RG
Ram Govind Yadav
CHEMISTRY EDUCATOR

ORGANIC

CH 01

Wurtz Reaction — Mechanism & Limitations

01

Complete mechanistic walk-through, limitations with secondary/tertiary halides, the Wurtz–Fittig variant, comparison table, exam traps and mnemonics.

WHAT YOU WILL BE ABLE TO DO

- Predict the Wurtz product of any alkyl halide in one step — count carbons, double them
- Explain both mechanisms and use side products as evidence for radicals
- Spot why mixed halides, 3° halides and wet ether fail — the favourite exam traps
- Choose between Wurtz, Wurtz–Fittig, Fittig and Corey–House for a given target

INSIDE

A The reaction at a glance
B Mechanism, step by step
C Scope and limitations
D Intramolecular Wurtz
E Fittig and Wurtz–Fittig
F Choosing a coupling method
G Exam trap gallery
H Practice MCQs · revision

USEFUL FOR CLASS 12 NEET JEE TGT / PGT

RAMGOVINDYADAV.COM
EDITION 3 · NOVEMBER 2026

HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

The reaction at a glance

A

Take two alkyl halides, add sodium metal in dry ether, and the two alkyl groups join. That single new C–C bond is the whole point of the Wurtz reaction.

IN ONE LINE Wurtz joins two identical alkyl groups: C_n halide ⟶ C_{2n} alkane.

THE WURTZ REACTION



Two ethyl groups (C2 each) join to give n-butane (C4). Sodium takes the halogen as NaBr.

$$2\ R\text{–}X + 2\ Na \longrightarrow R\text{–}R + 2\ NaX$$

R = alkyl group, X = Cl, Br or I. Conditions: sodium metal, dry (anhydrous) diethyl ether, warm.

THINK OF IT LIKE THIS

Picture each sodium atom as a hand that pulls the halogen off. Once the halogen is gone, the two 'loose' alkyl pieces grab each other. Two halides in, one bigger alkane out.

What each condition is doing

Condition	Best choice	Why it matters
Halogen	R–I > R–Br > R–Cl	C–I is the weakest bond, so sodium cleaves it most easily. R–F does not react.
Alkyl group	Primary (1°)	2° gives low yields; 3° mostly gives alkene (Section C)
Metal	Sodium (Na)	Strong electron donor. Zn gives the related Frankland reaction.
Solvent	Dry diethyl ether	Does not react with Na; water would destroy Na and the intermediates
Product	Symmetrical alkane R–R	Always an even number of carbons from one halide

KEY IDEA

The carbon count rule does most of the work in MCQs:

$C_nH_{2n+1}X \longrightarrow C_{2n}H_{4n+2}$

Methyl (C1) ⟶ ethane (C2) · Ethyl (C2) ⟶ butane (C4) · n-Propyl (C3) ⟶ n-hexane (C6)

SOLVED EXAMPLE 01 CARBON COUNTING

1-Bromopropane is heated with sodium in dry ether. Name the product and give its molecular formula.

SOLUTION

1. Identify R: $CH_3CH_2CH_2-$ is n-propyl, 3 carbons.
2. Wurtz joins two R groups end to end through the carbon that carried Br.
3. R–R = $CH_3CH_2CH_2-CH_2CH_2CH_3$, a straight chain of 6 carbons.

ANSWER n-Hexane, C_6H_{14}

SOLVED EXAMPLE 02 WORKING BACKWARDS

Which alkyl bromide gives 2,3-dimethylbutane in a Wurtz reaction?

SOLUTION

1. 2,3-Dimethylbutane is $(CH_3)_2CH-CH(CH_3)_2$. Cut it at the central bond.
2. Each half is $(CH_3)_2CH-$ — an isopropyl group.
3. The two halves are identical, so one halide is enough.

ANSWER 2-Bromopropane, $(CH_3)_2CHBr$. (Yield is modest because it is a 2° halide.)

CHECK YOURSELF

C1 Which alkane forms from methyl iodide in Wurtz reaction?

C2 Why is diethyl ether, not ethanol, used as the solvent?

C3 Arrange in order of reactivity: CH_3CH_2Cl, CH_3CH_2I, CH_3CH_2Br.

