CARBANIONS

Carbanions are units that contain a negative charge on a carbon atom. The negative charge gives good nucleophilic properties to the unit that can be used in the formation of new carbon carbon bonds. Carbanions thus act as nucleophiles in substitution reactions, in carbonyl addition and substitution reactions, and in 1,4-addition (Michael) reactions.

\[
\begin{align*}
\text{a carbanion} \\
R & \quad \text{C} \quad R \\
\text{R} & \\
\end{align*}
\]

Carbanions bear many substituents that can affect the structure and reactivity of the carbanion, and can affect the acidity of a parent C-H precursor. Halogens stabilize carbanions in the order of Br > Cl > F. A prominent I-π repulsion between the F and Carbanionic center causes some destabilization in alpha-fluorinated carbanions. The magnitude of the destabilization depends on the carbanion structure. The destabilization maximizes as the carbanion structure approaches a planar configuration. Thus, fluorinated carbanions possess pyramidal structures with high barriers to inversion.

Carbanion Structure

Carbanions are trivalent with sp\(^3\) hybridization. The lone pair of electrons occupies one of the sp\(^3\) orbitals. The geometry is thus tetrahedral. The tetrahedron can undergo inversion or retain its stereochemistry depending on the attached substituents. A methyl carbanion has a barrier to inversion of about 2 kcal/mole. The trifluoromethyl carbanion has a barrier of 120 kcal/mole. A fluorine atom is however more stabilizing than a hydrogen atom because of the fluorine electronegativity.

\[
\begin{align*}
\text{inversion} & \\
\end{align*}
\]
The rate of inversion in hydrocarbon system is slowed by incorporation of the carbanion into a three membered ring.

Experiments involving the use of chiral substrates aids the study of carbanion stereochemistry as inversion causes loss of optical activity. Cleavage of the methyl ketone below with amide ion give a carbanion with a slow rate of inversion. The carbanion abstracts a proton to give an optically active product. Carbanions that contain fluorine atoms often show a slow rate of inversion.

When the rate of deuterium exchange at a chiral center is not equal to the rate of racemization it shows that an intermediate is involved as an ion pair. Carbanion ion-pairs are show to be present through labeling at a chiral center. The rate of d exchange is different from the rate of inversion, indicating that the ion pair is encumbered with the cation or the solvent.
Carbanions containing beta fluorine atoms are strongly stabilized. Electronegativity of the fluorine atom is the main reason but some consideration must be given to "Negative hyperconjugation", as has been found from the crystal structure of the compound below. Negative hyperconjugation is possible because fluorine atoms have a very low energy sigma * orbital to accept the electron. In the structures below the fluorine atom position is identical in each structure.

The formation of carbanion intermediates in the elimination of HF from fluorcarbons often occurs (E1Cb) as shown below.
**Acidity**

The conversion of carboxylic acids and phenols to carboxylate or phenolate ions is common because the proton is acidic, thus the proton is easily removed to form the anion in weakly basic medium. Most organic compounds are much less acidic than carboxylic acids, and thus need stronger basic medium to ionize a carbon-hydrogen bond. Because of the high electronegativity of a fluorine atom, fluorinated compounds are always more acidic than non-fluorinated compounds. Fluorination alpha to an anionic site can sometimes be destabilizing depending on the geometry of the anion. Thus the p-π backbonding from fluorine is maximized in planar carbanions. But fluorinated carbanions tend not to be planar. Beta fluorination increases acidity dramatically, and trifluoromethyl groups very much increase acidity.

In the planar fluroene systems shown below the decreasing acidity effect of the fluorine by p-π interaction of the non-bonding fluorine atoms with the occupied p orbital is evident, as the rate of C-D exchange in the fluorinated compound is the slowest of all the compounds. The mechanism for exchange involves a carbanion intermediate which in this case is planar.

