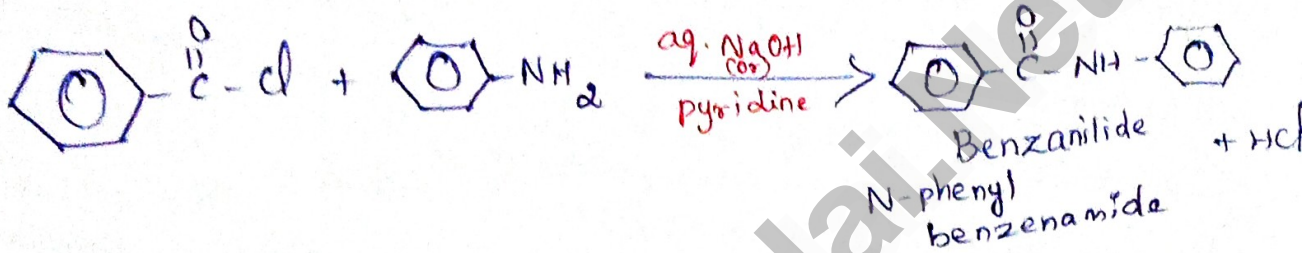
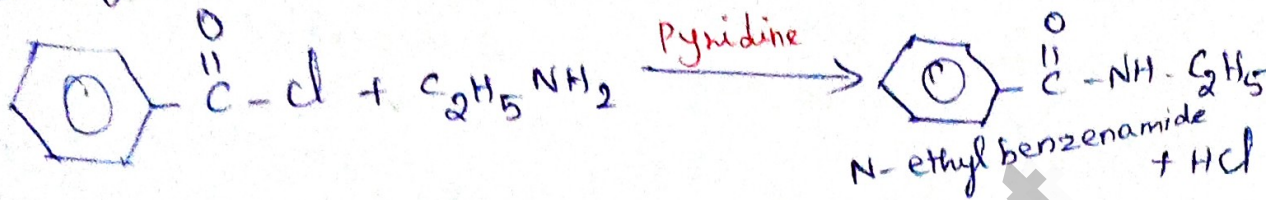
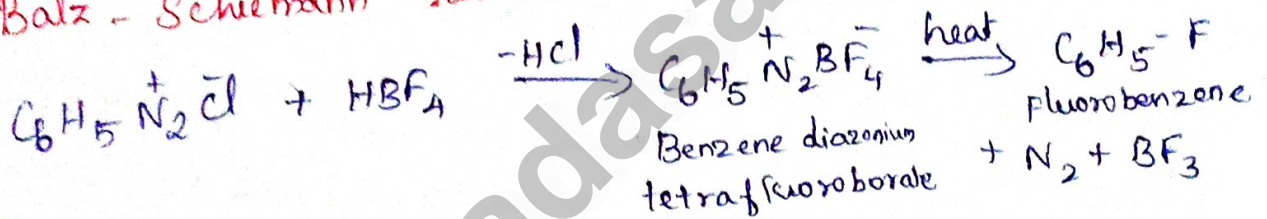
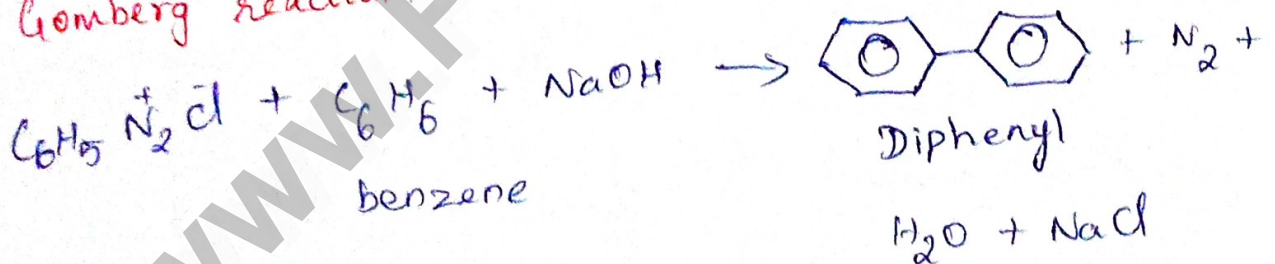