Answers at the end of the chapter.

SECTION B

Mechanism, step by step

B

Textbooks show two pathways. Both start the same way — sodium hands over one electron. They differ in what the alkyl radical does next. You need both, because exams ask for evidence.

IN ONE LINE Na gives an electron ⟶ alkyl radical ⟶ either two radicals pair up, or the radical becomes a carbanion that attacks R–X.

Step 1 · Single-electron transfer (common to both pathways)

Sodium has one loosely held 3s electron. It pushes that electron into the C–Br bond. The bond breaks; bromine leaves as Br^- (with Na^+ as NaBr) and carbon is left with one unpaired electron — an **alkyl radical**. Half-headed (fish-hook) arrows show single electrons moving.

STEP 1 — ELECTRON TRANSFER



single-electron transfer (SET)

Fish-hook arrows: each moves one electron. The ethyl radical has 7 electrons around carbon.

Pathway I · Two radicals pair up

Radicals are unstable and meet quickly. When two ethyl radicals collide, each contributes one electron to a new C–C bond. No activation barrier, no leftover pieces.

PATHWAY I — RADICAL COUPLING



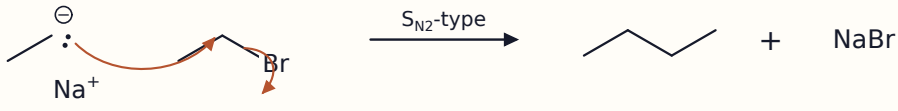
Pathway I · radical coupling

One electron from each radical forms the shared pair of the new C–C bond.

Pathway II · Radical becomes a carbanion, then attacks

If the radical meets a second sodium atom first, it picks up another electron and becomes an **alkylsodium** (R^-Na^+), a carbanion. The carbanion's lone pair then attacks the carbon bearing bromine in another R–X — an S_N2-type displacement.

PATHWAY II — CARBANION (SN2-TYPE) ROUTE



Pathway II · carbanion route

Full arrows: each moves an electron pair. The lone pair forms the C–C bond; C–Br pair leaves with Br.

$$R\text{–}X + Na \longrightarrow R^{\bullet} + NaX \qquad R^{\bullet} + Na \longrightarrow R^{-}Na^{+}$$

$$R^{-}Na^{+} + R\text{–}X \longrightarrow R\text{–}R + NaX$$

The evidence: why we believe radicals are involved

When ethyl bromide is used, the flask also contains a little **ethane** and **ethene**. Neither can come from simple coupling. They come from **disproportionation**: one radical removes a β-hydrogen from another.

SIDE REACTION — DISPROPORTIONATION



A takes a β-H from B; B becomes an alkene

Two ethyl radicals give ethane + ethene. The same radicals that couple can also swap a hydrogen.

WHY IT HAPPENS

Why the ether must be completely dry: sodium reacts with water ($2Na + 2H_2O \longrightarrow 2NaOH + H_2$), and any $R^{-}Na^{+}$ is instantly protonated to R–H.

So in wet ether, ethyl bromide gives mostly **ethane** (C2), not butane (C4). Same carbon count as the halide = water got in.

SOLVED EXAMPLE 03 MECHANISM EVIDENCE

Ethyl bromide + Na in dry ether gives butane, but small amounts of ethane and ethene are also found. Explain.

SOLUTION

1. Ethyl radicals ($CH_3CH_2^{\bullet}$) form in step 1.
2. Most pairs combine (coupling) ⟶ butane.
3. Some pairs disproportionate: one radical takes a β-H from the other ⟶ ethane + ethene.
4. Ethene can only appear if radicals with a β-H are present, so this supports the radical mechanism.

ANSWER **Ethane and ethene come from radical disproportionation — evidence for free-radical intermediates.**

CHECK YOURSELF

C4 How many electrons surround the carbon of an alkyl radical?

C5 In Pathway II, what is the nucleophile and what is the electrophile?

Answers at the end of the chapter.

SECTION C

Scope and limitations

C

Every limitation comes from one of three facts: radicals couple at random, carbanions are strong bases, and sodium attacks almost any polar group. Learn the reason and you will never need to memorise the list.