![Fluorene systems](image)

<table>
<thead>
<tr>
<th>R</th>
<th>Ka</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>6090</td>
</tr>
<tr>
<td>Cl</td>
<td>3480</td>
</tr>
<tr>
<td>H</td>
<td>8.7</td>
</tr>
<tr>
<td>F</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The equilibrium expression below how the pKa is related to the basic medium where H⁻ is the base constant. Thus for compounds of weak acid strength (high pKa) a large base constant is needed to form the carbanion.

\[
\begin{align*}
R-H & \quad + \quad \text{base} \quad \rightleftharpoons \quad R^- & \quad + \quad \text{base-H} \\
\text{Ka} & = \frac{[R^-][\text{base-H}]}{[R-H][\text{base}]} \\
p\text{Ka} & = -\log \left[ \frac{[R^-][\text{base-H}]}{[R-H][\text{base}]} \right] \\
p\text{Ka} & = pK_a + \log \frac{R\text{H}}{R^-}
\end{align*}
\]
The pKa values of some common organic compounds are shown below. Hydrocarbons which have pKa of about 48 are almost non-acidic, but with special structural features such as added benzene rings or adjacent carbony groups, the pKa values approaches that of weak organic acids.

pKa

**OH Compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$COO-H</td>
<td>4.8</td>
</tr>
<tr>
<td>CF$_3$COO-H</td>
<td>0.5</td>
</tr>
<tr>
<td>C$_6$H$_5$-OH</td>
<td>10</td>
</tr>
<tr>
<td>C$_6$F$_5$-OH</td>
<td>5.5</td>
</tr>
<tr>
<td>(CH$_3$)$_3$C-OH</td>
<td>19</td>
</tr>
<tr>
<td>(CF$_3$)$_3$C-OH</td>
<td>5.4</td>
</tr>
</tbody>
</table>

**Hydrocarbons**

<table>
<thead>
<tr>
<th>Compound</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCH$_2$-H</td>
<td>41</td>
</tr>
<tr>
<td>Ph$_2$CH-H</td>
<td>33</td>
</tr>
<tr>
<td>Ph$_3$C-H</td>
<td>31</td>
</tr>
<tr>
<td>CH$_3$CH$_2$H</td>
<td>48</td>
</tr>
<tr>
<td>H</td>
<td>49</td>
</tr>
<tr>
<td>H</td>
<td>16</td>
</tr>
<tr>
<td>H</td>
<td>26</td>
</tr>
<tr>
<td>H</td>
<td>11</td>
</tr>
<tr>
<td>(CH$_3$)$_3$C-OH</td>
<td>19</td>
</tr>
<tr>
<td>(CF$_3$)$_3$C-OH</td>
<td>5.4</td>
</tr>
<tr>
<td>F</td>
<td>14</td>
</tr>
<tr>
<td>F</td>
<td>14</td>
</tr>
<tr>
<td>F</td>
<td>8.5</td>
</tr>
</tbody>
</table>
Several basicity constants are show below. When a system has a basicity constant higher that the pKa of an acid then a reaction will occur to form a carbanion. Thus a number of bases are now known that can be used for the generation of carbanions that are then used in some synthetic process.

\[

t-1 \\
\text{RLi} & 50 \\
0.01 \text{M NaOCH}_3 \text{ in DMSO/MeOH} & 15 \\
6\text{M KOH} & 16 \\
10\text{ M KOH} & 17-18 \\
\]

Solvents and Bases

The formation of carbanions can occur in several solvent systems. Very strong bases cannot be formed in protic solvents because they abstract a hydrogen atom from the solvent to form a hydrocarbon.

Commonly Used Solvents

Water, Alcohols---polar protic
Ether, THF, Hexane--covalent aprotic
DMSO, DMF, HMPA---polar, aprotic

The strongest bases are obtained from the reaction of metal with organohalogen compounds to give reagents known as Grignard reagents or organolithium reagents.

Bases

Organolithium reagents

n-BuLi, PhLi, MeLi commercially available

t-BuLi > sec-BuLi> n-BuLi in base strength

\[
\text{Bu-Br} + 2 \text{Li} \xrightarrow{\text{cold}} \text{Bu-Li} + \text{LiBr}
\]

ether or hexane
The organolithium reagents tend to exist as tetramers because of the covalent nature of lithium to carbon bonds. The tetramers are still very strong bases and strong nucleophiles, and can be converted to even stronger bases on coordination with tetramethylethlenediamine as shown.

Postassium tert-butoxide, commercially available, and lithium diisopropamide (LDA), easily prepared in the lab, are frequently used for reaction with the alpha hydrogen of carbonyl compounds to produce enolates.