Unit - 13 - Amines.Schotten - Baumann reaction

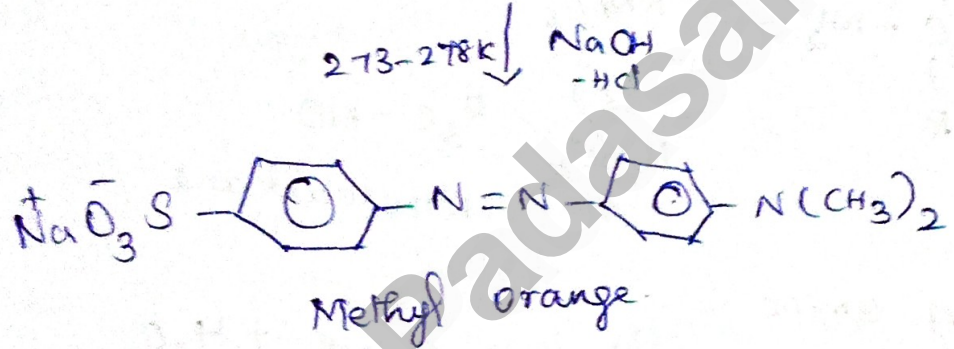
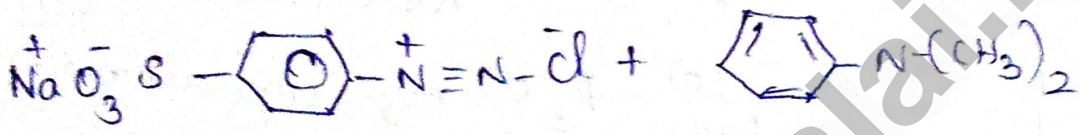
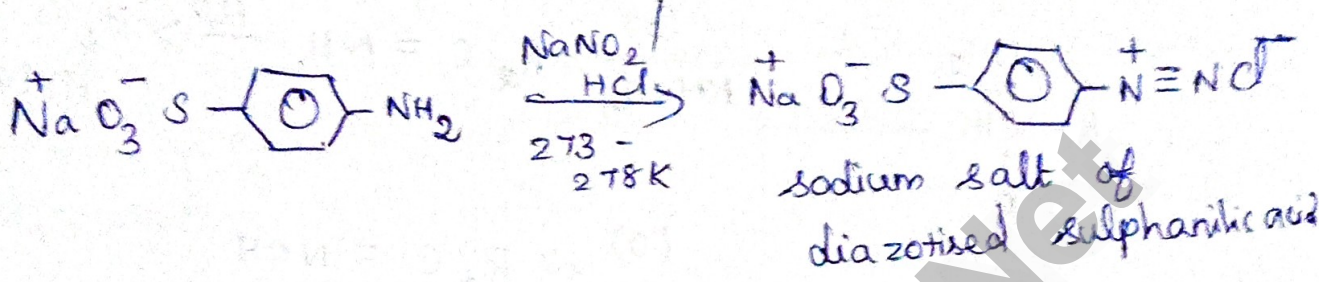
Benzoylation of compounds containing active hydrogen such as alcohols, phenols and amines with benzoyl chloride in presence of dil. aq. NaOH solution.

2. Balz - Schiemann reaction:3. Gomberg reaction:4. Coupling reactions:

Coupling takes place at para position with respect to phenolic (-OH) or amino (-NH<sub>2</sub>) group. If p-position is not free, coupling takes place at o-position.

