Carbocations

terminology: historically, \( R_3C^+ \) was referred to as a “carbonium ion” but:

碳正离子 (超共价)

碳正离子 (共价)

5 bonds to C - rare

3 bonds to C - commonplace

moot point until the advent of super acids (George Olah, Nobel ’96)

\[
\begin{align*}
\text{CH}_4 & \xrightarrow{\text{FSO}_3\text{H} - \text{SbF}_5} \text{SO}_2 (l) \\
& \text{“super acid” (also HF - SbF}_5) \\
& \text{methanonium ion} \\
& \text{extremely non-nucleophilic, non-basic counterion}
\end{align*}
\]

ex: (see Olah, *JACS* 1972, 94, 808; *CHEMTECH* 1971, 1, 566)

structure:

\[
\text{empty p orbital}
\]

sp\(^2\) hybridized \(\rightarrow\) planar structure

note: it lacks an octet \(\Rightarrow\) unstable

What about \(\text{?}\)

- can’t rehybridize to give empty p orbital
contrast this with benzenonium ion:

and benzylic cation:

**stability**: 

+18 +27 +38 kcal  

general trend:  

3° > 2° > 1° > CH₃  

(due to hyperconjugation of β C-H bonds)  

special case:  

very stable (hyperconjugation of C - Si)  

extra stability:  

(resonance)  

overlap of empty p orbital with cyclopropyl  

p orbital  

special case:  

(Doering, JACS 1954, 76, 3203)  

α - heteroatom:  

Y = Cl < OR < NR₂ < SR
Why this order?

consider resonance:

\[
\begin{align*}
\ce{Y@} & \leftrightarrow \ce{Y}=\ce{C} \\
\end{align*}
\]

so, order is dictated by a balance of electronegativity & \(\pi\) bond energy

Why is \(\ce{Y}=\ce{C}\) so stable when \(\ce{Y}\) is more electronegative than \(\ce{C}\)?

\[\Rightarrow \ce{Y}=\ce{C}\] is hypervalent, not hypovalent \(\Rightarrow\) has a full octet

unstable cations:

Bridgehead carbocations (can’t planarize)

\(-\text{sp}^2, \text{sp} \text{ carbocations (can’t empty a p orbital)}\)

Hypovalent heteroatoms (\(\text{R-}\ce{O}^+, \text{R-}\ce{N^2}, \text{etc.})\)

“Non - Classical” Carbocations

used to describe carbocations stabilized by 3-center, 2e\(^-\) interactions

\[\text{ex:}\]

question: what is the structure of the cation? \(1 \leftrightarrow 2\) or \(3\)?

The answer to this question has been debated for 35 years

players: Winstein (3) vs. Brown (1 \(\leftrightarrow\) 2)

We will discuss this question more later on ...
Methods of Generation of Carbocations

1) Ionization by heterolytic bond cleavage

\[ \text{C} \overset{\text{LA}}{\text{Y}} \rightarrow \overset{\text{\text{@}}} \text{C} + \text{Y-LA} \]

\[ \text{Y} = \text{Cl, Br, I, OR, SR} \]

LA depends on Y

<table>
<thead>
<tr>
<th>Y</th>
<th>LA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl, Br, I</td>
<td>Ag⁺, FeX₃, AlX₃, SnX₄ (F with SbF₅)</td>
</tr>
<tr>
<td>OR</td>
<td>TiCl₄, TMS-OTf, TMS-I, BF₃, R₂AlCl; H⁺, Li⁺, Sc³⁺, Yb³⁺, Eu³⁺</td>
</tr>
<tr>
<td>SR</td>
<td>Hg²⁺, Cu⁺</td>
</tr>
</tbody>
</table>

Example:

2) Addition of an electrophile to a multiple bond

\[ \text{E}^+ = \text{H}^+, \text{X}^+, \text{RSe}^+, \text{RS}^+, \text{R₃C}^+, \text{Pt}^+ \]

<table>
<thead>
<tr>
<th>Y</th>
<th>E⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>TiCl₄, Sn(OTf)₂, BF₃, TMS-OTf, Et₂AlCl, H⁺</td>
</tr>
<tr>
<td>S</td>
<td>HgCl₂, Hg(BF₄)₂</td>
</tr>
<tr>
<td>NR</td>
<td>BF₃, TiCl₄, Yb(OTf)₃, Sc(OTf)₃</td>
</tr>
</tbody>
</table>