**Stabilization of Carbanions**

The negative charge on a carbanion is stabilized by neighboring electron withdrawing groups (WEG) such as carbonyl, nitro, and sulfone.

\[
\text{EWG} = \text{C=O, NO}_2, \text{CN, SO}_2
\]

The stabilizing dispersal of the electrons into the EWG is shown in the examples below. Carbonyl functions are very effective in stabilizing adjacent negative charge and when two carbonyl groups are present (as in diethyl malonate or acetylacetone) a very useful carbanionic intermediate is produced. The intermediate is called an enolate. The dithane system is capable of stabilizing the carbanion by dispersal of the charge into the d orbitals of the sulfur atoms.
When carbanions are formed in unsymmetrical ketones, two carbanions is possible. One, the more substituted carbanion and more stable, is called the thermodynamic anion; while the least substituted and first formed anions is called the kinetic anion. LDA is a base of choice for formation of kinetic products while hydroxide and alkoxides give the thermodynamic anion.
Fluorine atoms alpha to a carbonyl group oppose the normal polarization of the carbonyl which contains positive charge on the carbon and negative charge on the oxygen. Thus fluorinated aldehydes and ketones show higher enol content than the hydrogen counterparts.

**Synthetic Applications of Enolates**

Processes in organic chemistry used for synthesis generally include functional group changes and formation of new carbon-carbon bonds. Carbanions are very useful intermediates for the formation of new carbon-carbon bonds. **Thus carbanions participate in 1) SN2 alkylation reactions, 2) in 1,2 additions to carbonyl functions, and 3) in 1,4-additions such as Michael Reactions.** Fluorinated carbanions are very common useful intermediates for the synthesis of new fluorinated materials. As already noted, the fluorine atom will act in a stabilizing manner to withdraw electrons from the carbanion when the carbanion has a pyramidal shape. Fluorine backbonding would be just the opposite in donating electrons to the carbanion center, and thus be destabilizing. The overall result is that fluorinated carbanions are pyramidal and therefore stabilized by the fluorine. There appears to be little difference between fluorinated and non-fluorinated carbanions in synthetic procedures.

**Enolate Reactions with Carbonyl Groups**

**Aldol Condensation**

An aldehyde or ketone that has a hydrogen next to the carbonyl group, an alpha-hydrogen, can form an enolate in basic solution, and the enolate can react by nucleophilic addition at the carbonyl group of another molecule. This process is a very important synthetic procedure and is known as the **Aldol Condensation.** The final product from aliphatic aldehydes or ketones contains both a carbonyl and an alcohol group. The product is called an aldol.

\[
\text{CH}_3\text{CH}=\text{O} \xrightarrow{\text{OH}} \text{CH}_2\text{CH}=\text{O} \rightleftharpoons \text{CH}_2=\text{CH}-\text{O}^-
\]

\[
\text{CH}_3\text{CH}=\text{O} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}-\text{O}^- \xrightarrow{\text{CH}_2\text{CH}=\text{O}} \text{CH}_3\text{CH-OH}
\]

Some examples of the aldol condensation from aldehydes and ketones are shown below.
The aldol products react readily with acid to undergo dehydration and give α,β-unsaturated carbonyl compounds that are also very useful in synthetic organic and biological chemistry.

Intramolecular aldol condensations are useful in the formation of cyclic α,β-unsaturated ketones.

**Crossed-Aldol Condensation**

The main aldol condensation involves reaction between two aldehydes or ketones of the same structure. But, the procedure can be modified so that the enolate can react with another aldehyde of different structure. The requirement is that the other aldehyde has to be more reactive than the first and it contains no α-hydrogens. Formaldehyde, CH₂C=O, and benzaldehyde, PhCH=O, both meet these requirements and are useful in this procedure called the crossed-aldol condensation. All three of the α-hydrogens in acetaldehyde can react in a crossed-aldol condensation with formaldehyde.
Aromatic ketones bearing α-hydrogens give aldol reaction products readily, but in this case the aldol product spontaneously loses water to form the unsaturated ketone. When benzaldehyde is used in the crossed-aldol condensation the final product is the unsaturated aldehyde or ketone. Conjugation of the double bond with the aromatic ring is the reason for the spontaneous dehydration.

Fluoroacetonitrile condenses with carbon disulfide in an interesting aldol-type reaction as shown below.

