SYNTHETIC APPROACHES TO SILOXANES AND SILOXANOLS

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INDIAN INSTITUTE OF TECHNOLOGY DELHI

DECEMBER 2023

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by

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Submitted

In fulfilment of the requirements of the degree of Doctor of Philosophy

to the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

DECEMBER 2023

Dedicated to My Family

CERTIFICATE

This is to certify that the thesis entitled ***"SYNTHETIC APPROACHES TO SILOXANES AND SILOXANOLS"*** being submitted by **Ms. Ragini Jain** to the Department of Chemistry, Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. She has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis, which to my knowledge has reached the requisite standard. The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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Acknowledgements

First and foremost, I would like to express my sincere gratitude to Prof. Ravi Shankar for giving me the opportunity to work on this project, providing valuable guidance and feedback, and challenging me to grow as a scientist. He has always been there when I needed his support, reviewing my progress constantly, and guiding me through my Ph. D. studies.

I must thank IIT-Delhi for the award of Institute fellowship which has supported me during my research.

A special thanks to the staff of the Instrumentation Laboratory of Chemistry Department, especially Mr. Narugopal Kuily and Mr. Sandeep Kumar whose dedication and flexibility went a long way in the completion of the work.

I want to thank the former and present Head of Chemistry Department, Prof. Narayanan D. Kurur and Prof. Siddharth Pandey for providing the necessary facilities for carrying out my research work.

I would also like to extend my thanks to Central Research Facility at IIT Delhi and Sonipat campus for sample analysis and characterization data recorded in this thesis. In addition, special thanks are due to Mr. Manjeet and Mr. Manoj Kumar for ^{29}Si *NMR studies. I am highly obliged to Mr. Jitendra, Ms. Aastha and Mr. Shivprakash Solanki for TEM and FESEM analysis.*

I want to give my deepest appreciation to Dr. Nidhi Mahavar who took her time to help teach me Schlenk line operations and offered unlimited support besides unconditional guidance during my initial days as research scholar in the laboratory. She has been always there for discussions about anything that I was unsure on. I also wish to express my warm feelings to my seniors Dr. Ekta Jakhar, Dr. Archishmati Dubey and lab mates, Dr. Priyanka Chauhan and

Aishwarya Chauhan for their well wishes and help. In addition, I would like to mention the assistance of M.Sc. project students, Vinit Kumawat and Azad K. Pandey in discussion and set up of experiments.

I owe a deep sense of gratitude to Dr. Seema Kewat who has offered invaluable advice that will benefit me throughout my life. She gave me the best company in hostel and made my stay memorable. I thank my friends Nancy Varshney, Monika and Kirandeep for making the past 5 years much more enjoyable and keeping me sane throughout the whole process. I am highly obliged to Dharmendra and Rahul for their help and support during the course of this work.

Words fail to express my sentiments for my loving and respectable parents Mr. Rajnish Jain and Mrs. Sandhya Jain. Without their unconditional love, encouragement and continuous support, it would have been impossible for me to arrive where I am today. I deeply thank my paternal grandparents, (D. K. Jain and Chandra Jain) and maternal grandparents (J. K. Jain and Usha Rani Jain) who understood my vision and put their trust in me always. I am grateful to my brother Sushant Jain for standing by my side in difficult times.

Finally, but most importantly, I would like to thank GOD and BK Shivani for providing me the strength to continue moving forward, come what may.

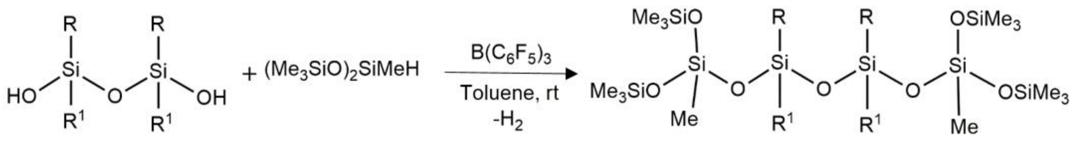
Ragini Jain

Abstract

The study embodied in the present thesis is divided into three sections. Initial studies relate to thiol-ene “click” reactions between appropriate vinyl-substituted cyclic siloxane precursors and thiols to afford functional siloxanes bearing polar organic groups. The affinity of these siloxanes to act as molecular scaffolds for surface-passivation of gold nanoparticles (AuNPs) has been examined in detail. The dispersion of the NPs in aqueous medium act as efficient catalysts for hydrolytic oxidation of organosilanes, R_nSiH_{4-n} (n=1, 2) and provides a viable route to organosilica-AuNP hybrid, organosilanols and disiloxane-1,3-diols.

$$RR^1SiH_2 \xrightarrow[\text{rt}]{\text{AuNP-H}_2\text{O}} (RR^1SiOH)_2O$$

Further, these functional siloxanols are important precursors to study hetero dehydrocoupling reactions between Si−H/Si−OH groups with $B(C_6F_5)_3$ catalyst (Figure 1) as well as O-silylation of Si−OH groups using disilazanes. A significant outcome emanating from this study is the synthesis of well-defined siloxanes with extended chain lengths and their functionalization *via* hydrosilylation approach. The study also demonstrate the utility of $B(C_6F_5)_3$-catalyzed dehydrocoupling between difunctional precursors $(HRR^1Si)_2O$ and $(RR^1SiOH)_2O$ (R, R^1= alkyl/aryl) to afford linear polysiloxanes with different aryl/alkyl substituents on silicon.



