]{CH_3COCl}$

The above reaction is an example of :

(A) *acetylation* (B) *benzoylation*
(C) *Schotten-Baumann reaction* (D) *Reimer-Tiemann reaction*

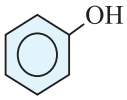
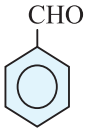
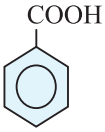
Paragraph for Q.11 - 13

An organic compound (X) on treatment with $CHCl_3$ and KOH gives (Y) and (Z) both of which in turn gives the same compound (T) when distilled with Zn. X on esterification with acetic acid yields a product with V.D. = 68. (T) is oxidised to give (S), which on decarboxylation gives (P). (X) on distillation with Zn also gives (P).

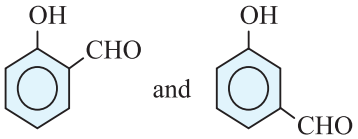
11. *The molecular weight of compound (X)* is :

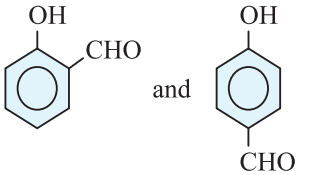
(A) 122 (B) 94 (C) 106 (D) 78

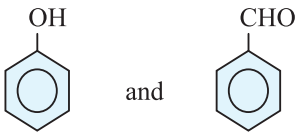
12. *The compound (T) is* :

(A)  (B)  (C)  (D) 

13. *Compound (Y) and (Z) could be* :

(A) 

(B) 

(C) 

(D)