IN ONE LINE Wurtz is clean only for one primary halide with no other functional group.

Limitation 1 · Two different halides give a mixture

Sodium does not know which alkyl group should pair with which. With CH_3Br and C_2H_5Br you get every possible pair:

$$CH_3\text{-}CH_3 \;+\; CH_3\text{-}C_2H_5 \;+\; C_2H_5\text{-}C_2H_5$$

ethane propane n-butane

Three alkanes with close boiling points — hard to separate. This is why propane is not made by Wurtz.

COUNTING PRODUCTS

With **k** different alkyl halides, the number of coupling combinations is **k(k + 1) / 2**.

- k = 2 ⟶ 3 combinations - k = 3 ⟶ 6 combinations - k = 4 ⟶ 10 combinations

Then **check for duplicates**: two different pairs can give the same alkane (see the next example).

SOLVED EXAMPLE 04 THE DUPLICATE TRAP

A mixture of CH_3Br, CH_3CH_2Br and $CH_3CH_2CH_2Br$ is treated with Na in dry ether. How many ***different*** alkanes form?

SOLUTION

1. k = 3, so k(k+1)/2 = 6 pairs: C1+C1, C2+C2, C3+C3, C1+C2, C1+C3, C2+C3.
2. Products: ethane, n-butane, n-hexane, propane, n-butane, n-pentane.
3. C1+C3 (methyl + n-propyl) gives $CH_3\text{–}CH_2CH_2CH_3$ = n-butane — the same as C2+C2.

ANSWER 5 different alkanes (6 combinations, but n-butane appears twice).

Limitation 2 · Odd-carbon alkanes cannot be made cleanly

A single halide always gives 2n carbons — an even number. Propane (C3), n-pentane (C5) and n-heptane (C7) need two different halides, which brings back Limitation 1.

Limitation 3 · Methane cannot be made

The smallest possible Wurtz product is ethane, from two methyl groups. Wurtz never gives a one-carbon product.

Limitation 4 · Secondary and tertiary halides

As the carbon gets more crowded, the alkyl groups struggle to reach each other, and there are more β-hydrogens to remove. Disproportionation and elimination (the carbanion acting as a base) take over.

Halide type	What you mainly get	Reason
1° (RCH_2X)	Good yield of R–R	Unhindered carbon; coupling and S_N2 attack both easy
2° (R_2CHX)	Low yield of R–R, plus alkene and alkane	More β-H atoms; more hindrance
3° (R_3CX)	Mainly alkene (+ R–H); almost no R–R	Very hindered; R^- acts as a base (E2)

WHY 3° HALIDES FAIL



tert-BUTYL BROMIDE — ISOBUTYLENE (major) — ISOBUTANE

coupled alkane: C_8H_{18} trace

tert-Butyl bromide gives isobutylene and isobutane — not 2,2,3,3-tetramethylbutane.

Limitation 5 · Other functional groups are destroyed

Groups with an acidic H or an electrophilic carbon react with Na or with R^- first: –OH, –COOH, $–NH_2$, C=O, –CN, $–NO_2$. The substrate must be a plain alkyl halide.

CHECK YOURSELF

C6 Can n-pentane be made in good yield by Wurtz reaction? Why?

C7 Four different alkyl halides are coupled. What is the maximum number of combinations?

Answers at the end of the chapter.

SECTION D

Intramolecular Wurtz: building rings

D

When both halogens sit on the same molecule, the two reactive ends can find each other faster than they find another molecule. The result is a ring.

IN ONE LINE Two halogens on one chain, close in space ⟶ the ends join ⟶ a ring.

RING FORMATION



Left: 1,3-dihalide ⟶ cyclopropane (Freund reaction). Right: the classic JEE example.

1,3-Dibromopropane gives cyclopropane; 1,4-dibromobutane gives cyclobutane. With zinc instead of sodium, the 1,3-case is called the **Gustavson reaction**.

SOLVED EXAMPLE 05 THE JEE FAVOURITE

Predict the product when 1-bromo-3-chlorocyclobutane is treated with 2 Na in dry ether.

SOLUTION

1. Both halogens are on the same molecule, on C1 and C3 of the ring.
2. C1 and C3 are directly across the small ring — close in space.
3. Na removes both halogens and a bond forms across the ring between C1 and C3.

