

CHAPTER-WISE NOTES

Organic Chemistry

Named Reactions

NAMED REACTIONS

1. ALDOL CONDENSATION

Two molecules of an aldehyde or a ketone undergo condensation in the presence of a base to yield a β -hydroxyaldehyde or a β -hydroxyketone. This reaction is called the aldol condensation

$$H_3C$$
 — C — CH_3 CH_3 — CH_3

2. <u>DIECKMANN CONDENSATION</u>

The Dieckmann condensation is the intramolecular chemical reaction of diesters with base to give β-ketoesters

3. CLAISEN CONDENSATION

An α -hydrogen in an ester is weaker than the α -hydrogen of aldehydes or ketones, because the carbonyl group helps accommodate the negative charge of the carbanion to a lesser extent.

When ethyl acetate is treated with sodium ethoxide, and the resulting mixture is acidified, ethyl 3-oxobutanoate, generally known as ethyl acetoacetate or acetoacetic ester, is obtained.

4. PERKIN REACTION

The reaction between aromatic aldehydes and alkanoic anhydrides in the presence of alkanoate is called the Perkin reaction. The reaction is similar to aldol condensation.

5. KNOEVENAGEL REACTION

The condensation of aldehydes and ketones with compounds containing an active methylene group in the presence of a basic catalyst to form α,β -unsaturated compounds is known as the Knoevenagel reaction. The basic catalyst may be ammonia or its derivative. Thus, 1°, 2°, and 3° amines, i.e., aniline, dior tri-alkyl amines, pyridine, or piperidine, are used.

6. REFORMATSKY REACTION

It involves treating an aldehyde or ketone with an α -bromo ester in the presence of zinc metal; the solvent most often used is benzene. The initial product is a zinc alkoxide, which must be hydrolyzed to yield the β -hydroxy ester.

$$R_2C \longrightarrow O$$
 + $BrCH_2COOC_2H_5 \longrightarrow R \longrightarrow R$ $CH_2COOC_2H_5$

7. MICHAEL ADDITION

The best Michael reactions are those that take place when a particularly stable enolate ion, such as that derived from a β -keto ester or other 1,3-dicarbonyl compound, adds to an unhindered α,β -unsaturated ketone. For example, ethyl acetoacetate reacts with 3-buten-2-one in the presence of sodium ethoxide to yield the conjugate addition product.

8. MANNICH REACTION

The Mannich reaction is an organic reaction that involves the amino alkylation of an acidic proton adjacent to a carbonyl functional group by formaldehyde and a primary or secondary amine, or ammonia. The final product is a β-amino-carbonyl compound, also known as a Mannich base.

SUBSTITUTION REACTIONS

1. SANDMEYER REACTION

2. GATTERMANN REACTION

Similar to Sandmeyer, but uses Cu powder and HCl.

3. FINKELSTEIN REACTION

Alkyl iodides are often prepared by the reaction of alkyl chlorides or bromides with NaI in dry acetone or DMSO.

4. SWARTZ REACTION

This reaction is for the synthesis of alkyl fluorides via heating of alkyl halide or bromide in the presence of metallic fluoride, i.e., AgF, Hg₂F₂, CoF₂, or SbF₃.

5. WILLIAMSON ETHER SYNTHESIS

This is an SN2 reaction between an alkoxide and alkyl halide to form ether. It is an important laboratory

method for the synthesis of symmetrical and unsymmetrical ether.

$$H_3C$$
 CH_3
 O^-Na^+
 $+$
 H_3C
 CH_3
 CH_3
 CH_3

ELECTROPHILIC AROMATIC SUBSTITUTION

1. FRIEDEL-CRAFT ALKYLATION REACTION

In this reaction, benzene is treated with an alkyl halide in the presence of anhydrous AlCl₃ to form alkylbenzene

2. FRIEDEL-CRAFT ACYLATION REACTION

3. GATTERMAN-KOCH SYNTHESIS

When benzene is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride, benzaldehyde is obtained

AROMATIC AND MISCELLANEOUS REACTIONS

1. REIMER-TIEMANN REACTION

2. KOLBE'S REACTION

Phenol on treatment with sodium hydroxide give orthohydroxybenzoic acid as the final product

3. DIAZOTIZATION

When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, then as a result diazonium salt is obtained

4. COUPLING REACTION

In this reaction, benzene diazonium chloride reacts with phenol or aniline to give an azo dye

OXIDATION-REDUCTION REACTIONS

1. WOLF-KISHNER REDUCTION REACTIONS

When a ketone or an aldehyde is heated in a basic solution of hydrazine, the carbonyl group is converted to a methylene group this process is called Deoxygenation because oxygen is removed from the reactant. The reaction is known as the Wolf-Kishner Reduction.

2. CLEMMENSEN REDUCTION

The reduction of carbonyl groups of aldehydes and ketones to methylene groups with amalgamated zinc and concentrated hydrochloric acid is known as Clemmensen reduction.

$$R_1$$
 R_2 $Zn, Hg/HCl$ R_1 R_2

3. BAEYER-VILLIGER OXIDATION REACTIONS

In this reaction, when ketone is treated with hydrogen peroxide or peracid, a formal insertion of oxygen takes place to give a carboxylic ester.

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4. OPPENAUER OXIDATION

This reaction is carried out by treating the substrate with aluminium tri-t-butoxide in the presence of acetone to give the ketone and isopropanol

5. MEERWEIN-PONDORFF-VERLEY REDUCTION

In this reaction, reduction of ketones takes place to form secondary alcohols, and for aldehydes, primary alcohols are formed in the presence of aluminum isopropoxide. This reaction is the reverse of Oppenauer oxidation.

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ADDITION REACTIONS

1. CANNIZZARO REACTION

Those aldehydes (aliphatic or aromatic), which do not have an α -hydrogen atom, on treatment with a strong base, undergo a reaction involving two moles. One molecule is oxidized to yield a carboxylic acid, and the other is reduced to an alcohol.

2. WITTIG REACTION

$$R_1$$
 $C = PR_3$
 R_2
 R_4
 R_4
 R_2
 R_4
 R_4

3. TIESCHENKO REACTION

In this reaction, aldehydes react with Al(OEt)3 to give an ester in the presence of alkoxide catalyst

4. OXYMERCURATION-DEMERCURATION REACTION

5. HYDROBORATION OXIDATION REACTION

$$R_1 \longrightarrow R_3 + H_2O_2 \longrightarrow HO \longrightarrow R_1 \longrightarrow R_2 \longrightarrow R_3 + BH_2OH \longrightarrow HV$$
Alkene

Alcohol

ELIMINATION AND REARRANGEMENT REACTIONS

1. BECKMANN REARRANGEMENT

2. CURTIUS REARRANGEMENT

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3. COPE ELIMINATION

4. SCHMIDT REACTION

$$R - c + HN_3 - HV_3 - R - NH_2 - NH_2$$
OH
OH

Carboxylic acids

5. FRIES REARRANGEMENT

Para-acyl phenols

6. HOFFMANN ELIMINATION

This reaction is for the preparation of alkenes from amines. In this reaction amine is first converted to the quaternary ammonium salt by exhaustive methylation

7. HOFFMANN REARRANGEMENT

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