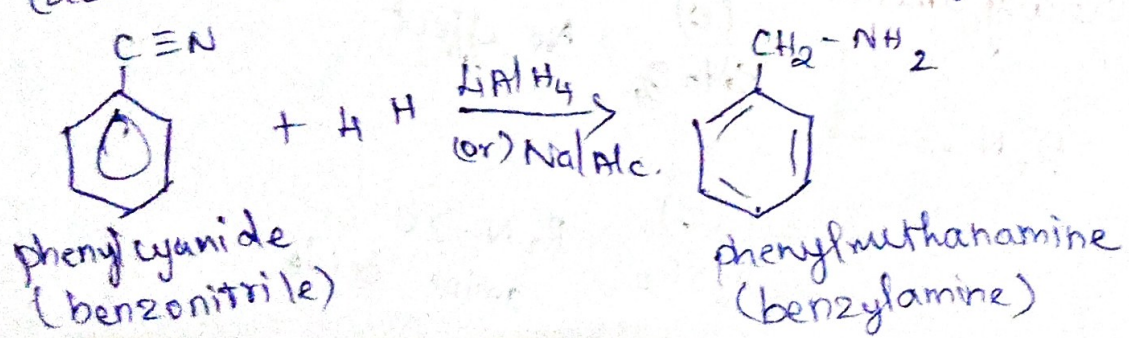
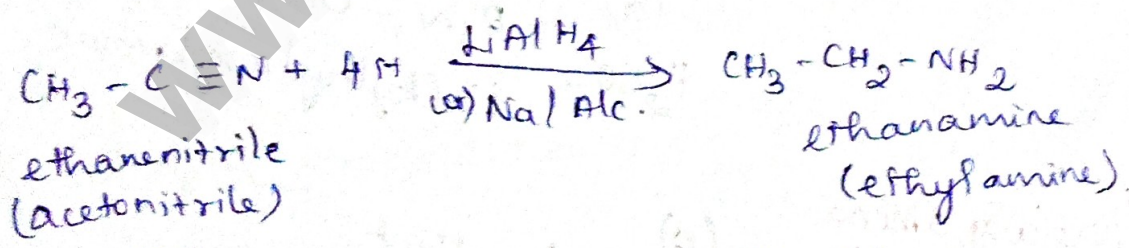
The well known indicator methyl orange is also an dye (azo dye)

It is obtained by coupling of diazonium salt of sulphanic acid with N,N-dimethyl aniline.