R, R^1= Me, Ph; Me, c-Hex; Ph, Ph

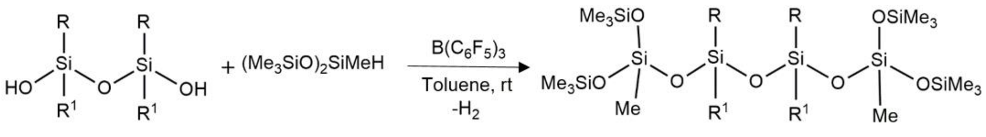
Figure 1. Catalytic synthesis of oligosiloxanes *via* heterodehydrocoupling reaction

शोध सार

वर्तमान थीसिस में सन्निहित अध्ययन को तीन खंडों में विभाजित किया गया है। प्रारंभिक अध्ययन ध्रुवीय कार्बनिक समूहों को प्रभावित करने वाले कार्यात्मक सिलोक्सेन को वहन करने के लिए उपयुक्त विनाइल-प्रतिस्थापित चक्रीय सिलोक्सेन अग्रदूतों और थिओल्स के बीच थिओल-ईन "क्लिक" प्रतिक्रियाओं से संबंधित हैं। सोने के नैनोकणों (AuNP) के सतह-निष्क्रियण के लिए आणविक मचान के रूप में कार्य करने के लिए इन सिलोक्सेन की आत्मीयता की विस्तार से जांच की गई है। जलीय माध्यम में NP का फैलाव ऑर्गेनोसिलेन्स, R_nSiH_{4-n} (n=1, 2) के हाइड्रोलाइटिक ऑक्सीकरण के लिए कुशल उत्प्रेरक के रूप में कार्य करता है और ऑर्गेनोसिलिका- AuNP हाइब्रिड, ऑर्गेनोसिलानोल और डिसिलोक्सेन-1,3-डायोल्स के लिए एक व्यवहार्य मार्ग प्रदान करता है।

$$RR^1SiH_2 \xrightarrow[\text{rt}]{\text{AuNP-}H_2O} (RR^1SiOH)_2O$$

इसके अलावा, ये कार्यात्मक सिलोक्सानोल $B(C_6F_5)_3$ उत्प्रेरक (चित्र 1) के साथ Si−H/Si−OH समूहों के बीच हेटेरो डिहाइड्रोकपलिंग प्रतिक्रियाओं का अध्ययन करने के साथ-साथ डिसिलज़ेन का उपयोग करके Si−OH समूहों के O-सिलिलेशन का अध्ययन करने के लिए महत्वपूर्ण अग्रदूत हैं। इस अध्ययन से निकलने वाला एक महत्वपूर्ण परिणाम विस्तारित लम्बी श्रृंखला के साथ अच्छी तरह से परिभाषित सिलोक्सेन का संश्लेषण और हाइड्रोसिलिलेशन दृष्टिकोण के माध्यम से उनका कार्यकरण है। अध्ययन सिलिकॉन पर विभिन्न एरिल/अल्काइल प्रतिस्थापन के साथ रैखिक पॉलीसिलोक्सेन को वहन करने के लिए डिफंक्शनल अग्रदूतों $(HRR^1Si)_2O$ और $(RR^1SiOH)_2O$ (R, R^1= एल्काइल/एरिल) के बीच $B(C_6F_5)_3$-उत्प्रेरित डिहाइड्रोकपलिंग की उपयोगिता को भी प्रदर्शित करता है।



R, R^1= Me, Ph; Me, c-Hex; Ph, Ph

चित्र 1. हेटेरोडाइड्रोकपलिंग प्रतिक्रिया के माध्यम से ऑलिगोसिलोक्सेन का उत्प्रेरक संश्लेषण

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	percent
δ	chemical shift
ν	frequency
℃	degree centigrade
AuNPs	gold nanoparticles
ATRP	atom transfer radical polymerization
b.p.	boiling point
m.p.	melting point
ESI	electrospray ionization
FESEM	field emission scanning electron microscopy
FT	fourier transform
GPC	gel permeation chromatography
h	hour
min	minute
i.e.	that is
IR	infrared
m	multiplet
br	broad
PDI	polydispersity index
Ph	phenyl
Pd	palladium
Ag	silver
MHz	mega hertz
kHz	kilo hertz
rt	room temperature
TEM	transmission electron microscopy
t-Bu	*tert*-butyl
cHex	*cyclo*-Hex
cm	centimeter
$CDCl_3$	deuterated chloroform
CD_3OD	deuterated methanol
dmso-d_6	deuterated dimethyl sulfoxide
DLS	dynamic light scattering
e.g.	for example
s	singlet
t_R	retention time
m/z	mass/charge
M^+	molecular ion
Me	methyl
ml	millilitre
mmol	millimol
M_n	number average molecular weight
nm	nanometer
NMR	nuclear magnetic resonance
T_g	glass transition temperature
TGA	thermogravimetric analysis
THF	tetrahydrofuran
wt	weight
UV	ultraviolet
µm	micrometer
DMAEMA	2-(dimethylamino)ethyl methacrylate
SEM	scanning electron microscopy