

Weak Interactions in Carbon-Hetero Atom Bond Forming Reactions

Anima Bose*^a and Prasenjit Mal*^b^aDepartment of Chemistry, Ravenshaw University, Cuttack, 753003, Odisha^bSchool of Chemical Sciences, National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar, PO Bimpur-Padanpur, Via Jatni, District Khurda, Odisha 752050, India.

Email: pmal@niser.ac.in

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Abstract

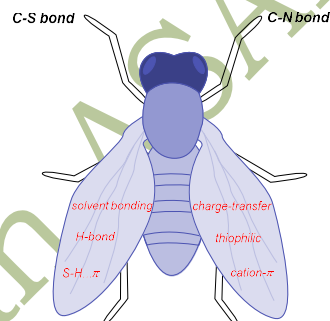
Controlling various reactions by multiple weak interactions or soft forces has become an widespread topic under supramolecular catalysis. This review has made a literature collection that explores cooperative weak or noncovalent interactions. These are charge transfer complexation, H-bonding, S-H... π , acid-base, cation- π , etc., towards C-hetero bond formation reactions. This review article will discuss the specific reactivity of chemical systems controlled by weak interactions.

Keywords: C-N bond formation; C-S Bond formation; Metal-free; Soft forces; Weak Interactions

1. Introduction

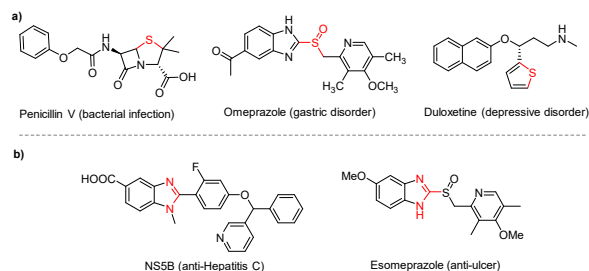
The development of the system chemistry approach on small molecules¹⁻² has become popular research topics that help to understand chemical reactions' complexity. Numerous chemical reactions are controlled by the proper use of noncovalent or weak interactions.³⁻⁵ The soft forces⁶ like charge transfer complexation,⁷ H-bonding, S-H... π ,⁸⁻⁹ acid-base,¹⁰⁻¹¹ cation- π ,^{7, 12-13} anion- π ,¹⁴ hydrophobic effect,¹⁵ etc., play a significant role in understanding the chemistry of life. The development of new materials with suitable functionality is achievable by choosing appropriate supramolecular interactions or a system chemistry approach. The systems chemistry approach delivers fundamental understandings into the self-assembly and self-sorting principles of molecular systems to design newer functional molecules.¹⁶ Thus, it becomes a popular approach in building complex molecules with high-purity from mixtures of starting components by fewer reaction steps. On the other hand, the accomplishment of system chemistry of small molecules in organic synthesis is less explored.¹⁷⁻¹⁸

Nitrogen and sulfur are essential elements of living systems.¹⁹ The nitrogen and sulfur-containing organic compounds are abundant in numerous non-natural and natural products, agrochemicals, pharmaceuticals, pesticides, medicines, and materials.²⁰⁻²³ Many sulfur-containing drugs are used regularly in day-to-day practice



Weak Interactions in C-Hetero Bond Formations

(Scheme 1).²⁴⁻²⁵ Amongst the many known carbon-nitrogen (C-N) and carbon-sulfur (C-S) bond formation reactions, cross-coupling reactions *via* transition-metal catalysis are the most convenient.²⁶⁻²⁸ However, these methods are often associated with several shortcomings like post-reaction contamination of harmful heavy metals, high catalyst loading, etc. Therefore, various sustainable strategies, including photocatalysis,²⁹⁻³⁰ metal-free transformations,³¹ etc., have been documented in the literature. In this review article synthesis of C-N and C-S bonds has been discussed with particular importance to weak interactions and supramolecular catalysis.³²⁻³⁶

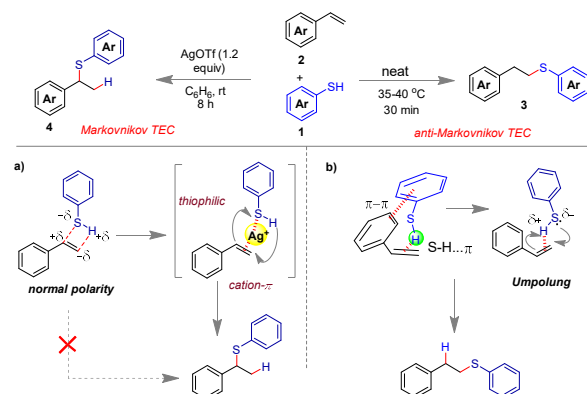


Scheme 1. Selected examples of a) C-S and b) C-N bond containing drugs.