ANSWER Bicyclo[1.1.0]butane, C_4H_6 — two fused three-membered rings.

EXAM TRAP

Students write a dimer (C_8) or cyclobutane. Remember: **intramolecular wins** when the two reactive carbons are 1,3 or 1,4 to each other. Count carbons: the product still has 4.

SECTION E

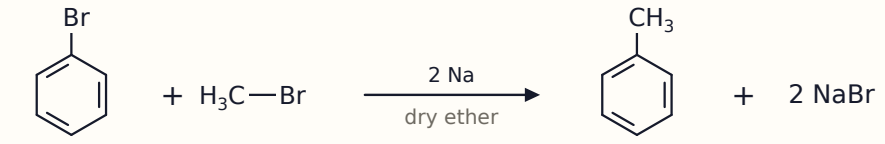
Fittig and Wurtz–Fittig

E

Aryl halides react with sodium too. Using them alone gives biaryls; mixing an aryl and an alkyl halide gives alkylbenzenes — the one mixed coupling that works well.

IN ONE LINE Ar–X + R–X + 2 Na ⟶ Ar–R. The partners are different enough that cross-coupling wins.

WURTZ–FITTIG REACTION



BROMOBENZENE METHYL BROMIDE TOLUENE (major)

Bromobenzene + methyl bromide ⟶ toluene. Biphenyl and ethane form in smaller amounts.

Reaction	Reactants	Product	Example
Wurtz	2 R–X + 2 Na	R–R	2 C_2H_5Br ⟶ n-butane
Fittig	2 Ar–X + 2 Na	Ar–Ar	2 C_6H_5Cl ⟶ biphenyl
Wurtz–Fittig	Ar–X + R–X + 2 Na	Ar–R	C_6H_5Br + CH_3Br ⟶ toluene

WHY IT HAPPENS

The aryl halide forms aryl-sodium (Ar^-Na^+) readily, and that carbanion attacks the **alkyl** halide (an aryl carbon resists S_N2). So Ar–R is favoured.

The side products (Ar–Ar and R–R) have very different boiling points from Ar–R, so separation is easy — unlike a mixed Wurtz.

SOLVED EXAMPLE 06 WURTZ–FITTIG

Chlorobenzene and ethyl chloride are treated with sodium in dry ether. Give the main product and the two side products.

SOLUTION

1. Aryl + alkyl halide with Na = Wurtz–Fittig ⟶ Ar–R.
2. Ar = C_6H_5, R = C_2H_5 ⟶ C_6H_5–C_2H_5.
3. Self-coupling: Ar–Ar = biphenyl; R–R = n-butane.

ANSWER Ethylbenzene (main); biphenyl and n-butane (side products).

SECTION F

Choosing a coupling method

F

In MCQs, Wurtz is tested against its relatives. Ask one question: is the target symmetrical or not?

IN ONE LINE Symmetrical R–R ⟶ Wurtz. Ar–R ⟶ Wurtz–Fittig. Unsymmetrical R–R′ ⟶ Corey–House.

Method	Reagent	Gives	Unsymmetrical product cleanly?
Wurtz	Na, dry ether	R–R	No — mixture
Frankland	Zn, heat	R–R	No — mixture
Fittig	Na, dry ether	Ar–Ar	No (biaryls only)
Wurtz–Fittig	Na, dry ether	Ar–R	Yes (aryl + alkyl)
Ullmann	Cu powder, heat	Ar–Ar	Mainly symmetrical biaryls
Corey–House	R_2CuLi + R′–X	R–R′	Yes — the clean route to odd-carbon alkanes
Kolbe electrolysis	RCOONa, electrolysis	R–R	No — two acids give a mixture

$$(CH_3)_2CuLi + CH_3CH_2Br \longrightarrow CH_3CH_2CH_3 + CH_3Cu + LiBr$$

Corey–House: lithium dimethylcuprate + ethyl bromide gives pure propane.

CHECK YOURSELF

C8 Best method to prepare 2-methylbutane free of other alkanes?

Answers at the end of the chapter.

SECTION G

Exam trap gallery

G

These are the mistakes examiners design options around. Read the left column, cover the right, and check you would have caught it.