Example:
3) Hydride abstraction (very exotic)

\[
\text{R}_3\text{C}^+ + \text{H}^+ \xrightarrow{\text{FSO}_3\text{H} - \text{SbF}_5} \text{CR}_3 + \text{H}_2 + \text{SbF}_6
\]

Olah, *JACS* 1967, 89, 4739

**Reactions of Carbocations**

1) Nucleophilic attack

\[
\text{R}_3\text{C}^+ + \text{Nuc} \rightarrow \text{R}_3\text{C}^-\text{Nuc}
\]

:|Nuc = ROH, RSH, X^-, alkene (produces new carbocation), Ar

note: this is the opposite of ionization (#1 of previous section)

2) β - elimination

also:

| Nuc: |  |  |  |
| SiR₃ |  |  |  |
| SnR₃ |  |  |  |

note: this is the opposite of generation method #2
3) Rearrangements

“1,2 hydride shift” - favors more stable cation (VERY fast reaction)

Wagner - Meerwein shift (less fast, but still fast)

Wagner-Meerwein rearrangement is an equilibrium reaction:

ex:

(note: this is not a good thing if you’re trying to synthesize something!)

Carbanions

occurs as a complex with $M^\oplus$, either ionic or covalent

$M^\oplus = \text{Li}^\oplus, \text{Na}^\oplus, \text{K}^\oplus, \text{Mg}^\oplus\text{X}, \text{Cu}^\oplus, \text{Zn}^{\text{II}}\text{X}, \text{Ce}^{\text{III}}\text{Cl}_2, \text{Cr}^{\text{III}}\text{Cl}, \text{Al}^{3+}$
structure:

- rapid epimerization of stereogenic carbanions, except when $R_1 = OR$

(Still, *JACS* 1978, 100, 1481 & *JACS* 1980, 102, 1201)

sp$^2$ does not easily invert

stability:

$3^\circ < 2^\circ < 1^\circ <$ allylic, benzylic

$sp^3 < sp^2 < sp$

[note: these trends are exactly opposite those of carbocations]

$R_3SiC\ominus < R_2NC\ominus < RSC\ominus << R=CH\ominus < RSC\ominus$ (enolate)

generation of carbanions

1) reduction of $\sigma$ bonds

$$R-X \xrightarrow{M^\ominus} R-M + M-X$$
ex:

\[
\begin{align*}
R-\text{Br} & \xrightarrow{\text{Mg}^0, \text{Et}_2\text{O}} R-\text{MgBr} \\
\text{Grignard Reaction} \\
\text{Yamamoto, } \textit{JACS} \text{ 1994, 117, 6130}
\end{align*}
\]

other bonds (besides R-X) can be reduced:

"lithium naphthalide" - single electron reductant

\[
\begin{align*}
\text{O} & \\
\text{SPh} & \xrightarrow{\text{Li}^+} \\
\text{Accts. Chem. Res. 1989, 22, 152}
\end{align*}
\]

Rychnovský, \textit{JACS} 1992, 57, 4336

2) Metallation (deprotonation)

-very basic reagents can deprotonate C-H
- like any acid / base chemistry, it’s an equilibrium dictated by pKₐ

so, we use n-BuLi, s-BuLi, t-BuLi, PhLi

\[
\begin{align*}
\text{OMe} & \xrightarrow{\text{tBuLi, THF, } 0^\circ} \text{OMe} \\
\text{ex: } & \textit{JOC} 1979, 44, 2004
\end{align*}
\]

Why that product? sp² C next to O most acidic (pKₐ ≈ 30) K_{eq} ≈ 10^{50-30} = 10^{20}
also:

```
\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]
```

Schlosser, JACS 1978, 100, 3258
structure of LICKOR base: Venturello, Tetrahedron 1996, 52, 7053

note that many hydrocarbons can’t be easily deprotonated due to kinetics

another special case:

```
\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]
```

also:

```
\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]
```

JOC 1977, 42, 1823

```
\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]
```