The carbanion for ethyl fluoroacetate reacts readily with benzaldehyde in a cross-aldol reaction to give the fluorinated alcohol. Alpha fluorinated carbonyl compounds are often very toxic materials because biologically they are converted to fluoroacetate which is toxic to the Krebs cycle. Thus extreme care is needed when using these compounds.

**Esters**

**Claisen Condensation**

Esters, like aldehydes and ketones, give an aldol-type reaction. The α-hydrogen of the ester is removed by base to give the enolate. The enolate reacts with another molecule of the ester in an addition-elimination reaction characteristic of esters, which appears as displacement of the alkoxide. The resulting product is a β-ketoester. The reaction is known as the **Claisen condensation**.
The α-hydrogens in the product β-ketoester are more acidic than the α-hydrogens in the starting ester. Thus a new enolate is formed that is more stable than the first enolate, thus helping the reaction go to completion.

**Crossed-Claisen condensation** occurs when a highly reactive ester with no α-hydrogens reacts with the enolate derived from another ester. Ethyl benzoate and ethyl formate are two frequently used esters that have no α-hydrogens.

Claisen condensation of ethyl benzoate with ethyl acetate affords ethyl benzoylacacetate in the crossed-Claisen method.

Intramolecular Claisen condensations go by the name of Dieckmann condensations and are useful for the preparation of five and six-membered rings.
Ethyl fluoroacetate reacts readily in a crossed-Claisen reaction with diethyl carbonate to give diethyl fluoromalonate. Diethyl fluoromalonate can be used synthetically just as diethyl malonate.

$$
\text{EtO}_2\text{C} + \text{EtO}_2\text{C} \rightarrow \text{EtO}_2\text{C} = \text{EtO}_2\text{C} \quad 90\%
$$

**Dieckmann condensation**

**Enolate Anion Alkylation Reactions**

**General Reaction**

When strong anhydrous bases such as sodium hydride, sodamide or lithium diethylamide LiN(C$_2$H$_5$)$_2$, are used to prepare the enolate anions at low temperatures, the resulting enolate reacts very slowly with carbonyl groups and can be used as nucleophiles in the SN2 reaction with primary alkyl halides. In the resonance stabilized enolate, a negative charge exists on both a carbon and an oxygen. Both sites are possible nucleophiles in the reaction but the carbon nucleophile predominates because it is a stronger nucleophile, but minor products from O-alkylation are found.

Alkylation of simple fluoroketones seems to be little studied, but alkylation of the cyclohexylimine of fluoroactone show temperature dependent regioselectivity. Mixtures are formed but the major isomer shown is produced in about 90 % yield. Imines are used because there is no competition for Aldol type additions.
The fluorinated oxazine below is alkylated easily with benzyl bromide. After reduction and hydrolysis a fluoro aldehyde is obtained. This is a fluoro modification of the Meyers synthesis.

\[
\begin{align*}
\text{N} & \quad \text{F} \\
\text{LiHMDS} & \quad \text{1)} \\
\text{CH}_3\text{I} & \quad \text{2)} \\
\text{F} & \quad \text{N} \\
\text{LiHMDS} & \quad \text{1)} \\
\text{CH}_3\text{I} & \quad \text{2)} \\
\end{align*}
\]

1) n-BuLi, THF, -78°
2) PhCH$_2$Br

\[
\begin{align*}
\text{O} & \quad \text{F} \\
\text{Ph} & \quad \text{Ph} \\
\text{76%} & \\
\end{align*}
\]

Alkylation of Ethyl Acetoacetate and Diethyl Malonate

β-Keto esters have earned a special place in organic chemistry for their value as compounds used in the synthesis of new carbon-carbon bonds. The general method for their use involves a) formation of the enolate between the carbonyl groups, b) reaction of the enolate in an S$_\text{N}$2 reaction with an alkyl halide, and c) removal of one of the carbonyl groups by decarboxylation. The result is the formation of methyl ketones or acetic acid derivatives.