✗ TRAP 01 · WHAT STUDENTS WRITE

Ethyl bromide + Na ⟶ ethane.

✓ WHAT IS ACTUALLY CORRECT

Ethyl bromide + Na (dry ether) ⟶ **n-butane** (C2 + C2 = C4).

WHY Wurtz doubles the carbon count. Ethane appears only as a minor side product, or as the main product in wet ether.

✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
$CH_3Br + C_2H_5Br + Na \longrightarrow$ propane only.	Gives **three** alkanes: ethane, propane, n-butane.

WHY Random coupling: every pair combination forms.

✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Three different halides ⟶ 6 different alkanes, always.	6 combinations, but check for **duplicates** — C1+C3 and C2+C2 both give n-butane.

WHY $k(k+1)/2$ counts pairs, not unique structures.

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
tert-Butyl bromide + Na ⟶ 2,2,3,3-tetramethylbutane.	Gives mainly **isobutylene** and isobutane.

WHY 3° carbon is too crowded; elimination/disproportionation win.

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Methane can be made from CH_3I by Wurtz.	CH_3I gives **ethane**. Methane is impossible by Wurtz.

WHY Product always has at least two carbons.

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
1-Bromo-3-chlorocyclobutane + Na ⟶ a dimer.	Gives **bicyclo[1.1.0]butane** (intramolecular).

WHY C1 and C3 are close; ring closure beats finding another molecule.

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Fittig reaction gives toluene.	Fittig gives **biphenyl**. Toluene needs **Wurtz–Fittig** ($Ar–X + CH_3X$).

WHY Fittig = aryl + aryl only.

MEMORY HOOK

"Wurtz makes twins." Two identical R groups join; one halide in, double the carbons out.

"Fittig sounds like Ph." Fittig is the aryl (Ph) version; Wurtz–Fittig brings one of each.

"Dry or die." Moisture kills Na and gives R–H.

"1° yes, 2° meh, 3° no." Yield trend with alkyl type.

SECTION H

Practice MCQs

H

Levels: Easy checks recall, Moderate needs one reasoning step, Tough combines two ideas. Full explanations follow.

Q01 Ethyl bromide is treated with sodium in dry ether. The main product is: [EASY]

(a) Ethane
(b) Ethene
(c) n-Butane
(d) Isobutane

Q02 Which alkane cannot be prepared by Wurtz reaction? [EASY]

(a) Ethane
(b) Methane
(c) n-Butane
(d) n-Hexane

Q03 Reactivity of alkyl halides in Wurtz reaction follows: [EASY]

(a) R–Cl > R–Br > R–I
(b) R–I > R–Br > R–Cl
(c) R–Br > R–I > R–Cl
(d) All equal

Q04 A mixture of CH_3I and C_2H_5I is treated with Na in dry ether. Number of alkanes formed: [MODERATE]

(a) 1
(b) 2
(c) 3
(d) 4

Q05 Small amounts of ethene form during the Wurtz reaction of ethyl bromide. This supports: [MODERATE]

(a) Carbocation intermediate
(b) Free-radical intermediate
(c) Carbene intermediate
(d) Benzyne intermediate

Q06 tert-Butyl bromide with Na in dry ether gives mainly: [MODERATE]

(a) 2,2,3,3-Tetramethylbutane
(b) 2-Methylpropene and isobutane
(c) n-Octane
(d) No reaction

Q07 Bromobenzene + methyl bromide + Na in dry ether gives mainly: [MODERATE]

(a) Biphenyl
(b) Toluene
(c) Ethylbenzene
(d) Benzene

Q08 If moist ether is used with C_2H_5Br and Na, the major organic product is: [MODERATE]

(a) Butane
(b) Ethane
(c) Ethanol
(d) Diethyl ether

Q09 2,3-Dimethylbutane can be prepared by Wurtz reaction using: [MODERATE]

(a) 1-Bromopropane
(b) 2-Bromopropane
(c) 2-Bromobutane
(d) 1-Bromo-2-methylpropane

Q10 1-Bromo-3-chlorocyclobutane + 2 Na in dry ether gives: [TOUGH]