2. Review

2.1 Hydrogen Bonding (H-bonding) as Reaction Controller

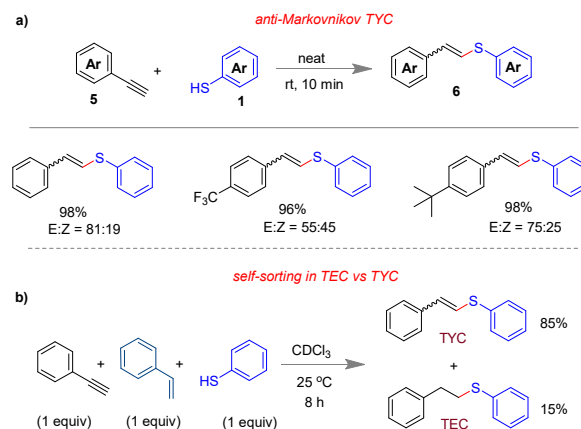
TEC by S-H... π H-bonding. S-H... π interaction or S-H... π H-bonding is one of the latest additions to the family³⁷⁻³⁸ of noncovalent interactions³⁹ used to control various chemical reactions.⁴⁰ However, organic synthetic research areas using S-H... π interaction still in their infancy. Mal and coworkers successfully demonstrated the selective synthesis of *anti*-Markovnikov or Markovnikov selective Thiol Ene Click (TEC) products (Scheme 2). The *anti*-Markovnikov selective thioethers **3** were obtained from neat mixing of styrenes **2** and thiophenols **1** at 35-40 °C (Scheme 2b).⁹ Conversely, when silver triflate was used as an additive, the reaction was switched entirely to the Markovnikov-selective products **4**. Authors proposed that silver(I), prompted cation- π and thiophilic interactions cooperatively dominated over S-H... π H-bonding to obtain the Markovnikov-selective products (Scheme 2a).



Scheme 2. System chemistry approach.⁹ Mechanism for a) Markovnikov selective and b) *anti*-Markovnikov selective TEC reaction.

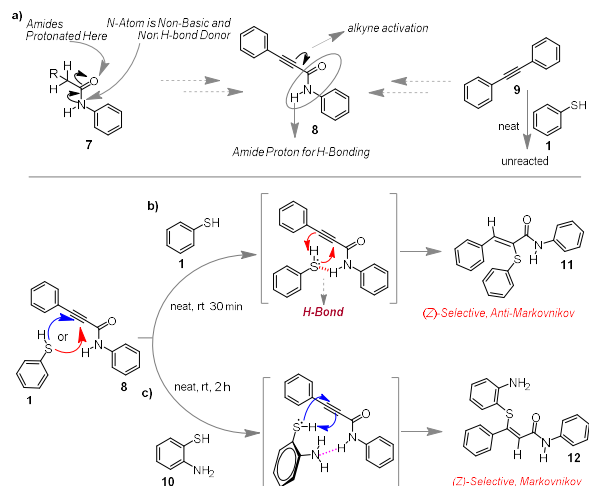
TYC via S-H... π H-Bonding. The Thiol-Yne-Click (TYC) or alkyne hydrothiolation reaction is one of the most encouraging C-S bond-forming reactions practiced in synthesis.⁴¹ Mal and coworkers extended their methodology using S-H... π H-bonding interactions to establish TYC reaction between phenyl acetylenes **5** and thiophenols **1** with exclusive *anti*-Markovnikov selectivity. The hydrothiolated products **6** were selectively synthesized under catalyst, additives, and solvents-free conditions (Scheme 3a).⁸ They have shown that S-H... π H-bonding and the π - π stacking among the aromatic rings helped to control the reaction. They had also established the concept of self-sorting⁴²⁻⁴⁴ when the components like phenylacetylene, styrene, and thiophenol reacted in one pot (Scheme 3b). The ethynyl (triple bond)-H

responded more rapidly over the vinyl (double bond)-H hydrogen bond due to the stronger preference of S-H... π interaction. Therefore, the TYC reaction dominated (yield 85%) than the TEC (yield 15%) reaction. This simple approach on TYC reaction helped to synthesized a series of vinyl sulfides with good yields, however, the products were isolated as combination of *-Z* and *-E* isomers.

