

The Laboratory for Organic and Inorganic Chemistry

Final MSc Seminar

Monday, July 3rd at 11:30 in the Seminar Room

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Apeloig Group

On the Topic of:

Synthesis of genuine germenyl lithiums and the first enol germenolate tautomer

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Synthesis of genuine germenyl lithiums and the first enol germenolate tautomer

Enolates are compounds containing an E=C-O⁻ moiety. They can exist as keto (Figure 1, A) and enol (Figure 1, B) tautomers. While organic enolates (E=C) are widely used in industry and academic research, the chemistry of "heavy" enolates (E=Si, Ge, Sn) remains challenging, and only a few examples were published.^{[1][2]} Contrary to organic enolates, most known heavy enolates exist as the keto tautomers. Only two examples of enol-form silanolates were published.^[3] **Germenolates in enol form have not been reported.**

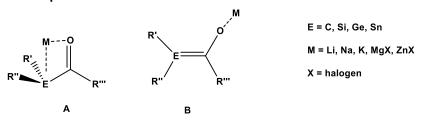
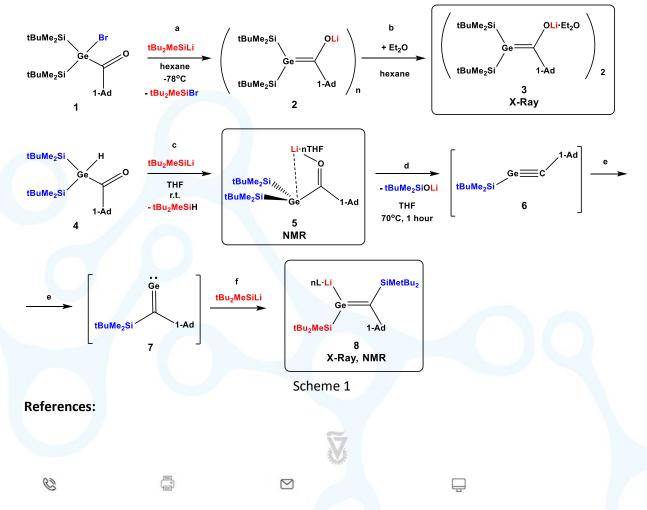


Figure 1. Keto (A) and enol (B) tautomersof enolates

In my MSc research we synthesized and isolated the **first enol-form germenolate**. Moreover, we have demonstrated that this germenolate exists as the enol (**3**) or the keto (**5**) tautomer, depending on the solvent.

Reaction of bromo-acylgermane **1** in hexane at -78°C produces unsolvated germenolate **2** (Scheme 1, step a), which crystallizes upon addition of Et_2O as **enol**-germenolate **3**, while reaction of acylgermane **4** with tBu₂MeSiLi in THF at r.t. yields **keto**-germenolate **5** (Scheme 1, step c).

Elimination of tBuMe₂SiOLi from germenolate **5** (Scheme 1, step d) produces transient germyne **6**, which rearranges to the more stable germylidene **7**, which inserts into the Si-Li bond of tBu₂MeSiLi (Scheme 1, step f), producing the **novel germenyl lithium 8.**^[4] This mechanism is also supported by detailed quantum mechanical calculations.



- [1] I. S. Biltueva, D. A. Bravo-Zhivotovskii, I. D. Kalikhman, V. Y. Vitkovskii, S. G. Shevchenko, N. S. Vyazankin, M. G. Voronkov, *J. Organomet. Chem.* **1989**, *368*, 163–165.
- [2] M. Haas, Chem. A Eur. J. **2019**, 25, 15218–15227.
- [3] R. Dobrovetsky, L. Zborovsky, D. Sheberla, M. Botoshansky, D. Bravo-Zhivotovskii, Y. Apeloig, *Angew. Chemie Int. Ed.* **2010**, *49*, 4084–4087.
- Y. Goldshtein, Y. Glagovsky, B. Tumanskii, N. Fridman, D. Bravo-Zhivotovskii, Y. Apeloig, Angew. Chemie Int. Ed. 2022, 61, e202202452.