JOC 1979, 44, 4463
3) Transmetallation

\[ R_1M_1 + R_2M_2 \rightleftharpoons R_1M_2 + R_2M_1 \]

equilibrium favors putting more electropositive M on more acidic R

ex:

\[ \text{tBuLi} + \text{ZnBr} \rightleftharpoons \text{tBuZnBr} + \text{Li} \]

corollary:

\[ R-Li \xrightarrow{\text{MgBr}_2} R-MgBr + LiBr \] (consider Br as R₂)

\[ R-Li \xrightarrow{\text{ZnBr}_2} R-ZnBr + LiBr \]

\[ R-Li \xrightarrow{\text{CeCl}_3} R-CeCl₂ + LiCl \] (very synthetically useful)

\[ R-Li \xrightarrow{\text{CuI}} R₂-CuI + Lil \] (very synthetically useful)

this follows electropositivity: \( \text{Li}^{\oplus}, \text{Na}^{\oplus}, \text{K}^{\oplus} > \text{Mg}^{\text{II}^{\oplus}}, \text{Ca}^{\text{II}^{\oplus}} > \text{Zn}^{\text{II}^{\oplus}} > \text{Cu}^{\text{I}^{\oplus}} > \text{Pd}^{\text{II}^{\oplus}} \)

(ionic) \hspace{1cm} (covalent)

“hard” \hspace{1cm} “soft”

related exchange reactions:

\[ \text{R-SnBu}_3 \xrightarrow{\text{BuLi}} R-Li + \text{Bu}_4\text{Sn} \]

stable, chromatographable \hspace{1cm} works if R is more acidic than butane \( (pK_a \approx 46) \)

also, metal - halogen exchange:

\[ R_1-X + R_2-Li \rightleftharpoons R_1-Li + R_2-X \]

\(-110^\circ \text{ to } -30^\circ \)

\( X = \text{Br, I} \)

-equilibrium governed by basicity of \( R_1, R_2 \)

(favors less basic R-Li)

-very fast reaction! (competes with proton transfer)
mechanism:
\[
R_1-X + R_2-Li \xrightarrow{(+ e^-)} [R_1-X]^\ominus \xrightarrow{-X^\ominus} \]
\[
[O^\oplus R_1Li + R_2-X \xrightarrow{(+ e^-)} R_1^\ominus + R_2^\ominus \rightarrow R_1R_2]
\]
sequential single electron transfers
evidence is the formation of \(R_1-R_2\) as a minor side-product (so-called Wurtz coupling)
this can be made irreversible:
\[
R-I \xrightarrow{tBuLi (2eq)} R-Li + [\text{H}] \xrightarrow{\Theta \text{Li}^\ominus \text{elimination}} R\text{Li} + \text{LiI} + \]
Seebach, *TL* 1976, 4839

**Characteristic Reactions**

1) acid / base chemistry

2) transmetallation / metal-halogen exchange

3) nucleophilic addition

\[
R-M + R'-\text{Y} \rightarrow R'O^\ominus M^\ominus
\]
(works best when \(Y = H, \text{OR, NR}_2, X\); \(R = \text{I}, \text{allylic, sp}^2, \text{sp})
4) nucleophilic substitution (uncommon)

\[
R-M + R'-X \rightarrow R-R' + M-X
\]

-note that this is the **Wurtz Coupling**, a side reaction of Li / X exchange
most common when \( M = Cu^+ \), but probably isn’t \( S_N1 \) or \( S_N2 \)

**Ylides - a special class of carbanions**

\[\begin{align*}
&H \\
&\text{R}_2\text{C} - Y\text{R}_n \\
&\text{base} \quad \rightarrow \quad \\
&\text{R}_2\text{C} - Y\text{R}_2
\end{align*}\]

When a carbon \( \alpha^- \) to a positively charged heteroatom is deprotonated, it forms an ylide

(“yl” = \( \oplus \); “ide” = \( \ominus \))

-very stable carbanions

ex: \( \text{R}_2\text{C} - PR_3 \), \( \text{R}_2\text{C} - SR_2 \), \( \text{R}_2\text{C} - NR_3 \) (less stable)

(note that \( \text{R}_2\text{C} - SO_2\text{R} \), \( \text{R}_2\text{C} - PO_3\text{R} \), \( \text{R}_2\text{C} - NO_2 \) can be viewed as ylides)

