HISTORY OF ORGANIC CHEMISTRY

Although it is most often taught as a dry subject devoid of major controversy or character, organic chemistry has a truly colorful history. My own interests in the history of organic chemistry are in the contributions of Russian organic chemists to the development of the science. Despite the fact that most students and teachers of organic chemistry tend to credit the major advances in the discipline to the German chemists (Kekulé, Liebig, Wöhler, Baeyer, and their ilk), many major advances were made by Russian organic chemists, whose names have also passed into the vocabulary of the science.

Some major Russian contributors to modern organic chemistry include:

Aleksandr Erminingel’dovich Arbuzov: the Arbuzov rearrangement of phosphites to phosphonates

<chemical formula image>

Aleksandr Porfir’evich Borodin: discovered the Borodin-Hunsdiecker reaction of silver carboxylates, the aldol addition, and made the first organic fluorine compound (he is the same person as the renowned composer, which is how he usually appears on "Jeopardy!")

<chemical formula image>
Aleksandr Mikhailovich Butlerov: an early champion of structural theory in organic chemistry; first synthesis of a tertiary alcohol and first synthesis (somewhat serendipitous) of a carbohydrate

Aleksei Yevgenievich Chichibabin: the Chichibabin reaction of pyridines; Chichibabin pyridine synthesis

Lev Aleksandrovich Chugaev: the Chugaev elimination of xanthate esters
Nikolai Yakovlevich Demyanov: the Demjanov rearrangement of β-aminoalcohols

\[ \text{NH}_2 \xrightarrow{\text{HNO}_2} \text{OH} \quad + \quad \text{OH} \xleftarrow{\text{HNO}_2} \text{H}_2\text{N} \]

Aleksei Yevgrafovich Favorskii: the Favorskii rearrangement of α-haloketones; Favorskii-Babayan synthesis of propargylic alcohols

\[ \text{Br} \xrightarrow{10\% \text{ KOH}} \text{HO}_2\text{C} \]

\[ \text{Me} \xrightarrow{\text{HC} \equiv \text{CH}} \text{OH} \xrightarrow{\text{KOH (powdered)}} \text{Me} \]

Vladimir Nikolaevich Ipatieff: pioneer in high-pressure hydrogenation
<table>
<thead>
<tr>
<th>Nikolai Matveyevich Kizhner (Kishner): the Wolff-Kishner reduction of ketones and aldehydes</th>
</tr>
</thead>
</table>
| \[
\begin{align*}
R' \quad \text{CH}_{2} \text{NH}_{2} & \quad \rightarrow \\
\text{RO} & \quad \text{KOH, } \Delta & \quad \rightarrow \\
n\text{R} \quad \text{H}
\end{align*}
\] |

| Karl Karlovich Klaus (Carl Ernst Claus): discoverer of ruthenium |

<table>
<thead>
<tr>
<th>Vladimir Vasilievich Markovnikov: Markovnikov's Rule for addition to alkenes; further exploration of structural theory; first cyclobutane and cycloheptane derivatives</th>
</tr>
</thead>
</table>
| \[
\begin{align*}
\text{Cl} \quad \text{CO}_{2} \text{H} & \quad \rightarrow \\
\text{CH}_{2} & \quad \text{H}_{2} \text{O} \text{C} & \quad \rightarrow \\
\text{Na, EtOH} & \quad \rightarrow \\
\text{H}_{2} & \text{O} \text{C} & \quad \rightarrow
\end{align*}
\] |
<table>
<thead>
<tr>
<th>Image</th>
<th>Name</th>
<th>Reaction/Description</th>
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</table>
| ![Nikolai Aleksandrovich Menshutkin](image1) | Nikolai Aleksandrovich Menshutkin: the Menshutkin reaction of tertiary amines; pioneer of physical organic chemistry | \[
\begin{align*}
\text{R} & \quad \text{R} - \text{N} \\
& \quad \text{R'} - \text{X} \\
\Rightarrow & \quad \text{R} + \text{R'} - \text{N} - \text{X} \\
& \quad \text{R} - \text{N} - \text{R'} - \text{X} 
\end{align*}
\] |
| ![Ivan Nikolaevich Nazarov](image2) | Ivan Nikolaevich Nazarov: the Nazarov cyclization | | ![Nikolai Aleksandrovich Prilezhaev](image3) | Nikolai Aleksandrovich Prilezhaev: epoxidation of alkenes with peracids (Prilezhaev reaction) | \[
\begin{align*}
\text{R} & \quad \text{R} - \text{C} = \text{O} \\
& \quad \text{R} - \text{OH} \\
\Rightarrow & \quad \text{R} + \text{R'} - \text{OH} \\
& \quad \text{R} + \text{R'} - \text{OH} \\
\Rightarrow & \quad \text{R} - \text{R'} - \text{O} \\
& \quad \text{R} - \text{R'} - \text{O} \\
\end{align*}
\] | \[
\begin{align*}
\text{R} & \quad \text{R} - \text{R} \\
\Rightarrow & \quad \text{R} + \text{R} - \text{C} = \text{O} \\
\Rightarrow & \quad \text{R} + \text{R} - \text{C} = \text{O} \\
\end{align*}
\] |
Nikolai Nikolaevich Reformatskii: the Reformatskii reaction of a-halocarbonyl compounds

\[ \text{Br} - \text{CO}_2\text{Et} \xrightarrow{1) \text{Zn, Et}_2\text{O}} \xrightarrow{2) \text{Me}_2\text{CHCHO}} \text{OH} - \text{CO}_2\text{Et} \]

Vyacheslav Yevgenievich Tishchenko: the Tishchenko reaction of aromatic aldehydes with aluminum alkoxides

\[ \text{Ph} - \text{CHO} \xrightarrow{\text{Al(O-}t\text{-Bu)}_3} \text{Ph} - \text{O} - \text{O} - \text{Ph} \]

Egor Egorevich Vagner (Georg Wagner): the Wagner-Meerwein rearrangement; the Wagner oxidation (permanganate) of alkenes

\[ \text{Et}_2\text{Zn} \xrightarrow{\text{HX}} \]

Kazan’ St. Petersburg and Warsaw
Aleksandr Mikhailovich Zaitsev (Saytzeff): Saytzeff’s Rule for elimination from alkyl halides; the discoverer of sulfoxides; pioneer in organozinc syntheses of alcohols

\[
\begin{align*}
R^1-S-R^2 & \xrightarrow{HNO_3} R^1-SO-R^2 \\
R^1 = \text{Me, Et} & \\
\end{align*}
\]

Nikolai Dmitrievich Zelinskii: the Hell-Volhard-Zelinskii reaction of carboxylic acids; Zelinskii-Stadnikov modification of the Strecker amino acid synthesis

\[
\begin{align*}
\text{RCONH}_2 & \xrightarrow{\text{KCN, NH}_4\text{Cl, H}_2\text{O}} \text{RNH}_2 \\
\text{RNCO} & \xrightarrow{\Delta} \text{RNCO}_2\text{H} \\
\end{align*}
\]

Nikolai Nikolaevich Zinin: discoverer of the reduction of nitrobenzene to aniline

\[
\begin{align*}
\text{NO}_2 & \xrightarrow{\text{NH}_3, \text{H}_2\text{S, EtOH, } \Delta} \text{NH}_2 \\
\end{align*}
\]
My own special interests are the chemists of the Kazan' School of Chemistry, among whose luminaries are Zinin, Butlerov, Markovnikov, Zaitsev, Vagner, Reformatskii, and Arbuzov.