(a) Cyclobutene
(b) Bicyclo[1.1.0]butane
(c) Cyclobutane
(d) A dimer, C_8H_{12}

Q11 CH_3Br, C_2H_5Br and $n\text{-}C_3H_7Br$ are coupled together with Na. Number of ***different*** alkanes formed: [TOUGH]

(a) 3 (b) 5
(c) 6 (d) 9

Q12 The best method to prepare propane free of other alkanes is: [TOUGH]

(a) Wurtz reaction (b) Corey–House synthesis
(c) Kolbe electrolysis (d) Frankland reaction

Answer key with explanations

Q01 (c) **n-Butane** — two C2 groups join: C2 + C2 = C4.

Q02 (b) **Methane** — the smallest Wurtz product is ethane.

Q03 (b) **R–I > R–Br > R–Cl** — weaker C–X bond, easier electron transfer from Na.

Q04 (c) **3** — ethane, propane, n-butane; k(k+1)/2 with k = 2.

Q05 (b) **Free radical** — ethene comes from radical disproportionation.

Q06 (b) — 3° halide: elimination and disproportionation dominate; coupling is negligible.

Q07 (b) **Toluene** — Wurtz–Fittig gives Ar–R.

Q08 (b) **Ethane** — the intermediate is protonated by water to R–H.

Q09 (b) **2-Bromopropane** — two isopropyl groups join at their central carbons.

Q10 (b) **Bicyclo[1.1.0]butane** — intramolecular C1–C3 coupling.

Q11 (b) **5** — 6 combinations but n-butane forms twice (C2+C2 and C1+C3).

Q12 (b) **Corey–House** — $(CH_3)_2CuLi + C_2H_5Br$ gives only propane.

SECTION J

Previous-year questions

J

Real exam questions on this topic, tagged with the exam and session. Stems are lightly edited for clarity; the chemistry and the answer are unchanged.

ABOUT THESE TAGS

KCET 2018 is reproduced with its original options. The two MHT CET 2026 questions (18 April and 11 April, morning shifts) appear in published question banks with damaged formula text, so the options here are re-set by me; the question and the correct answer are as asked.

Sources: getmarks.app (KCET 2018); questions.examside.com (MHT CET 2026).

Q01 n-Propyl chloride reacts with sodium metal in dry ether to give: [KCET 2018]

(a) n-Hexane (b) Propane
(c) n-Butane (d) n-Heptane

Q02 Which alkyl chloride gives 2,2,5,5-tetramethylhexane on Wurtz reaction? [MHT CET 2026]

(a) tert-Butyl chloride
(b) 1-Chloro-2,2-dimethylpropane
(c) 2-Chloro-2-methylbutane
(d) 1-Chloro-3,3-dimethylbutane

Q03 Wurtz reaction is NOT possible (in useful yield) with: [MHT CET 2026]

(a) $(CH_3)_3CCl$
(b) CH_3Br
(c) CH_3CH_2Cl
(d) $CH_3CH_2CH_2I$

Previous-year answer key

Q01 (a) **n-Hexane** — two n-propyl groups join: C3 + C3 = C6.

Q02 (b) **Neopentyl chloride** — cut the target at its central C–C bond: each half is $(CH_3)_3C–CH_2–$.

Q03 (a) **tert-Butyl chloride** — a 3° halide eliminates to isobutylene instead of coupling.

SECTION K

Advanced problems

K

Problems at JEE Advanced / PGT level. They reward reasoning from the mechanism rather than recall.

IN ONE LINE Each problem combines two ideas from this chapter. Try it before reading the solution.

SOLVED EXAMPLE 07 ISOMERIC HALIDES

A mixture of 1-bromopropane and 2-bromopropane is treated with Na in dry ether. How many coupled alkanes form, and what are they?

SOLUTION

1. Two different halides $\Longrightarrow$ $k(k+1)/2 = 3$ combinations.
2. n-Pr + n-Pr $\longrightarrow$ n-hexane. i-Pr + i-Pr $\longrightarrow$ 2,3-dimethylbutane.
3. n-Pr + i-Pr $\longrightarrow$ $CH_3CH_2CH_2–CH(CH_3)_2$ = 2-methylpentane.
4. All three are C_6H_{14} isomers with close boiling points — a separation nightmare.