**Enolates - another special class of carbanions**

\[
\begin{align*}
&\text{H} \\
&\text{O} \\
&\text{base} \quad \rightarrow \quad \\
&\text{H} \\
&\text{O}
\end{align*}
\]

Abstraction of acidic \( \alpha^- \)-proton produces resonance-stabilized carbanion \( \Rightarrow \) very useful
**Free Radicals** - Species containing unpaired electron(s)

\[
\begin{align*}
\text{hybridization of carbon varies between } & \text{sp}^3 \text{ & sp}^2 \text{ depending on the substituents} \\
(\text{CH}_3 \text{ is planar}) & \Rightarrow 7 \text{ valence electrons (electron deficient like carbocations)}
\end{align*}
\]

like carbanions, free radicals can be chiral, but invert too rapidly

**stability:**

look at C-H bond strengths (first handout)

\[
1^\circ < 2^\circ < 3^\circ < \text{benzylic, allyl, acyl (similar to cation)}
\]

\[
\text{sp} < \text{sp}^2 < \text{sp}^3
\]

\[
\text{EWG} - \text{CR}_2 \quad > \quad \text{CR}_3
\]

\[
\text{EWG} = \text{OR, NR}_2, \text{SO}_2\text{R, CN, } \text{O} \text{CY}
\]

Why do electron - withdrawing substituents stabilize α-radicals?

through resonance, primarily:

\[
\begin{align*}
\begin{bmatrix}
\text{RO} & \text{R}' \\
\end{bmatrix}
& \quad \leftrightarrow \\
\begin{bmatrix}
\text{RO} & \text{R}' \\
\end{bmatrix}
\end{align*}
\]

\[
\begin{align*}
\begin{bmatrix}
\text{N} & \text{C} & \text{R} \\
\end{bmatrix}
& \quad \leftrightarrow \\
\begin{bmatrix}
\text{N} & \text{C} & \text{R} \\
\end{bmatrix}
\end{align*}
\]

very stable radicals:

\[
\text{Ph}_3\text{C}\
\]

stable & isolable
unstable radicals:

\[ \text{RO}^\cdot, \text{R}_2\text{N}^\cdot, \text{phen}^\cdot \]

(note that RS^\cdot is quite stable)

**Methods of generation:**

1) homolytic bond cleavages

\[
\begin{align*}
\text{RO} & \underset{\Delta \text{ or } \text{hv}}{\rightarrow} \text{RO}^\cdot & \text{RO}^\cdot & \underset{-\text{CO}_2}{\rightarrow} & 2\text{R}^\cdot \\
\text{CN} & \underset{\Delta \text{ or } \text{hv}}{\rightarrow} & \text{CN} & \underset{-\text{N}_2}{\rightarrow} & 2\text{CN}^\cdot \\
\text{AIBN} & & & \text{AIBN} & \\
(\text{X} = \text{I}, \text{Br}, \text{Cl}) & & & & 
\end{align*}
\]
2) photochemical excitation of $\pi$ bonds

Characteristic reactions:

1) atom transfer

mechanism:

typically, $H^*$ & $X^*$ transfers are observed

(note: also a method of generating new radicals)
2) Addition to $\pi$ systems

![Reaction diagram](image)

the most common variant of this reaction is intramolecular:

![Reaction diagram](image)

mechanism:

![Reaction diagram](image)

review: Curran, *Synthesis* 1988, 417 & 489

- $\pi$ system can also be

![Radical structures](image)

radicals most easily detected by electron spin resonance (ESR)
- they appear as doublets
Radical Anions & Cations

These species consist of neutral molecules that have gained (R. A.) or lost (R.C.) a single electron.

\[ \text{ex: } \text{LiNH}_3 (\text{l}) \rightarrow \text{Li} \cdot \Theta \text{lithium naphthalide} \]

What is meant by the structure?

\[ [\text{anti-bonding MO}] \cdot \Theta \]

-an extra electron is delocalized throughout the \( \pi \) system
(Unlike free radicals, no addition/loss of atoms during formation)

MO description:

\[ \begin{align*}
\pi^* & \quad \text{e}^- \quad \pi^* \\
\pi_3 & \quad \text{e}^- \quad \pi_3
\end{align*} \]

