Experimental and Computational Study of Umpolung N-Bromoamines; Organocatalytic Bromination of Olefins

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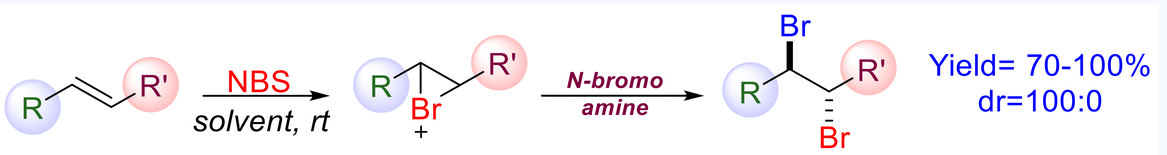
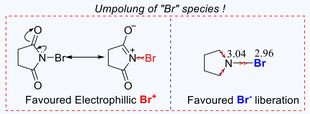
Abstract: ***N-bromoamines are the resultant of quick exchange between the cationic bromine souce (NBS) and amines. An unprecedented study of change in polarity (umpolung) of Br from NBS to N-bromoamines were supported by both experimental and computational data. Further, its application has been extended towards the bromination of various substituted olefins. This one-pot organocatalytic bromination protocol, is comparatively efficient as compared to conventional methodologies owing to the umpolung behaviour.***

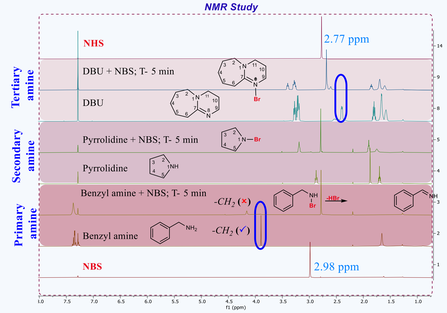


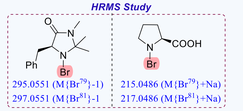
1. Introduction:

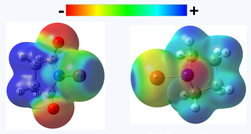
- "Umpolung" of cationic Br species has been achieved organocatalytically and implemented in an accelerated dibromination of inactivated olefins.
- An alternative to the conventional bromination methods such as; a) Br_2, b) Carrying agents supporting Br_2, c) Insitu generation of Br_2.



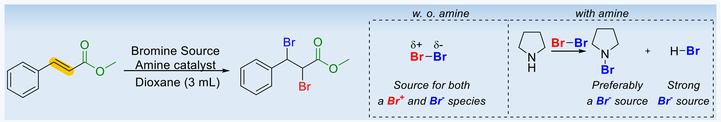
2. Experimental and Computational Evidence of N-Bromoamines:







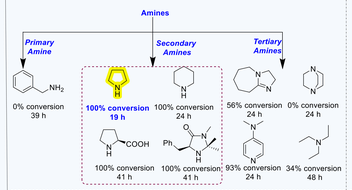
3.1. Experimental Evidence of Umpolung 'Br' in dibromination reaction:



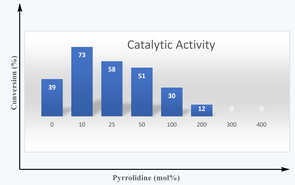
Sluggishness of reaction in presence of amine !!

Sl. No	Br Source (mol%)	Pyrrolidine (mol%)	Time (h)	Conversion (%)
1	NBS (200)	-	158	84
2	NBS (200)	50	74	74
3	NBS (300)	50	19	100
4	NBS (500)	50	12	100
5	Br_2 (100)	-	79	66
6	Br_2 (100)	100	78	18
7	NBS (100) HBr (100)	-	17	83

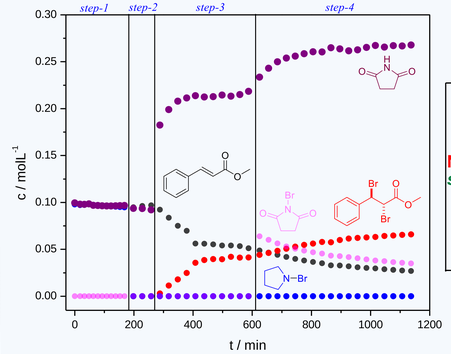
3.1. Amine Screening:

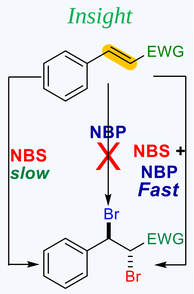


3.2. Catalyst Loading:

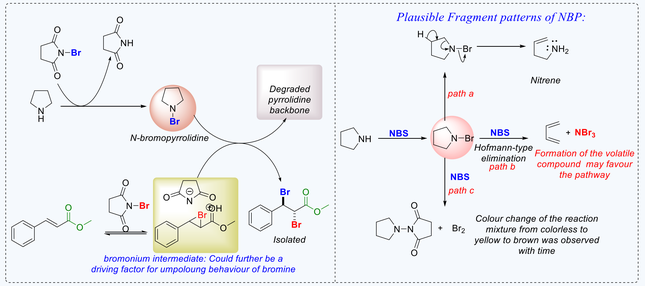


4. Elementary Steps via Control Experiment



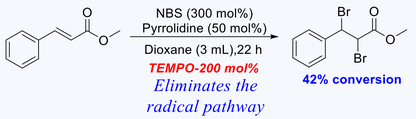


5. Mechanistic Interpretation:

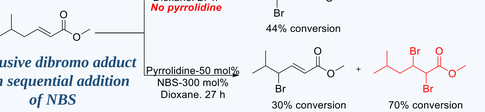


6. Control Experiment in Support of Mechanism:

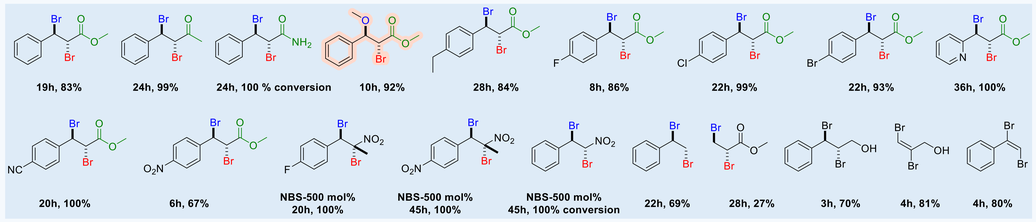
A. Ionic pathway Vs. Radical Pathway :



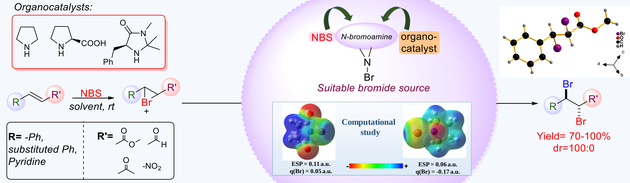
B. Allylic Bromination Vs. Dibromination:



6. Substrate Scope



7. Conclusion:



8. References

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2. ***Computational work was done in collaboration with Dr. H.K. Biswal, NISER Bhubaneswar.***
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