\[
\begin{align*}
\text{CH}_3\text{C}-\text{CH}_2-\text{C-OCH}_2\text{CH}_3 & \quad \text{base} \\
\text{O} & \quad \text{O} \\
\text{CH}_3\text{C}-\text{CH}_2-\text{C-OCH}_2\text{CH}_3 & \quad \text{CH}_3\text{C}-\text{CH}-\text{C-OCH}_2\text{CH}_3 \\
\text{Ethyl Acetoacetate} & \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{O}-\text{C}-\text{CH}_2-\text{C-OCH}_2\text{CH}_3 & \quad \text{base} \\
\text{O} & \quad \text{O} \\
\text{CH}_3\text{CH}_2\text{O}-\text{C}-\text{CH}-\text{C-OCH}_2\text{CH}_3 & \quad \text{CH}_3\text{CH}_2\text{O}-\text{C}-\text{CH}_2-\text{C-OCH}_2\text{CH}_3 \\
\text{Diethyl Malonate} & \\
\end{align*}
\]
**Ethyl Acetoacetate**

The α-hydrogens of ethyl acetoacetate are acidic enough (pKa =11) to be removed by a variety of bases. The enolate anion can be used to displace a halogen in an alkyl halide. Hydrolysis of the product gives a β-ketoacid which loses CO₂ on mild heating. A derivative of acetone is the final product.

```
CH₃CCHCO₂C₂H₅ + C₂H₅O⁻ → CH₃CCHCO₂C₂H₅ + R-X
H₂O⁺ → CH₃CCHCO₂H → CH₃CCH₂O⁻ → CH₃CCH₂
```

substituted acetone

The decarboxylation occurs readily because it proceeds through a favorable cyclic transition state as shown below.

```
CH₃
R-O
```

```
CH₃-O
R-H
```

Double alkylation of ethyl acetoacetate in sequential steps can provide a synthesis of highly branched derivatives of acetone after the hydrolysis and decarboxylation steps.

```
CH₃CCH₂CO₂C₂H₅ + C₂H₅O⁻ → CH₃CCHCO₂C₂H₅ + C₂H₅-Br
1) C₂H₅O⁻ 2) CH₃Br → CH₃CCHCO₂C₂H₅ + H₃O⁺ → CH₃CCHCH₃
```

**Diethyl malonate**

Diethyl malonate also possess acidic α-hydrogens and may be used instead of ethyl acetoacetate in the above sequence. The difference is found in the final product that contains an acetic acid structural unit instead of an acetone structural unit.
The Michael Reaction

Enolate Addition

Enolates may also be alkylated with $\alpha,\beta$-unsaturated carbonyl substrates. The enolate adds in the 1,4 fashion to give a unit extended by three carbon atoms in a process known as the Michael reaction. Many $\alpha,\beta$-unsaturated carbonyl systems may be prepared by the dehydration of aldol products. Examples of the Michael reaction using methyl vinyl ketone and acrylonitrile, two common units in the reaction, are shown below.

Enamine Additions

Enamines, the products of the acid-catalyzed addition of secondary amines to aldehydes or ketones, can be viewed as weakly nucleophilic enolate anions. Enamines will react with $\alpha,\beta$-unsaturated carbonyl systems in the Michael reaction in method that permits introduction of new carbon-carbon bonds adjacent to the carbonyl group.
Enamine Addition

\[
\text{EN}(\text{NH}) \rightarrow \text{enamine} \quad \text{H}^+ \\
\text{CN} \quad \text{CH}_2=\text{CHCN} \\
\text{CN} \quad \text{H}_2\text{O}^+ \\
\text{enamine} \rightarrow \text{EN} + \text{CN}
\]

Robinson Ring-forming Reaction

A unique reaction that produces a new ring containing an \(\alpha,\beta\)-unsaturated ketone is the Robinson reaction. When an enolate derived from a ketone reacts with methyl vinyl ketone, the enolate adds in the Michael reaction, then a second enolate in the ketone product is formed that cyclizes in an Aldol condensation to give the final product.

Robinson Reaction

\[
\text{Michael} \quad \text{OH} \\
\text{aldol} \quad 2\text{) H}^+
\]

The dithane system is capable of stabilizing the carbanion by dispersal of the charge into the \(d\) orbitals of the sulfur atoms. When the dithiane carbanion is used as a nucleophile, the dithiane unit can be hydrolyzed to a carbonyl group. This the dithane functions as a masked aldehyde.
Organometallics

Organometallic reagents are well-known in organic chemistry. The Grignard reagent (RMgX), organo lithium reagents and organozinc reagents are used as nucleophiles in the addition to carbonyl groups, in SN2 reaction and in Michael reactions. A few examples of their counterparts in organofluorine chemistry are shown here.