Extra electron is placed in antibonding MO

Likewise we can place an extra electron in \( \sigma^* \) orbital:

\[ \text{very common example: } \]

sodium benzophenone ketyl (blue-purple)
radical cations are somewhat more rare; most commonly encountered when single electron oxidants are used (also in mass spectroscopy)

ex:

\[ \text{R-O-} \begin{array}{c} \text{O} \\ \text{OMe} \end{array} \xrightarrow{\text{Ce}^{IV}} \text{R-O-} \begin{array}{c} \text{O} \\ \text{OMe} \end{array}^{*} \]

para-methoxybenzyl (PMB) group

\[ \begin{array}{c} \text{OR} \\ \text{OR} \end{array} \xrightarrow{\text{++}} \begin{array}{c} \text{OR} \\ \text{OR} \end{array}^{*} \xrightarrow{\text{=} \rightarrow} \begin{array}{c} \text{OR} \\ \text{OR} \end{array}^{*} \xrightarrow{\text{etc.}} \]

MO description

\[ \begin{array}{c} \pi_{1}^{*} \\ \pi_{2} \end{array} \xrightarrow{-e^{-}} \begin{array}{c} \pi_{1}^{*} \\ \pi_{2} \end{array} \]

vacant bonding orbital ("hole" in \( \pi_{2} \))

Radical cations also arise in the oxidations produced by DDQ

\[ \text{O} \xrightarrow{\text{(- e-)}} \left( \begin{array}{c} \text{NC} \\ \text{Cl} \end{array} \right) \xrightarrow{\text{(- e-)}} \begin{array}{c} \text{H} \\ \text{H} \end{array} \]

very e\(^{-}\) deficient

\[ \begin{array}{c} \text{NC} \\ \text{Cl} \end{array} \begin{array}{c} \text{NC} \\ \text{Cl} \end{array} \xrightarrow{\text{(- e-)}} \left( \begin{array}{c} \text{NC} \\ \text{Cl} \end{array} \right) \text{H} \]
radical ions can also be distonic (Kenttamaa)
ex:

\[ \text{O}^{\bullet^*} \quad \text{vs.} \quad \text{O}^+ \]

-differing stabilities, reactivities
(these species are very important in mass spectrometry experiments)

**Carbenes** - neutral molecules lacking an octet

\[
\begin{array}{c}
\text{R}_1 \\
\text{C} \\
\text{R}_2
\end{array}
\]

divalent carbon with two non-bonded electrons
\[ \Rightarrow \text{VERY reactive & unstable} \]

two different spin states:

\[
\begin{array}{c}
\sigma_2 \\
\sigma_1
\end{array}
\]

\[
\begin{array}{c}
\text{singlet (J = 0)} \\
\text{triplet (J = 1)}
\end{array}
\]

at first approximation, we can consider them as:

\[
\begin{array}{c}
\text{R}_1 \quad \text{sp}^3 \\
\text{R}_2
\end{array}
\]

\[
\begin{array}{c}
\text{R}_1 \quad \text{sp}^2 \\
\text{R}_2
\end{array}
\]

triplet

-singlet behaves as isolated radicals

-singlet behaves as zwitterion
structure:

much debate on structure of methylene (CH₂)

\[
\begin{align*}
\text{triplet} & : \quad \text{Wasserman, JACS 1970, 92, 7491} \\
\text{singlet} & : \quad \text{Herzberg, Nature 1959, 183, 1801}
\end{align*}
\]

- same bent structure holds for most other carbenes

stability:

methylene (CH₂) is a ground state triplet (by 8 - 10 kcal/mol)

normally, carbenes are generated as singlets

carbenes are stabilized by resonance:

\[
\begin{align*}
\text{H}_2\text{C} & \quad < \quad \text{HC-COR} \quad < \quad \text{HC} \quad < \quad \text{X-C-H} \quad < \quad \text{X-C-X} \\
(X & = \text{Cl, Br})
\end{align*}
\]

a very stable carbene has been reported:

