Mendeleev 2021

XII International Conference on Chemistry for Young Scientists

BOOK OF ABSTRACTS

St Petersburg University

XII International Conference on Chemistry for Young Scientists “MENDELEEV 2021“

St Petersburg, Russia

September 6-10,

2021

ISBN 978-5-9651-1364-4

Book of abstracts contains theses of plenary, keynote, oral and poster presentations which were presented on **Mendeleev 2021**, the XII International Conference on Chemistry for Young Scientists. The Mendeleev 2021 Conference hold in Saint Petersburg (September 6–10, 2021).

Abstracts presented in the original edition

CONTENTS

REGIOSELECTIVE DINITROARENE REDUCTION METHODS: DEVELOPMENT, OPTIMIZATION AND COMPARISON

Maksutova A.I., Tsymliakov M.D., Bezsonova E.N., Zakharova D.V., Tafeenko V.A., Sosonyuk S.E., Lozinskaya N.A.

Moscow State University, Moscow, Russia
Student
anita.maksutova@gmail.com

The regioselective reduction reaction, shown in Figure 1, is highly convenient synthetically while being crucial for obtaining of some substances, which cannot be synthesized otherwise. The information about this reaction in literature is fragmented: most authors report either only 1-2 successfully reduced model compounds per article, or the method is not completely regioselective. Moreover, most methods require expensive reagents, for example noble metals. Both methods, proposed in this work, are far more versatile and highly selective, while being rapid in mild conditions and use only cheap and accessible reagents.

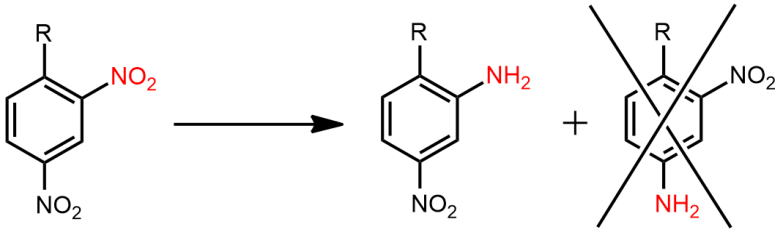

Figure 1. Regioselective dinitroarene reduction (R=Alk, OH, NH_2, Alk_2N, ArNH, BnNH, COOH, Cl).

The method A (Table 1) is versatile and preparative, but problems with isolation upscaling led us to searching for another reducting system. Next, method B was found and studied. Despite the high yields, method B is not entirely multipurpose. High nucleophilic properties of hydrazine somewhat narrow its applicable scope compared to sodium dithionite.

Table 1. Comparison of the condition and results of the two methods.

	Method A	Method B
Reagents; solvent	$Na_2S_2O_4$; H_2O/THF	N_2H_4*H_2O, $FeCl_3$*$6H_2O$, C_{act}; EtOH
Yield	Average at 30-40%, up to 69%	Average at 70-80%, up to 92%

Catalytic and regioselectivity mechanisms were proposed. N-monosubstituted 2,4-dinitroanilines form an intramolecular hydrogen bond with the *ortho*-nitrogroup, which activates the regioselective reduction by withdrawing and rearranging the electron density within a six-membered system. In case of N,N-disubstituted anilines, the ortho-nitro group is out of the plane because of more sterically hindered substituents, which interrupts its conjugation with the aromatic system. Assumptions about regioselectivity were additionally substantiated by single crystal X-ray structural data, obtained in this work. (Figure 2).

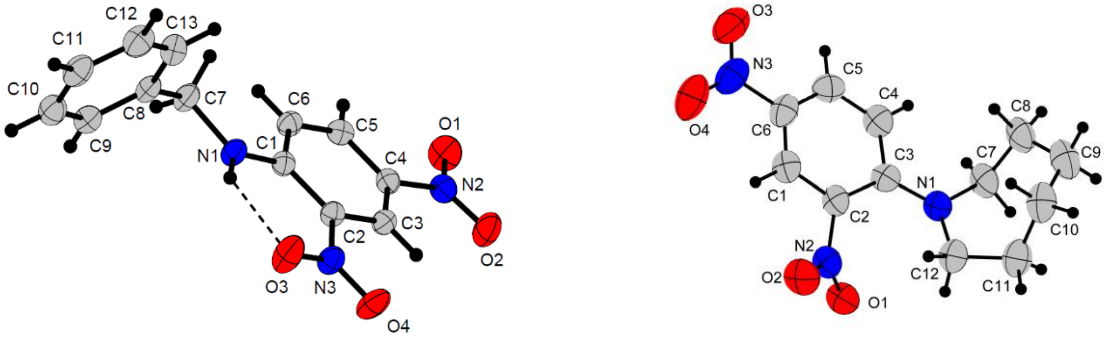

Figure 2. Single crystal X-ray diffraction study of 2,4-dinitro-N-benzylaniline and 1-(2,4-dinitrophenyl)azepane

Thus, two different preparative methods A and B (Table 1) of regioselective reduction were developed in this work. A sheer library of 2-amino-4-nitroarenes were successfully obtained with high to excellent yields.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (Project 20-03-00915).