Introduction

- Proceedings of the USSR Academy of Sciences (Doklady Akademii Nauk SSSR) was a Soviet science journal published by the academy of sciences of the USSR.

- The journal covered academic research papers in biology, mathematics, physics, chemistry, and geology.

- It was published from 1933 to 1992 and is continued nowadays by Doklady Akademii nauk by the Russian Academy of Sciences (RAN) (Impact Factor: 0.609)

Translations

- In 1956 the American Institute of Physics began publishing translating "Soviet Physics Doklady", followed by most other sections including chemistry.

- Nevertheless it is often problematic to find the matching English translation journal for articles published in Doklady due to translation errors and incorrect indexing of translated articles.

- One approach to overcome this issue is to search in SciFinder for the original publication, yielding the subject section of Doklady by which one knows in which translation journal the article can be found. The print version of the translated journal provides a table of contents with the page numbers of the Russian original and the translated English version.

Content of this seminar

- Providing a selected overview of Soviet research published and translated in "Doklady Chemistry".

- Setting the focus on selected publications in the field of organic chemistry

- Covering translations ranging from the 1966 to 1990.

Synthesis and Properties of New Phosphorylides (Phosphinemethylene) with Phosphorane-Phosphonium Type Conjugation


New representations of the mechanism of the Wittig reaction

- Mechanism proposed and widely accepted (Speziali et al. J. Am. Chem. Soc., 85(23), 3878 (1963))

- However, this experiment by no means demonstrates reversibility of the first step of the Wittig reaction (and does not contradict a one-step mechanism).
Aryl- and Allyldemetalation of RSnMe₃ in the Presence of Palladium Complexes

\[
R'^{1}\quad +\quad R'^{2}SnMe_3 \xrightarrow{2 \text{ mol}\% \text{(MeCN)}_2PdCl_2} \text{DMF, 20 °C, 1 min - 24 h} \quad R'^{1} + \text{Me}_3SnI \quad R'^{2}\text{SnMe}_3
\]

- no phosphine ligands necessary, in fact, addition of 2 eq. of PPh₃, with respect to Pd-cat. hampered the reaction and much harsher conditions were required (120 - 130 °C)

\[
\text{Br} + R''\text{SnMe}_3 \xrightarrow{24 \text{ h, 94% in acetone}} \text{R''} + \text{Me}_3\text{SnI}
\]

\[
\text{Ph} \quad \text{NO}_2 \quad \text{O} \quad \text{Ph} \quad \text{R''} \quad \text{O} \quad \text{Me}_3\text{SnI}
\]

\[
\text{O}_2\text{N} \quad \text{NO}_2 \quad \text{O} \quad \text{R''} \quad \text{O} \quad \text{Me}_3\text{SnI}
\]

Conversions of Thienopyrillium Salts in Alkaline Medium - A New Way to Synthesize The Thienonaphthene System

\[
\text{Me} \quad \text{OH} \xrightarrow{\text{H}_2\text{O}} \text{Et} \quad \text{CHO}_4 \quad \text{Et} \quad \text{H}_2\text{O} \quad \text{35%}
\]

Synthesis of Aryltrimethylstannanes by the Reaction of Me₃SnSnMe₃ with Aryliodides, Catalyzed by "Ligand-Free" Palladium

Total synthesis of the first representative of A, B-Indolosteroids

HOOC

Me

SnMe₃

MeO

AchN

Cl⁻ · H₂N

HNO₂

Me

Cl⁻ · H₃N

57%

Cl⁻ · ClN₂

50 °C, 80 min, 74%  
20 °C, 15 min, 97%  
20 °C, 15 min, 95%  
20 °C, 10 min, 98%  
20 °C, 5 min, 100%

20 °C, 5 min, 100%  
20 °C, 10 min, 98%  
20 °C, 5 min, 100%  
20 °C, 5 min, 93%

crystallized from a mixture of decarboxylation isomers
A New Reaction of Electrophilic C=C Bonds. Fixation of the Amide Anion, an Intermediate Formed in the Hofmann and Lossen Reactions


\[ \text{RCONH}_\text{X} + B \xrightarrow{-\text{BH}} \text{RCON}_\text{X}^- \xrightarrow{-\text{X}} \text{O=C=N=R} \]

\( X = \text{Hal}, \text{OCOR}^* \)