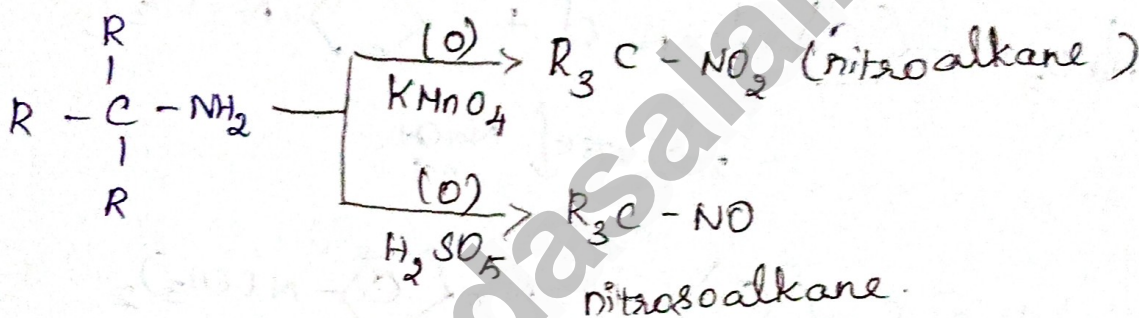
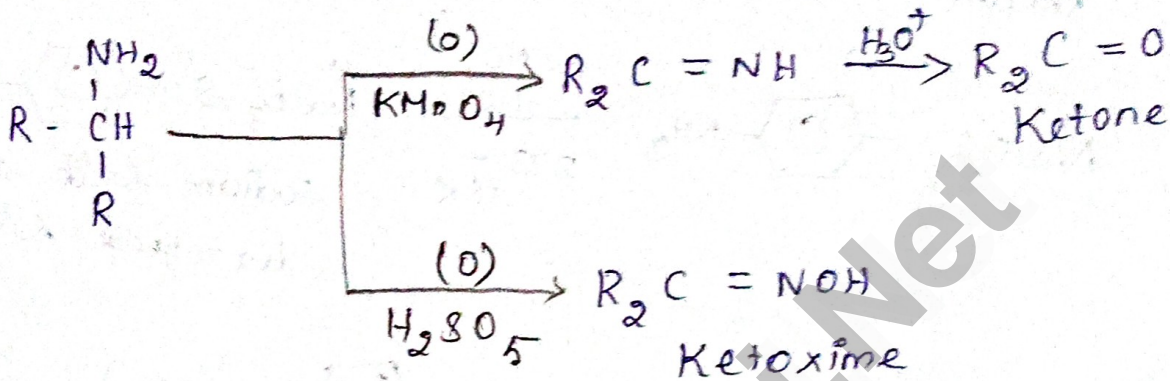
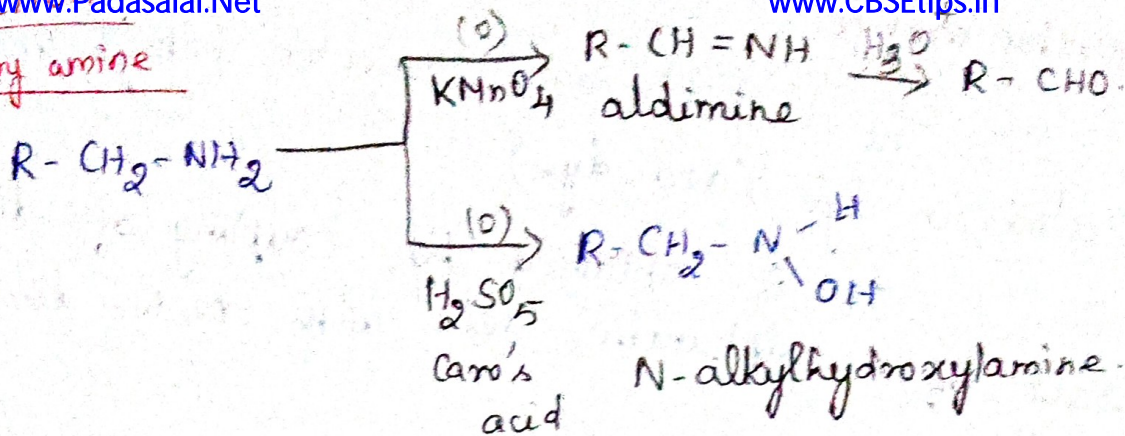


5. Mendius reaction:

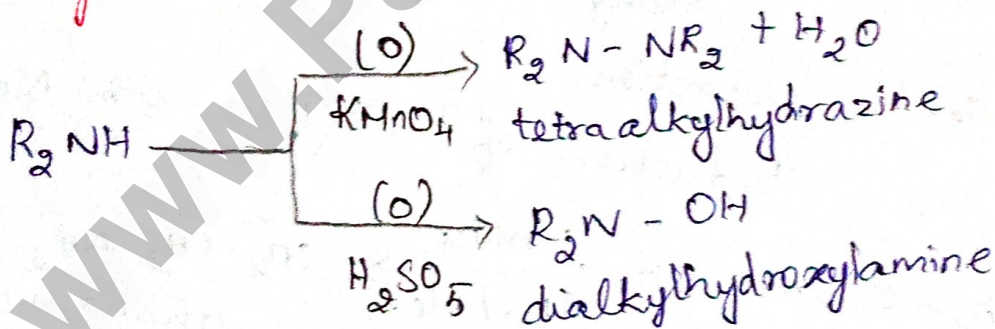
Reduction of nitrile with Na/C<sub>2</sub>H<sub>5</sub>OH