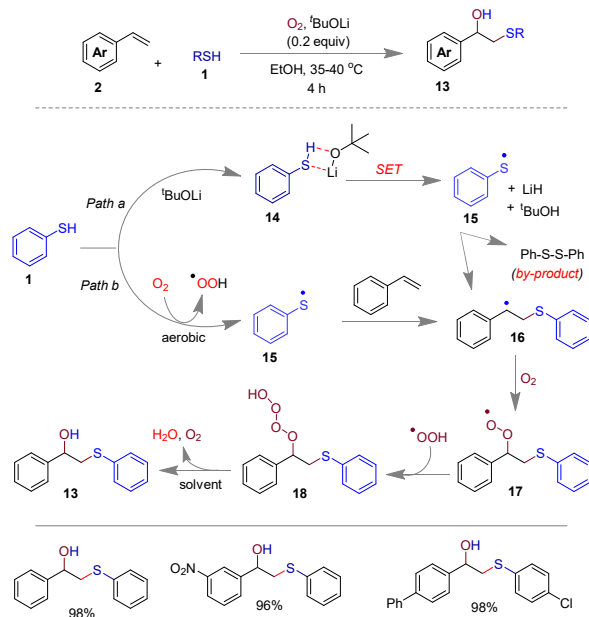


Scheme 3. a) The *anti*-Markovnikov selective TYC reaction.⁸ b) Concept of self-sorting in TEC vs. TYC.

TYC Reaction via Amide Hydrogen Bond Control. Mal and coworkers overcame the stereoselective issues⁴⁵ on the alkyne hydrothiolation reactions of internal alkynes.⁴⁶ The oxygen atom in enolizable carbonyls of **7** makes amide nitrogen non-basic. Therefore, the amide N-H hydrogens do not prefer to form any H-bonding. The diphenyl acetylene **9** (internal alkyne) was reported to be unreactive with thiophenols upon neat mixing (Scheme 4a).⁴⁶ However, incorporating an amide functionality next to the alkyne group activated the alkyne and made the N-H hydrogen available for hydrogen bonding. The compound *N*,3-diphenylpropionamide **8**, was activated by the amide hydrogen, acting as a directing group. The *anti*-Markovnikov (*Z*)-selective products **11** were obtained exclusively from internal alkynes **8** and thiophenols **1** (Scheme 4b). Probably, N-H...S hydrogen bonding amongst N-H and S- of thiophenol could regulate the regioselectivity. However, the (*Z*)-selectivity of **8** was conserved because of the C-H...O and N-H...S hydrogen bonding interactions. On the other hand, switching of selectivity from *anti*-Markovnikov to Markovnikov vinyl sulfide was observed with *ortho*-amino thiophenol **10**. Here, the Markovnikov product **12** was observed due to the higher preference of N-H...N between -NH₂ and S-H over N-H...S hydrogen bonding (Scheme 4c).⁴⁶ Overall, the reactions were performed under solvents and additive-free conditions to obtain the selective products of choices within a system.



Scheme 4. a) The amide hydrogen bond in the (Z) -selective b) *anti*-Markovnikov or c) Markovnikov TYC reactions.⁴⁶

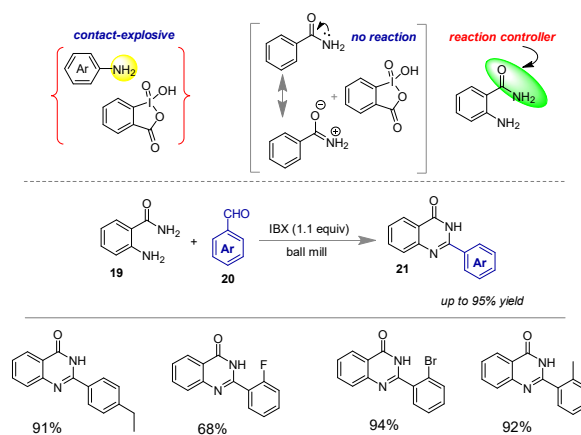


Scheme 5. Mal's approach for β -hydroxy sulfenylation using $^t\text{BuOLi}$ as radical initiator.⁹

Mal and coworkers also showed the preparation of β -hydroxy sulfides **13** by using styrene derivatives **2** and thiophenols **1** in ethanol solvent using $^t\text{BuOLi}$ as a radical initiator⁴⁷ (Scheme 5).⁹ Both $^t\text{BuOLi}$ and molecular oxygen acted as the promoter for the formation of thiyl radical. The catalyst $^t\text{BuOLi}$ could bind with $-\text{SH}$ of thiophenol *via* the complex **14** in EtOH, to generate the thiyl radical. Next, the thiyl-radicals attacked the styrene to offer stable benzylic-radical intermediate **16**. Then aerial dioxygen insertion on **16** might have produced the radicals **17** or **18**, responsible for forming β -hydroxy sulfides **13**.

