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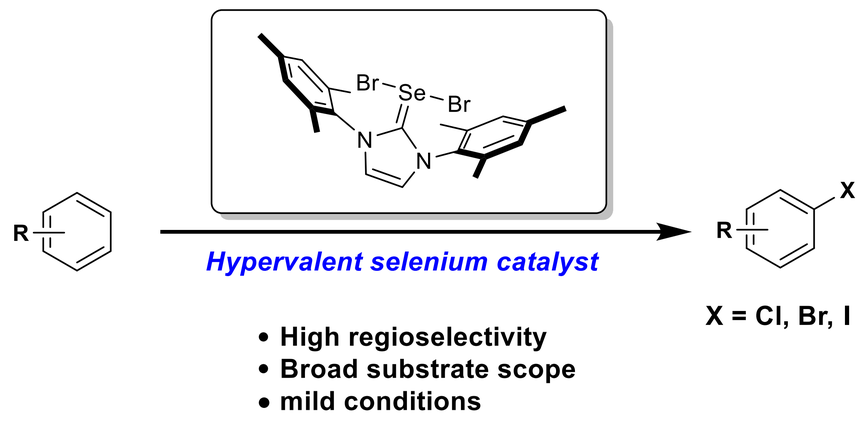
Study on the mechanism of chalcogen catalysts in halogenation reactions

Huang, Jingxian, Yeung, Ying-Yeung*
Department of Chemistry, The Chinese University of Hong Kong

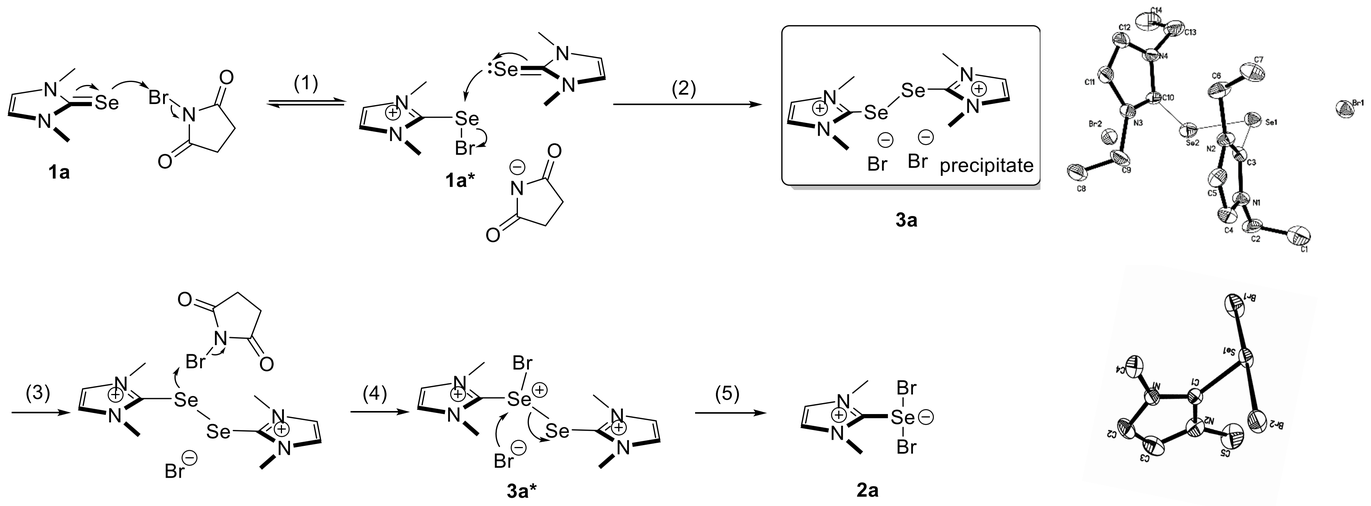
Abstract

Lewis base organocatalysts are widely used to improve the reactivity for N-Haloamide reagents, among which imidazole-2-selenone has shown its ability to achieve mild reaction conditions and excellent functional groups. However, the reaction mechanism remains unclear. The Lewis base imidazole-2-selenone catalyzed bromination reaction has been studied in this research. It was found that the hypervalent selenium was in situ generated and it was found to be the active catalytic species for the reactions.

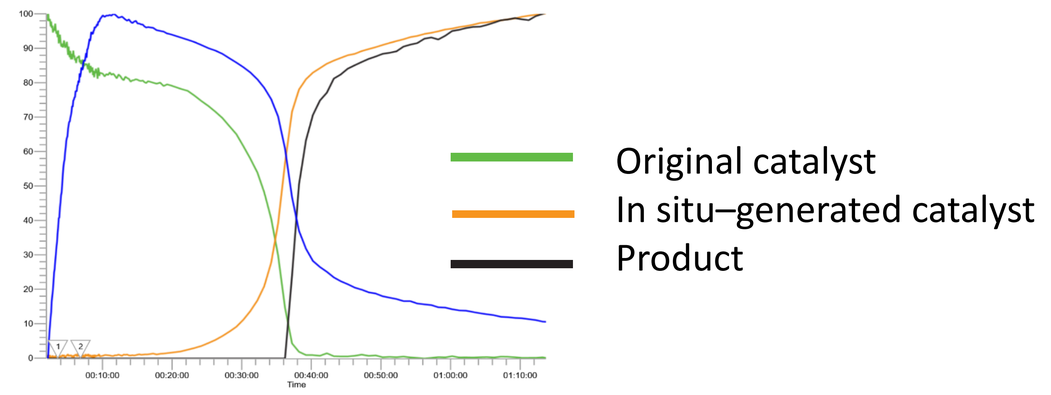


Mechanism study

According to the spectroscopic and crystallographic studies, it is believed that imidazole-2-selenone could be brominated to in situ generate dibromoimidazoleselone, which could then activate N-bromosuccinimide in the electrophilic halogenation reactions.



