Mendeleev 2024

XIII International Conference on Chemistry for Young Scientists

BOOK OF ABSTRACTS

St Petersburg University

BOOK OF ABSTRACTS

XIII International Conference on Chemistry for Young Scientists “MENDELEEV 2024”

St Petersburg, Russia
September 2-6,
2024

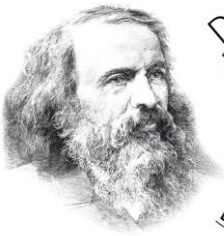
XIII International Conference on Chemistry for Young Scientists “MENDELEEV 2024”. St Petersburg. September 2–6, 2024. Book of abstracts.— St Petersburg.: VVM Publishing LLC, 2024.— 822 p.

ISBN 978-5-9651-1584-6

Book of abstracts contains theses of plenary, keynote, oral and poster presentations which were presented on **Mendeleev 2024**, the XIII International Conference on Chemistry for Young Scientists. The Mendeleev 2024 Conference hold in Saint Petersburg (September 2–6, 2024).

Abstracts are presented in the author's edition with minimal technical corrections.

DEDICATED TO



DECADE OF BICENTURY
190 YEARS SINCE THE BIRTH OF DMITRI IVANOVICH MENDELEEV

300 years Russian Academy of Sciences

300 YEARS of SPbU

@mendeleev.spbu

@Mendeleev_spbu

EXPERIMENTAL STUDY OF «FLIPPING» METALATION OF 4-DIMETHYLAMINOPYRIDINE

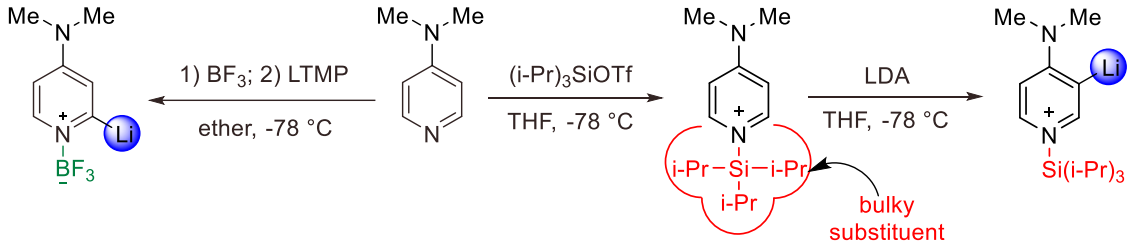
Gubanova A.N.[1], *Verkhov V.A.*[1], *Antonov A.S.*[2]

[1] St. Petersburg State University, St. Petersburg, Russia
[2] University of Regensburg, Regensburg, Germany
Student
st097979@student.spbu.ru

For a long time, it was believed that the metalation of 4-dimethylaminopyridine (DMAP) is possible only in the position 2(6), due to the conjugation of the NMe_2 group with the ring and as a result, the absence of the DOM-effect. It was only in 2006 that DMAP metalation was achieved in the position 3(5) using sterically hindered Caubère's salt [1].

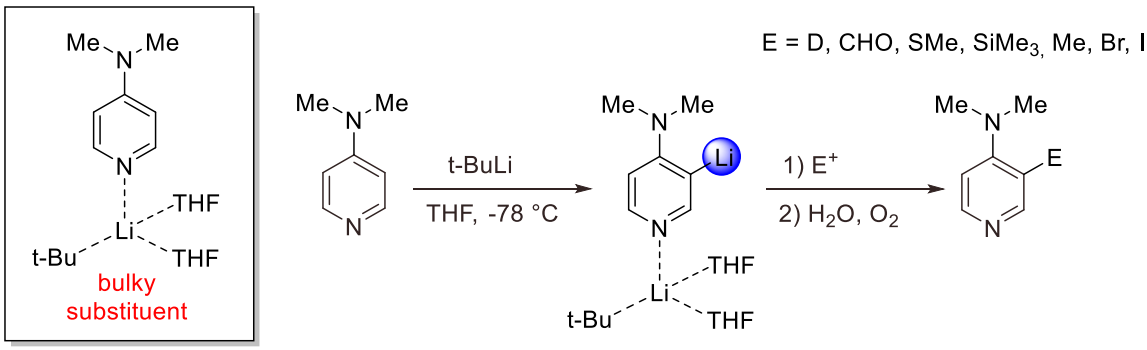
In the early work of our laboratory, it was shown that the introduction of bulky groups leads to a change in the direction of metalation reactions. Thus, the main idea of this work is to study the effect of various substituents on the direction of metalation.

In our work, we have investigated the interaction of the DMAP molecule with weakly nucleophilic organometallic reagents such as lithium diisopropylamide (LDA) and lithium tetramethylpipyridine (LTMP). Usually, these reagents do not react with DMAP. For this reason, the nitrogen atom of the aza group was quaternized by various groups, such as BF_3 and Alk_3Si, to increase the acidity of the CH-bonds. It was found that an increase in the volume of the substituent leads to a change direction of the metalation reaction from positions 2(6) to positions 3(5) (scheme 1).



Scheme 1. Interaction of DMAP and its 1-derivatives with weakly nucleophilic organometallic reagents.

In addition, the interaction of strong base organolithium reagents such as tert-BuLi with DMAP·Me3Si leads to an increase in conversion. Moreover, as theoretical calculations have shown, the organometallic reagent itself coordinates to the aza group and blocks positions 2(6), thus it leads to metalation at position 3(5). This made it possible to obtain a set of different products with high yields (scheme 2).



Scheme 2. Interaction of DMAP with strong nucleophilic organometallic reagents.

References

[1] *Chem. Commun*. **2006**, 2673

Acknowledgements
This work was supported by the Russian Science Foundation (project No 21-73-10040).