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VI NORTH CAUCASUS ORGANIC CHEMISTRY SYMPOSIUM

BOOK OF ABSTRACTS

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VI СЕВЕРО-КАВКАЗСКИЙ СИМПОЗИУМ ПО ОРГАНИЧЕСКОЙ ХИМИИ
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The book of abstracts of the VI North Caucasus Organic Chemistry Symposium held from 18 to 22 April 2022 at the Faculty of Chemistry and Pharmacy of the North-Caucasus Federal University. Includes lectures of plenary, key-note and invited speakers, as well as oral reports and poster session. The present publication is aimed at popularization of scientific research activity in the field of organic chemistry and to discuss modern chemical problems on the international level. The digest is intended for scientists, students, postgraduates, and a wide range of readers interested in current chemistry problems.

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18-22 APRIL 2022

HALOGEN-LITHIUM EXCHANGE IN 2,4,5,7-TETRABROMO-1,8-BIS(DIMETHYLAMINO) NAPHTHALENE

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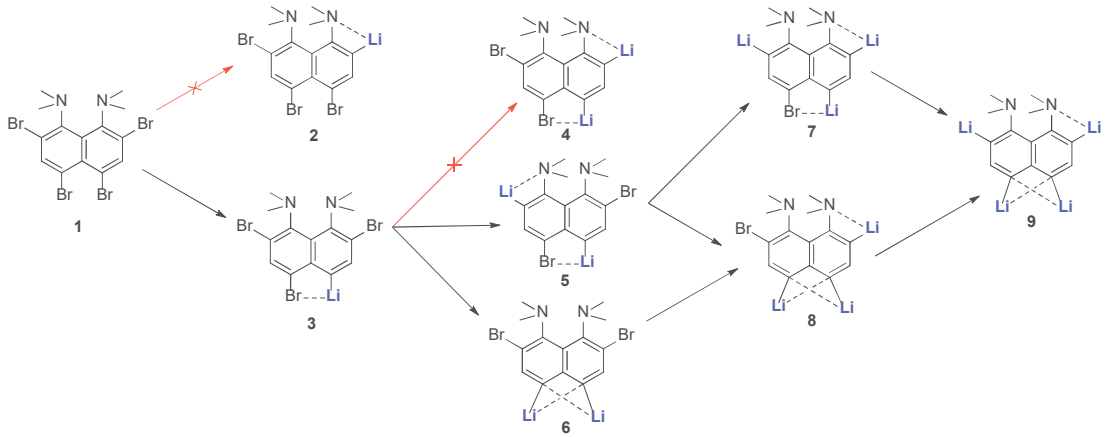
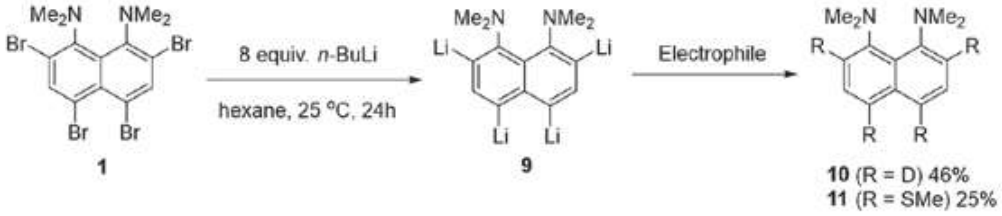
Nowadays organolithium reagents play indispensable role in organic synthesis. Featured by Karl Ziegler, halogen-lithium exchange remains one of the most common ways for the preparation of organolithiums. This phenomenon is well investigated in the benzene series, while multiple halogen-lithium exchanges in the synthesis of naphthyllithiums are much less studied. Thus, the influence of directing groups and the steric strain effects, as well as the possibility of more than two halogen atoms exchange, remain unknown. Here, we present the study on bromine-lithium exchanges in 2,4,5,7-tetrabromo-1,8-bis(dimethylamino)naphthalene **1**, a convenient model compound with different directing situations, a significant steric strain of *peri*-substituents, and the possibility of an exchange of up to four bromine atoms.



Scheme 1

We have shown that step-by-step lithiation proceeds precisely as shown on the Scheme 1. Thus, first exchange occurs in position 4 with formation of **3** due to the significant decrease of a steric strain of the molecule. The second exchange takes place in either position 5 or 7 leading to the formation of the mixture of **5** and **6** due to the more even negative charge distribution in the naphthalene core. As a result, the third exchange leads to the species containing lithium in positions 2,4,7 (**7**) or 2,4,5 (**8**). Using a large excess of n-BuLi in hexane, 2,4,5,7-tetralithio-1,8-bis(dimethylamino)naphthalene **9** was successfully prepared. The latter was used for the synthesis of several tetrasubstituted derivatives of 1,8-bis(dimethylamino)naphthalene by quenching with different electrophiles (Scheme 2).



Scheme 2

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