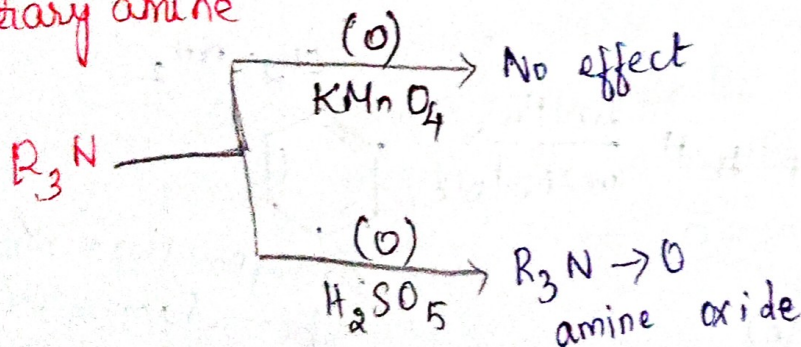
Primary amine



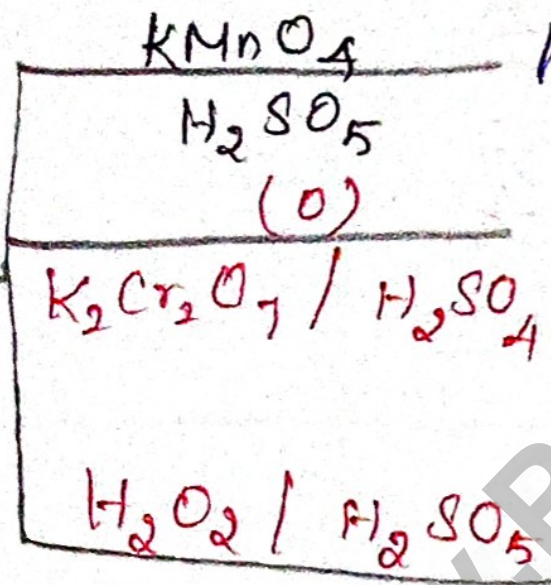
Secondary amine



Tertiary amine



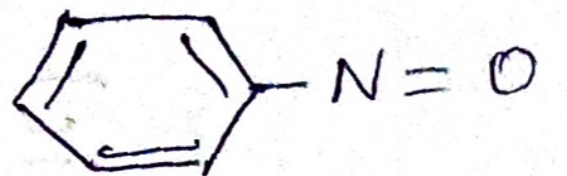
# Aromatic primary amine



Aniline Black

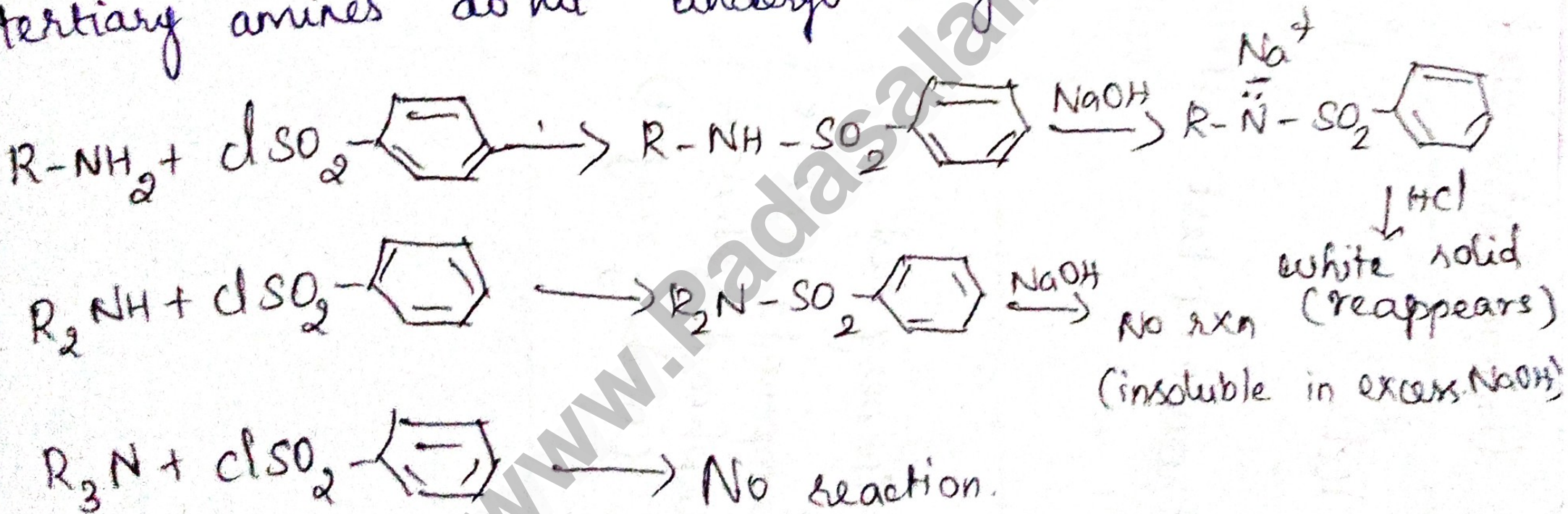


p-benzoquinone



# Reactions of Hinsberg test.

With benzenesulphonyl chloride and an alkali like NaOH, 1° amines form soluble sulphonamide, 2° amines form insoluble sulphonamides (which form white ppt) while tertiary amines do not undergo any rxn.



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## Tests to distinguish 1°, 2°, 3° amines

| S.No | Test   | Primary amines   | Secondary amines  | Tertiary amines  |
|------|--|--|---|--|
| 1.   | Reaction with alkyl halides                      | Combines with three molecules of alkyl halides to form the quaternary salts. | Combines with two molecules of alkyl halide to form the quaternary salts. | Combines with one molecule of alkyl halide to form the quaternary salts.                       |
| 2.   | Reaction with acid chlorides and acid anhydrides | Form monoalkyl substituted amide.  | Forms dialkyl-substituted amide.  | No reaction.   |
| 3.   | Reaction with nitrous acid                       | Forms mixture of alcohols and alkenes with evolution of nitrogen gas.        | Forms yellow oily nitrosoamines characterised by Liebermann's test.       | Forms nitrite salts which on decomposition give mixture of nitrosoamine, alcohols and ketones. |
| 4.   | Carbylamine reaction                             | Forms Carbylamine with offensive odour.                                      | No reaction   | No reaction  |

①

| S.No  | Test   | Primary amines  | Secondary amines   | Tertiary amines |
|---|--|---|--|-----------------|
| 5.  | Action with Hinsberg's reagent i.e., benzene Sulphonyl chloride ( $C_6H_5SO_2Cl$ ) | Forms monoalkyl sulphonamide which on treatment with alkali gives a water soluble salt. | Forms dialkyl sulphonamide which does not dissolve in alkali | Does not react. |
| Distinction between ethylamine and aniline (aliphatic + aromatic amine) |  |   |  |                 |
|   | Property / test  | Ethyl amine   | Aniline  |                 |
|   | Boiling point  | 292 K   | 457 K  |                 |
|   | Smell  | Fishy   | Unpleasant   |                 |
|   | Solubility in water  | Highly soluble  | Practically insoluble  |                 |
|   | Oxidation  | Not easily oxidised   | Readily oxidised to a brown coloured compound                |                 |
|   | Reaction with nitrous acid   | Gives primary alcohol   | Gives diazonium salts in ice cold solution.                  |                 |
|   |  | (2)   |  |                 |

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