▶ Video explanation (YouTube)

Nucleophilic Addition Reactions: One Carbonyl, Five Pathways

The C=O carbon of an aldehyde or ketone is δ+, so a nucleophile adds to it. The same carbonyl compound gives a different product with each reagent. Learn the reagent → product pairs below; the mechanism itself (attack, tetrahedral intermediate, protonation) is in note 06.

1. The five pathways at a glance

Reagent (condition)	What attacks C	Product	From CH_3CHO
HCN (base)	CN^- (through C)	cyanohydrin	$CH_3CH(OH)CN$
$NaHSO_3$	HSO_3^- (through S)	bisulphite addition compound	$CH_3CH(OH)SO_3^-Na^+$
R′MgX (dry ether), then H_3O^+	R′ (new C–C bond)	alcohol	$CH_3CH(OH)CH_3$ (with CH_3MgBr)
ROH, dry HCl	O of ROH	hemiacetal → acetal	$CH_3CH(OH)OCH_3$ → $CH_3CH(OCH_3)_2$
H_2N–Z (acid)	N of NH_2, then H_2O leaves	C=N–Z	CH_3CH=N–Z

2. HCN → cyanohydrin

Pure HCN adds very slowly. A base generates CN^-, the stronger nucleophile, which adds to the carbonyl carbon; the alkoxide O^- then takes H^+. Result: CN and OH on the same carbon. Example: CH_3COCH_3 + HCN → $(CH_3)_2C(OH)CN$.

3. $NaHSO_3$ → bisulphite addition compound

HSO_3^- attacks through sulphur; a proton shift gives $R_2C(OH)SO_3^-Na^+$, a crystalline solid. The equilibrium lies to the right for most aldehydes and to the left for most ketones (steric crowding). Dilute mineral acid or alkali gives the carbonyl compound back, so the reaction is used to separate and purify aldehydes.

4. Grignard reagent → alcohol (new C–C bond)

Carbonyl + CH_3MgBr, then H_3O^+	Product	Class
HCHO	CH_3CH_2OH (ethanol)	1°
CH_3CHO	$CH_3CH(OH)CH_3$ (propan-2-ol)	2°
CH_3COCH_3	$(CH_3)_3COH$ (2-methylpropan-2-ol)	3°

Trick: count the carbon groups on the carbon that carries the OH.

5. Alcohols → hemiacetal, acetal, cyclic ketal

In dry HCl, one molecule of alcohol adds to an aldehyde: **hemiacetal** (OH + OR on one carbon). A second molecule replaces the OH, which leaves as water: **acetal** (OR + OR). Ketones react with **ethylene glycol** to give a **cyclic ketal** (a five-membered ring) and water. Aqueous acid reverses these reactions.

6. Ammonia derivatives → C=N–Z (addition–elimination)

H_2N–Z adds to the C=O carbon, then water is lost, so C=O becomes C=N–Z. The reaction is acid catalysed and reversible; rapid dehydration drives it forward. NH_3 or a primary amine gives an imine (Schiff base).

Reagent	Product
NH_2OH (hydroxylamine)	oxime, >C=N–OH
NH_2NH_2 (hydrazine)	hydrazone, >C=N–NH_2
$C_6H_5NHNH_2$ (phenylhydrazine)	phenylhydrazone, >C=N–NHC_6H_5
$NH_2NHCONH_2$ (semicarbazide)	semicarbazone, >C=N–$NHCONH_2$
2,4-dinitrophenylhydrazine (2,4-DNP)	2,4-DNP hydrazone (yellow-orange precipitate; a test for C=O)

Solved example

Q. Give the products of CH_3CHO with (i) HCN (ii) CH_3MgBr then H_3O^+ (iii) $NH_2NHCONH_2$.
A. (i) $CH_3CH(OH)CN$, a cyanohydrin (ii) $CH_3CH(OH)CH_3$, propan-2-ol, a 2° alcohol (iii) $CH_3CH{=}NNHCONH_2$, acetaldehyde semicarbazone.

Key takeaways

- One C=O group, five pathways: HCN, $NaHSO_3$, RMgX, ROH, H_2N–Z.
- CN^- (from HCN + base) and HSO_3^- (through S) add; O^- then takes H^+.
- Grignard: new C–C bond; HCHO 1°, other aldehydes 2°, ketones 3°.
- 1 ROH → hemiacetal; 2 ROH → acetal; ketone + glycol → cyclic ketal.
- H_2N–Z: addition, then H_2O lost → C=N–Z (addition–elimination).

Practice questions

1. (MCQ) The nucleophile in the addition of HCN to a carbonyl compound is: (a) HCN (b) H^+ (c) CN^- (d) OH^-
2. (MCQ) Acetone with CH_3MgBr followed by hydrolysis gives: (a) ethanol (b) propan-2-ol (c) 2-methylpropan-2-ol (d) propan-1-ol
3. (Very short) Name the product of an aldehyde with two molecules of methanol in dry HCl.
4. (Very short) Through which atom does HSO_3^- bond to the carbonyl carbon?
5. (Short) Why do ketones form bisulphite adducts less readily than aldehydes?
6. (Short) Why is the reaction with NH_2OH called addition–elimination?
7. (Application) Write the products of CH_3COCH_3 with (i) HCN (ii) NH_2NH_2 (iii) ethylene glycol in dry HCl.
8. (Application) Which carbonyl compound and Grignard reagent give $(CH_3)_2CHOH$?

Answer key

1. (c) CN^-.
2. (c) 2-methylpropan-2-ol, $(CH_3)_3COH$.
3. An acetal, $RCH(OCH_3)_2$.
4. Sulphur.
5. The two alkyl groups crowd the carbonyl carbon (and make it less δ+), so the equilibrium lies to the left for most ketones.
6. NH_2OH first adds to C=O, then a molecule of water is eliminated to give C=N–OH.
7. (i) $(CH_3)_2C(OH)CN$ (ii) $(CH_3)_2C{=}NNH_2$ (iii) the cyclic ketal 2,2-dimethyl-1,3-dioxolane.
8. CH_3CHO with CH_3MgBr, then H_3O^+ (an aldehyde other than HCHO gives a 2° alcohol).

▶ Watch the video explanation