ANSWER 3 alkanes: n-hexane, 2,3-dimethylbutane, 2-methylpentane (plus some propane/propene from side reactions).

SOLVED EXAMPLE 08 DOUBLE RING CLOSURE

Pentaerythrityl tetrabromide, $C(CH_2Br)_4$, is heated with zinc dust. Predict the hydrocarbon formed.

SOLUTION

1. Each pair of CH_2Br groups on the central carbon is 1,3 to each other — set up for ring closure.
2. First closure: two CH_2Br groups join ⟶ a cyclopropane ring containing the central carbon.
3. Second closure: the remaining two CH_2Br groups join on the same central carbon ⟶ a second cyclopropane.

ANSWER **Spiropentane (spiro[2.2]pentane), C_5H_8 — two cyclopropane rings sharing one carbon (Gustavson-type).**

SOLVED EXAMPLE 09 CHOOSING A ROUTE

You need pure n-propylbenzene. A classmate suggests Friedel–Crafts alkylation of benzene with n-propyl chloride/$AlCl_3$. Why does that fail, and what is the better route?

SOLUTION

1. Friedel–Crafts goes through a carbocation. The 1° n-propyl cation rearranges (1,2-hydride shift) to the 2° isopropyl cation.
2. So the main product is isopropylbenzene (cumene), not n-propylbenzene.
3. Wurtz–Fittig has no carbocation: bromobenzene + 1-bromopropane + 2 Na (dry ether) joins the aryl group to C1 of the propyl chain without rearrangement.

ANSWER **Friedel–Crafts gives cumene by rearrangement; use Wurtz–Fittig (C_6H_5Br + $CH_3CH_2CH_2Br$ + 2 Na) for n-propylbenzene.**

Check-yourself answers

C1 Ethane, $CH_3–CH_3$.

C2 Ethanol has an acidic O–H; it reacts with Na and protonates the carbanion. Ether has no O–H.

C3 $C_2H_5I > C_2H_5Br > C_2H_5Cl$.

C4 Seven (three bonds + one unpaired electron).

C5 Nucleophile: the carbanion R^-. Electrophile: the carbon bonded to X in R–X.

C6 No. C5 is odd, so it needs two different halides (e.g. C2 + C3), giving a mixture of three alkanes.

C7 $k(k+1)/2 = 4 \times 5 / 2 = 10$.

C8 Corey–House: lithium diisopropylcuprate $[(CH_3)_2CH]_2CuLi$ + ethyl bromide (a primary halide works best).

QUICK REVISION

One-page revision

Read this page the night before the exam. Every line points back to a section in these notes.

The reaction

- 2 R–X + 2 Na ⟶ R–R + 2 NaX, dry ether
- C_n ⟶ C_{2n}; always even carbons from one halide
- Reactivity R–I > R–Br > R–Cl; R–F does not react

Mechanism

- Step 1: Na gives one electron ⟶ R• + NaX
- Path I: R• + R• ⟶ R–R
- Path II: R• + Na ⟶ R^-Na^+; then S_N2 on R–X
- Evidence: alkane + alkene from disproportionation

Limitations

- Mixed halides ⟶ mixture; k(k+1)/2 pairs, check duplicates
- No methane; odd alkanes not clean
- 1° good, 2° poor, 3° gives alkene
- No –OH, –COOH, C=O, $–NH_2$; wet ether ⟶ R–H

Rings

- 1,3-dihalide ⟶ cyclopropane (Freund); Zn = Gustavson
- 1,4-dihalide ⟶ cyclobutane
- 1-Br-3-Cl-cyclobutane ⟶ bicyclo[1.1.0]butane

Relatives

- Fittig: Ar–X ⟶ Ar–Ar
- Wurtz–Fittig: Ar–X + R–X ⟶ Ar–R (works well)
- Frankland: Zn; Ullmann: Cu, biaryls
- Corey–House: R_2CuLi + R′X ⟶ R–R′ (unsymmetrical)

Memory hooks

- Wurtz makes twins
- Fittig sounds like Ph
- Dry or die
- 1° yes, 2° meh, 3° no

SHARE FREELY · DO NOT SELL