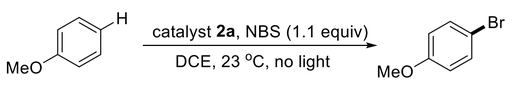
Mechanism study



The original catalyst was consumed from the beginning, but the brominated product was not detected. A new signal was observed upon the consumption of imidazole-2-selenone. After experimentations, the new signal was found to be dibromoimidazoleselone. This in situ generated species was found to be the actual active catalyst.

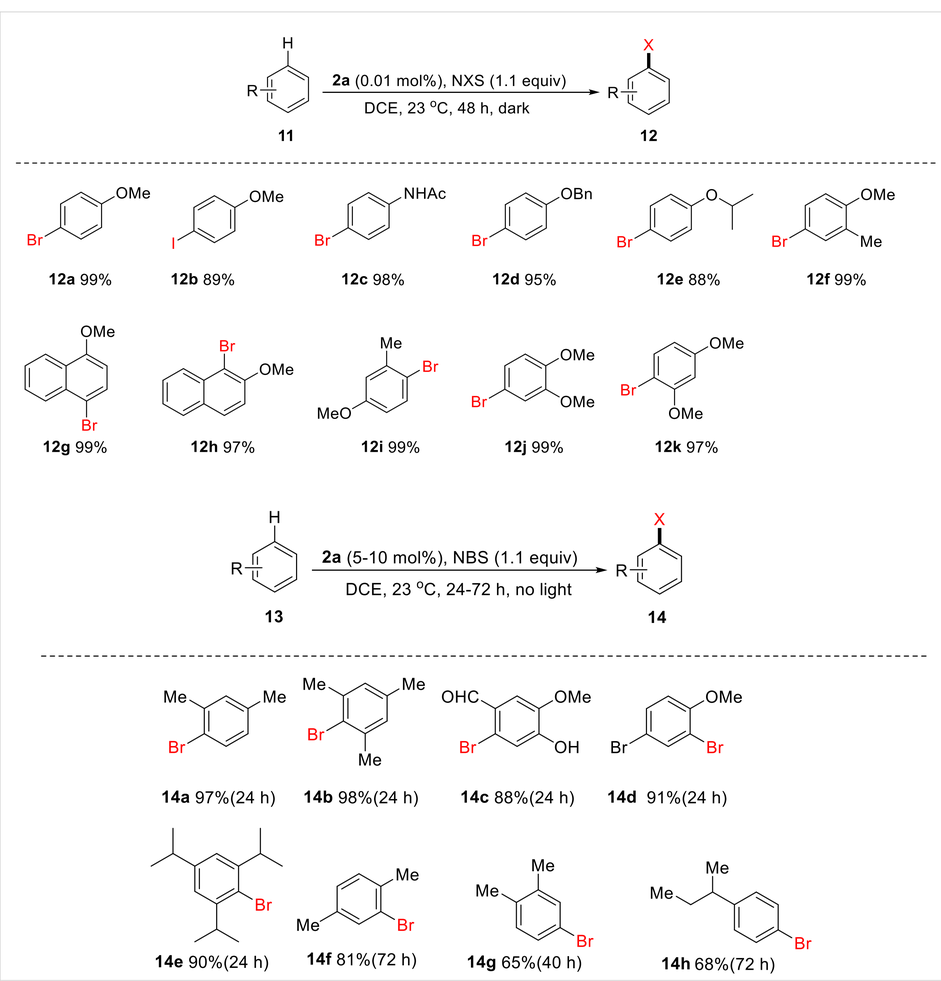
Condition screening

High product yields were still obtained even when the catalyst loading was adjusted to 0.01 mol%.

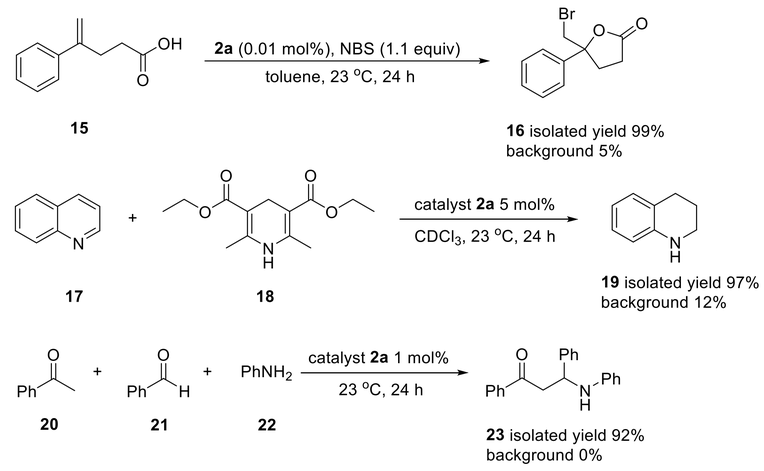


entry	catalyst	loading	time	yield[b]
1	-	-	24 h	0%
2	**2a**	0.05 mol%	24 h	99%
3	**2a**	0.02 mol%	48 h	100%
4	**2a**	0.01 mol%	48 h	97%
5	**2a**	0.01 mol%	72 h	98%

Aromatic halogenation



Catalyst ability



Conclusions

We have developed a highly efficient halogenation catalytic protocol. The efficiency is high and the reaction conditions are mild. Mechanistic studies suggested that the hypervalent selenium catalyst is responsible for the high catalytic efficiency in the reactions.

Acknowledgments

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Contact information

Huang, Jingxian (1155149672@link.cuhk.edu.hk), Yeung, Ying-Yeung* (yyyeung@cuhk.edu.hk)