Hoffman-Lossen reaction

\[ \text{PhCO}_\text{X} + \text{F}_3\text{C-CF}_3 \xrightarrow{\text{F}_3\text{C-CF}_3} \text{PhC(OF)}_2 \text{CF}_3 \xrightarrow{-\text{X}} \text{PhC(OF)}_2 \text{CF}_3 \]

\( X = \text{Cl}, \text{OCOCF}(\text{CF}_3) \)

66%

(1) Perfluoroisobutene (nowadays a schedule 2 substance on the chemical weapons convention and considered to be ten times more toxic than phosgene)

Total Synthesis of Shikalkin


\[ \text{Shikalkin} \]

- high antimicrobial activity
- antitumor activity
- clear anti-inflammatory effects
- rapid healing effects

Total Synthesis of Shikalkin

- High antimicrobial activity
- Antitumor activity
- Clear anti-inflammatory effects
- Rapid healing effects
A New Method of Preparation of Aromatic Fluorine-Containing Compounds (Anodic Substitution of Fluorine for Hydrogen)

Use of Lanthanide β-Diketonates to Increase the Regioselectivity of Organic Reactions
Komarov et al., Doklady Akademii Nauk SSSR, Vol. 313(6), pp. 1465-1467, 1970

- Coordinationally unsaturated tris β-Diketonates of lanthanides can form labile adducts with a wide variety of organic compounds which contain electron-donating moieties.
- This effect is often exploited in NMR-spectroscopy, when paramagnetic lanthanides are added to the NMR sample in order to increase the resolution.

**a)** Shows the H-NMR spectrum of pentane-1-ol without Eu(tmhd)$_3$.
**b)** Shows the H-NMR spectrum of pentane-1-ol with Eu(tmhd)$_3$.[1]

c) Tris(2,2,6,6-tetramethylheptan-3,5-dionato-0,0')europium

d) Tris(7,7-dimethyl-1,1,2,2,3,3-heptafluoroocta-7,7-dimethyl-4,6-dionato)lanthanide

**[1]** Chem Reviews, 1973, 73, 553

**This work's hypothesis:** According to the Pearson concept, Ln(fod)$_3$ prefers hard Lewis bases as adduct partners over soft Lewis bases or other Lewis acids.

*thereby it can be assumed that such hard groups can be protected by means of Ln(fod)$_3$ in the presence of soft groups.*

Dependence of the relative NMR-signal intensities of the aldehyde moiety and the olefinic moiety of the time (min). Left: without the addition of Ln(fod)$_3$. Right: with the addition of an equimolar amount of Ln(fod)$_3$. 
Is it also possible to tolerate an α,β-unsaturated ketone?

\[
\begin{align*}
\text{Citral} & \xrightarrow{\text{H}_2, \text{cat. Pd/C}} \text{O-C-O} \\
\text{Cyclohexane-d12} & \xrightarrow{20 ^\circ C} \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me}
\end{align*}
\]

Dependence of the relative NMR-signal intensities of the aldehyde moiety and the olefinic moiety of the time (min). Left: without the addition of Ln(fod)_3. Right: with the addition of an equimolar amount of Ln(fod)_3.

**Stereoselective Synthesis of 3,4-trans-1,2,3,4-Tetrahydropyridines**

**In-situ preparation of pyridinium-ylids**

\[
\begin{align*}
\text{N} & \text{X} \\
\text{R} & \xrightarrow{\text{EtOH}} \text{N} \\
\text{R} & \xrightarrow{-\text{HNEt}_3} \text{N}
\end{align*}
\]

**Cyanoacetic acid building block**

One-pot procedure

<table>
<thead>
<tr>
<th>R'</th>
<th>R</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONH_2</td>
<td>Ph</td>
<td>59%</td>
</tr>
<tr>
<td>COPh</td>
<td>R' = p-Cl-C_6H_4</td>
<td>97%</td>
</tr>
<tr>
<td>R</td>
<td>Ph</td>
<td>67%</td>
</tr>
<tr>
<td>R = COOMe</td>
<td>R' = p-F-C_6H_4</td>
<td></td>
</tr>
<tr>
<td>R = CSSMe</td>
<td>R' = 3-Py</td>
<td></td>
</tr>
<tr>
<td>R = COPh</td>
<td>R' = 3-Py</td>
<td></td>
</tr>
</tbody>
</table>

79% 54% 94% 92%