SUMMARY

- The pentafluorophenyl radical and halobenzene radical cation

In this thesis, we report here first time the analysis of the pentafluorophenyl radical (2.6) generated by the photolysis of matrix-isolated precursors such as iodopentafluorobenzene (2.1), bromopentafluorobenzene (2.2), 2,3,4,5,6-pentafluorobenzoic peroxyanhydride (2.3), and 1,2-bis(2,3,4,5,6-pentafluorophenyl)diazene (2.4) or by flash vacuum pyrolysis of its precursors and subsequent trapping of the products at cryogenic temperatures in inert gas matrices. Pulse pyrolysis at a higher temperature of iodopentafluorobenzene (2.1) leads to the formation of \( \alpha \)-benzyne (\( \alpha \)-C\(_6\)F\(_4\), 2.7) along with other decomposition products as well as radical 2.6 confirmed the F atom generation in pyrolysis, which is still unknown to the literature.

Rare gas discharge (Argon, Neon) irradiation on the halobenzene precursor 2.1 and 2.2 to generate the pentafluorophenyl cation 3.7 instead gives radical cation of halobenzene 3.8 and 3.9 respectively through ionization which is confirmed with literature value. The interaction between the pentafluorophenyl radical (2.6) and oxygen resulted in the formation of pentafluorophenylperoxy radical (2.21). The radical 2.6 is a very reactive species and rapidly reacts with CO to give pentafluorobenzoyl radical (2.24), which can be isolated and spectroscopically characterized in an argon matrix. On irradiation of matrix-isolated 2.24, it forms back the radical 2.6 and CO but as soon as the radical produce it reacts with already formed CO\(_2\) to generate the benzoate 2.13 confirming the photolability.

Chart 1. Pentafluorophenyl radical and its reaction, halobenzene radical cation.
• The phenylethynyl radical

The phenylethynyl radical (4.4) represents a carbon radical with unpaired electron occupies a hybrid $sp$ orbital. The radical generation was carried out by the photolysis as well as pyrolysis of the (iodoethynyl)benzene (4.1), 1,4-diphenylbuta-1,3-diyne (4.2), and 3-phenylpropionic peroxanhydride (4.3). Characterization of the radical through IR spectroscopy was difficult as it is highly reactive although the formation of phenyl acetylene as well as the other decomposition product as an intermediate confirmed the radical 4.4 generation in the matrix after pyrolysis. Previously studied photolysis experiment on 1,4-diphenylbuta-1,3-diyne (4.2) confirms the generation of radical cation 4.15 by EPR spectroscopy. IR spectrum of photolysis product of matrix isolated 4.2 combined with annealing experiment confirms the formation of at least two types of compound. One of this unknown product could be due to the formation of radical cation 4.15 as a theoretical spectrum of 4.15 matched very well with the experimental spectrum. Additionally, we could not exclude the possibility of formation of phenylethynyl radical (4.4) due to peaks in C≡C stretching region of the IR spectrum. Only few experiment on 3-phenylpropionic peroxanhydride (4.3) precursors were done, and finding the deposition condition for 4.3 was difficult as it is easily decomposed. It will be an appropriate precursor for the generation of the radical once the deposition condition is improved. From our experiment in matrix isolation till now, it was difficult to confirm the radical formation in matrix isolation via IR spectroscopy.

Chart 2. Phenylethynyl radical generation.

• Noncatalyzed azide-alkyne cycloaddition (In Prof. Igor Alabugin group)

The investigation of alkynyl radical made my research deepen into pure organic synthesis in the group of Prof. Igor Alabugin where we tried to synthesize strained cyclooctyne for the non-catalyzed azide-alkyne cycloaddition. Analogous to 5.3, unlike the halogenated system, 5.2 were
first prepared via double Mitsunobu reactions in high yield, although synthesis of 5.3 via a similar scheme doesn’t give product due to the stereochemistry of bromine which doesn’t permit ring cyclization.

We used another approach for the synthesis of 5.3 via S_N2 reaction using Cs_2CO_3 as a base. For the first series of experiment, 5.2 was prepared by reacting catechol 5.9 either with 5.16 or with 5.17, in high yield. An analogous experiment performed to synthesize 5.3 by reaction of catechol 5.9 with 5.18 or with 5.19. In a three month of research in the group of Igor Alabugin, we succeeded to synthesize the precursor for the generation of the cyclic 8-membered alkyne, and with a slight investigation on the precursor with a various reagent, we already knew the generation of cyclic alkyne as an intermediate based on the reaction products.


- **Magnetically bistable arylcarbene**

  The singlet-triplet gap in carbene can be lowered by introducing electron donating substituent in the para position of phenyl ring or also with the strongly electron-withdrawing group -CF_3. Thus, we have shown that p-tolyl(trifluoromethyl) carbene (6.10), as well as 2-
fluorenyltrifluoromethylcarbene (6.13), are the structurally simplest carbene that shows magnetic bistability under the conditions of matrix isolation by IR, UV-vis, and EPR spectroscopy.

Carbene 6.10 and 6.13 was investigated in different matrices (Ar, Ne, N₂) at cryogenic temperatures showing the peculiar characteristics that both its lowest energy singlet and triplet state coexist indefinitely at 3 K. Warming of matrix above 10 K, results in a partial conversion of triplet to singlet, which is not reversible by cooling back to very low temperatures (3 K) as observed by EPR, IR and UV-vis spectroscopy. Irradiation at 450 nm results in an increase of singlet and decrease of the triplet, whereas 365 nm irradiation shifts the photostationary equilibrium towards Triplet. The bi-stability of both the carbene 6.10 and 6.13 can be attributed to the energetic degeneracy of the singlet and triplet state.


- **Mechanochemistry**

Considering Enediynes as mechanophores and applying external pressure by means of sonication, the reactivity of neighboring functional group can be altered. It is demonstrated how the distance between enyne, and thus enediyne reactivity, can be tuned by applying mechanical stress. In the beginning of my Ph.D. project, we focused on the synthesis of the cyclic enediyne moiety with polymer incorporation and to look how their reactivity towards Bergman cyclization (BC) is enhanced by substitution pattern in cyclic moiety by applying an external force. Synthesis of the cyclic 10-membered ring with oxygen corporation is tough though few approaches are scrutinized for the synthesis of 7.4. None of the approaches were successful for the preparation of 7.4. Our main idea was to polymerize the cyclic enediyne with O incorporation and check the behavior of the molecule as structural change by applying ultrasound force characterized via various spectroscopy but we didn’t obtain the desired molecule thus, our interest was not attained.
Chart 5. Polymer Mechanochemistry for 7.4.