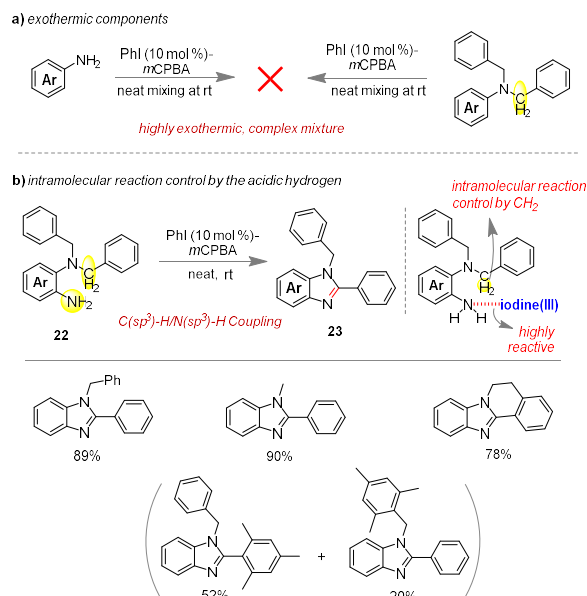
2.2 Intramolecular Amine-Iodine Reaction Control

Mal and coworkers reported an explosion of λ^5 -iodine reagent IBX⁴⁸ with aniline derivatives like *p*-toluidine and *p*-anisidine, when directly mixed under solvent-free conditions. Nevertheless, no reaction was observed amongst IBX and benzamide. They wisely designed compound **19** with an amide group *ortho*- to the $-\text{NH}_2$ group that possibly controlled the reaction. The reaction amongst 2-amino benzamide **19** and aryl aldehydes **20** was successfully performed under solvent-free ball-milling conditions using the IBX to obtain the quinazolin-4(3H)-ones **21** (Scheme 6).⁴⁹ The methodology was highly efficient with a wide substrate scope.



Scheme 6. Taming the reactivity iodine(V) reagent IBX with the amines.⁴⁹

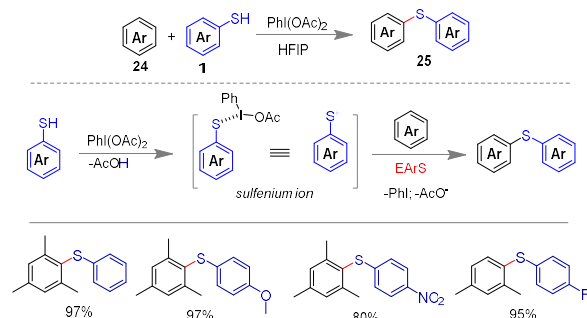
Mal and coworkers showed an organocatalytic method of controlling a very exothermic reaction of polyvalent iodine reagents with primary amines.⁵⁰ An *ortho*- tertiary amine group of aniline **22** helped to control the amine basicity towards acidic iodine reagents. The acidic methylene protons were the reaction controller for the acid-base amine-iodine reactions. The successful synthesis of benzimidazoles **23** are shown in the Scheme 7. They demonstrated a dehydrogenative acidic $\text{C}(\text{sp}^3)\text{-H}$ functionalization in a C-H imination reaction *via* $-\text{[4H]}$ elimination. The organocatalytic condition was accomplished using PhI (iodobenzene, 10 mol %)–*m*CPBA⁵¹ at room temperature conditions which generates the iodine(III) reagent *in situ*.



Scheme 7. a) Exothermic and uncontrollable reaction from the amines. b) Successful synthesis of the benzimidazoles.⁵⁰

2.3 Iodine(III) Reagents in Aromatic C-H Sulfonylation Reaction

Mal and coworkers described a dehydrogenative aryl C-S coupling method from the combination of arenes **24** and thiophenols (**1**) via sulfenium ion intermediate.⁵² Electrophilic sulfenium ions⁵³⁻⁵⁴ were generated *in situ* from thiols with hypervalent iodine reagent PIDA or PhI(OAc)₂ as the sole oxidant in hexafluoroisopropanol (HFIP)⁵⁵ and successively used for aromatic electrophilic substitution (EArS) with arenes to synthesized the C-S coupled products **25** (Scheme 8).⁵²