Arduengo, JACS 1991, 113, 361
Methods of Generation

1) $\alpha$ - elimination

\[
\begin{array}{c}
\text{H} \quad \text{X} \\
\text{R} \quad \text{R} \\
\end{array}
\xrightarrow{\text{base}}
\begin{array}{c}
\Theta \\
\text{C} \\
\text{R} \\
\text{X} \\
\text{R} \\
\end{array}
\xrightarrow{\text{slow}}
\begin{array}{c}
\bullet \\
\text{C} \\
\text{R} \\
\end{array}
\]

ex:

\[
\begin{align*}
\text{HCCl}_3 & \xrightarrow{\text{KOH}} \text{CCl}_2 \\
& \xrightarrow{\text{H}_2\text{O}, 35^\circ} \text{(dichlorocarbene)}
\end{align*}
\]

also:

\[
\begin{align*}
\text{HCCl}_3 & \xrightarrow{\text{MeLi, THF, -78^\circ}} \Theta \text{CHCl}_2 \\
& \xrightarrow{-78^\circ \text{ to } 25^\circ} \bullet \text{CHCl} \\
& \text{(chlorocarbene)}
\end{align*}
\]

In many cases, one can get a carbenoid instead:

\[
\begin{align*}
\text{CH}_2\text{I}_2 & \xrightarrow{\text{Zn^0}} \text{Zn(CH}_2\text{I})_2 \\
& \equiv \Theta^2 \Theta \text{Zn(CH}_2\text{I})_2
\end{align*}
\]

stable to $\alpha$ - elimination but behaves like a carbene

“Simmons - Smith” reagent

2) decomposition of diazo compounds

\[
\begin{align*}
\begin{array}{c}
\text{R} \\
\text{C} \equiv \text{N}_2 \\
\end{array} & \xrightarrow{\text{hv or } \Delta} \\
& \begin{array}{c}
\text{R} \\
\text{C} \bullet \\
\end{array}
\end{align*}
\]

($\Delta$ gives singlet, hv gives excited state)
mechanism:

\[
\begin{align*}
R_C &= N = \Theta \\
R_1 &= + \\
\end{align*}
\]

also works with diazirines:

\[
\begin{align*}
R_2C &= N \\
R_2 &= + \\
\end{align*}
\]

most important to synthetic chemists is the metal-catalyzed decomposition:

\[
\begin{align*}
R_C &= N_2 \\
R_1 &= + \\
\end{align*}
\]

Characteristic Reactions

1) Cyclopropanation

singlet and triplet behave differently

one isomer

mixture
singlet reacts in concerted fashion (no intermediate)

triplet reacts via diradical intermediate:

\[
\begin{align*}
\text{can rotate} & \\
\text{can invert} &
\end{align*}
\]


more commonly:

more commonly:

\[
\begin{align*}
\text{C} & \text{H} & \text{Cl} \\
\text{Cl} & \text{Cl} &
\end{align*}
\]

[25°]

2) C-H insertion

how? Maybe via 3-center, 2-electron transition state
for preparative purposes:

\[
\begin{align*}
\text{O} & \quad \text{Rh}_2(\text{OAc})_4 \quad \text{THF} \quad \text{O} \\
\text{N}_2 & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

Doyle in Comprehensive Organometallic Chemistry II, (1995), Vol. 2, Ch. 5.2

(very powerful transformation – stereoselective functionalization of methylene group)

this can also be intramolecular:

\[
\begin{align*}
\text{Br} & \quad \text{KOH} \quad -30^\circ \quad \text{Br} \\
& \quad >25^\circ \quad \text{C-H} \\
\text{insertion} & \quad \text{H} \\
\end{align*}
\]

Doering, Tetrahedron 1960, 11, 266

3) Rearrangements (like carbocations)

\[
\begin{align*}
\text{H} \quad \text{H} & \quad 1,2 \text{ shift} \quad \text{Schechter, JACS 1960, 82, 1002} \\
\end{align*}
\]

also:

\[
\begin{align*}
\text{R} & \quad \text{hv}, \Delta \quad \text{or Rh}_2(\text{OAc})_4 \\
\text{N}_2 & \quad (-\text{N}_2) \\
\end{align*}
\]

this is known as the Wolff rearrangement (JACS 1961, 83, 492)

when the ketene is trapped by an alcohol, it’s the Arndt - Eisnert rxn
The nitrogen equivalent (nitrenes) are also known:

\[
\text{very reactive}
\]

they behave similarly to carbenes, but are less stable and more reactive