The trifluormethyl anion is prepared from by reaction of trifluoromethyl trimethylsilane with fluoride ion. The strong affinity of fluoride for silane drives this reaction toward the trifluoromethy anion. The anion behaves like a good nucleophile in many reaction. Addition to a carbonyl group is shown here.

\[
\text{CF}_3\text{SiMe}_3 + \text{F}^- \rightarrow \text{FSiMe}_3 + \text{CF}_3^-
\]

Trifluormethyl copper shows good ability as a coupling reagent with arylaromatics.

\[
\text{CF}_3\text{Br} + \text{Cu} \rightarrow [\text{CF}_3\text{Cu}]
\]

\[
\text{ArI} + [\text{CF}_3\text{Cu}] \rightarrow \text{ArCF}_3
\]

Trifluorovinyl lithium is produced from chlorotrifluoroethene and butyl lithium. The lithium reagent adds easily to carbonyl groups.

\[
\text{CF}_2=\text{CFl} \xrightarrow{\text{n-BuLi}} \text{CF}_2=\text{CFl} \xrightarrow{\text{n-BuLi}} \text{CF}_3\text{CH}_2\text{F}
\]

Reformatsky Reaction

Instead of forming the enolate from an α-hydrogen, an α-bromine atom can also be used. Zinc reacts with ethyl α-bromoacetate to form a zinc enolate that reacts at the carbonyl function of aldehydes and ketones to produce α,β-hydroxyester. The method is made easier by addition of the bromoester to a mixture of zinc and the carbonyl compound.
Reformatsky Reaction

$$\text{BrCH}_2\text{CO}_2\text{C}_2\text{H}_5 \xrightarrow{\text{Zn/ether}} \text{BrZn}^- \xrightarrow{\text{ether}} \text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$$

$$\text{H}_3\text{C} \quad \text{CH}_3$$

$$\text{O} \quad \text{BrZn}^- \quad \text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$$

$$\xrightarrow{\text{BrZn}^-} \text{BrZnO} \xrightarrow{\text{ether}} \text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$$

$$\text{H}_3\text{C} \quad \text{CH}_3$$

$$\xrightarrow{\text{H}_2\text{O}} \text{HO} \quad \text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$$

$$\text{H}_3\text{C} \quad \text{CH}_3$$

Ethyl bromodifluoroacetate is used frequently in Reformatsky procedures to give high yields of alcohol products.

Keto-Enol Equilibrium

Ketones can exist as two equilibrated molecules. One molecule is the often written ketone structure while the other structure is a tautomer known as an enol. In some cases the enol contribution can be large. When fluorine atoms are present in the ring, the electron withdrawal by fluorine around the carbonyl increases the positive charge at the carbonyl. The molecule responds by forming the enol.
Rearrangements of Carbanions

Homoallylic rearrangements

The structures below represent allylic, homoallylic and homobenzylic. The “homo” means that there is one additional carbon atom. Some interesting rearrangements occur with the homoallylic systems.

The examples below show a homobenzylic rearrangement where the carbanion interacts with the aromatic ring. The carbanion appears to insert between the ring and the carbon containing the two methyl groups. The mechanism of the rearrangement is proven by isolation of the cyclopropane structure when a para phenyl group is present.
The examples below represent some well known reactions.

- **Wittig**
  
  \[
  \text{Ph-CH}_2\text{-O-CH}_3 \xrightarrow{\text{n-BuLi}} \text{Ph-CH-O} \text{CH}_3
  \]

- **Stevens**
  
  \[
  \text{PhCH}_2\text{-S-CHPh} \xleftarrow{\text{CH}_3} \text{SCH}_3
  \]

- **Sommelet-Hauser**
  
  \[
  \text{PhCH}_2\text{-N(C(CH}_3)_2} \xrightarrow{\text{CH}_2} \text{CH}_3 \text{CH}_2\text{-N(C(CH}_3)_2}
  \]

- **Rambourg-Backland**
  
  \[
  \text{O}_2 \text{Br} \xleftarrow{\ominus} \text{O}_2 \text{S} \xrightarrow{-\text{SO}_2} \text{ }
  \]