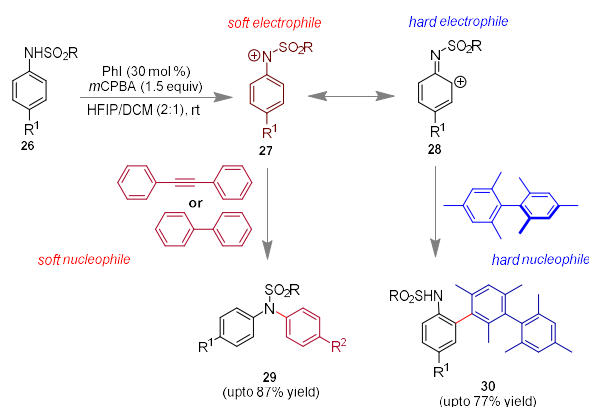


Scheme 8. Dehydrogenating C-S coupling using iodine(III) reagent PIDA.⁵²

2.4. Hard-Soft Acid-Base (HSAB) Control

Mal and coworkers reported the *N*-arylation of sulfonanilides by implementing the HSAB (hard-soft-acid-base) principle.¹¹ Nitrenium ions⁵⁶⁻⁵⁹ are soft, and carbenium ions^{10, 60-61} are

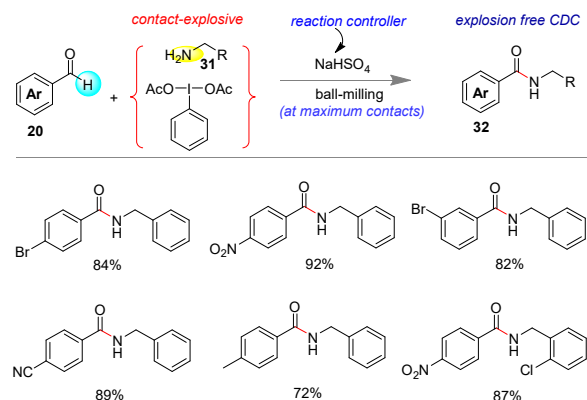
hard electrophiles in nature. Similarly, they considered the -alkyl or -alkoxy substituted arenes as hard and extended π -conjugated systems as soft nucleophiles. Due to soft-soft preference, biphenyl or diphenylacetylene led to the EArS through nitrenium ion. The authors validated the HSAB principle with bimesityl to isolate the product **30**. They described the intermolecular C-N bond formation by *in situ* generations of hypervalent iodine(III) reagent from PhI-mCPBA (Scheme 9).¹¹



Scheme 9. Mal's approach on *N*-selective arylation.¹¹

2.5. Reaction Control by External Influences

No explosion was reported when contact-explosive iodine(III) reagent PIDA and primary amine were grinded together under solvent-free mechanochemical conditions. The reaction produced CDC (cross dehydrogenative coupling) products from amines and aldehydes.^{48, 62-63} The reaction controller was the acid-salt NaHSO₄ (sodium bisulfate).⁷ Thus, highly exothermic amine-iodine(III) reaction control was demonstrated by choosing suitable additives. The acid-salt NaHSO₄ helped to control basic amine's reactivity to obtain CDC products **32** (Scheme 10).



Scheme 10. The acid-salt NaHSO₄ in an explosion-free CDC form iodine(III) reagents and amines with aryl aldehydes.⁷

3. Conclusions

In conclusion, herein, we have collected the literature to prescribe many efficient pathways to make desirable functional molecules using weak cooperative interactions. We hope this review will be a unique addition to supramolecular catalysis.⁵ Also, the research area of C-S and C-N bond constructions using weak interactions will be an important contribution in chemistry by bridging areas like supramolecular catalysis and heterocycle synthesis. So, reactions of several unactivated or inert reaction systems will be performed easily at ambient conditions by choosing suitable substrates.

4. Acknowledgements

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5. Notes and References

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6. About the author(s)

Anima Bose was born in 1989 in Odisha, India. She obtained her M. Sc. degree in 2011 from Utkal University (India). In 2014, she moved to the National Institute of Science Education and Research (NISER), Bhubaneswar, India



to start her doctoral studies under Prof. Prasenjit Mal on 'Peroxide promoted C-X (X = -O, -N) bond synthesis'. She obtained her PhD degree in 2019, and currently, she is working as a visiting faculty at Ravenshaw University, Odisha, India. Her research interest includes metal-free sustainable organic synthesis, hypervalent iodine chemistry, mechanochemistry, and organocatalysis.

Prasenjit Mal was born at Lokhesole, Bankura, West Bengal, India. He obtained his MSc degree from the Indian Institute of Technology Kharagpur and a PhD at the Indian Institute of Technology Kanpur in 2005. Then he undertook postdoctoral studies at the University of Siegen in Germany as Alexander von Humboldt Fellow (2006-2007) and at the University of Cambridge in the UK as Marie Curie Fellow (2008-2009). He started an independent research career at NISER Bhubaneswar in December 2009. His research is focused on supramolecular catalysis in organic chemistry.



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