Exploration of Disilylfunctionalization of Alkenes using N-methyl-p-tolylsulfonamide with Palladium Catalyst

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Abstract:

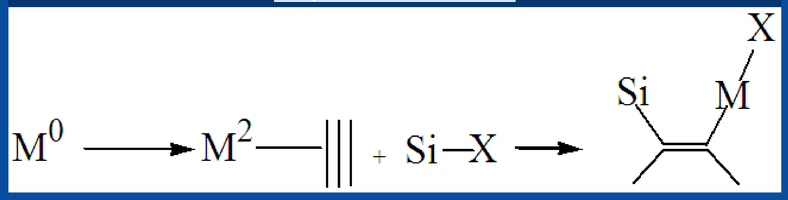
A new efficient method for silylfunctionalization with a transition metal catalyst using an alkyne can be beneficial to petroleum companies, who serve as the primary source of alkynes. This project focuses on beginning stages of creating a new reaction scheme that forms a new heteroatom-carbon bond and a new silicon-carbon bond across an alkene in one step instead of two. NMR and GCMS instruments were used to verify that disilylation was possible, after which different silicon reagents, solvents, palladium catalysts, phosphine ligands, and conditions were tested to confirm disilylfunctionalization with palladium catalyst and produce a Si-R_1 and a Si-C bond across an alkene.

Background:

Our proposed process would examine the possibility of adding two silicon atoms simultaneously across an alkene. Petroleum companies have access to an abundance of alkynes, which form when long chains of hydrocarbons from crude oil are broken. This diversifiable reaction would allow them to produce pharmaceuticals and other manufacturing goods from easily available resources, while reducing waste and excessive energy loss from this simultaneous reaction. Little research currently exists on performing difunctionalizations with silicon. This reaction would be a pi bond functionalization, where a pi and sigma bond are rearranged into two sigma bonds via the use of a catalyst. Although previous research confirms the possibility of a disilylation reaction, a metal-controlled oxidative 3-component silylfunctionalization is a new reaction method (Watanabe, Kobayashi, Higuchi, 1980). Past research has demonstrated success for the use of palladium as a catalyst for double silylation (Ozawa, Sugawara, Hayashi, 1994). This process would allow for a swift synthesis of vinyl silanes; the silicon atom can be switched out for other functional groups, allowing this reaction to be used in several different industries.

The gas-chromatography-mass spectrometry and nuclear magnetic resonance instruments were utilized to determine that the proposed products were attainable and verified the production of our experimental compounds. The NMR spectrometer applies a magnetic field to the nuclei in atoms, producing an electromagnetic signal in response to the energy transfer. Certain signals, appearing as peaks, correspond with certain types of bonds or functional groups, and are used to confirm their presence. The GCMS instrument vaporizes compounds into components that are eluted at different times depending on their polarity and melting point, and those components are ionized, fragmented, and separated by their mass-to-charge rations. Heights of peaks on the chromatogram correspond with the amount of that fragment in the sample, with the right-most peak showing the initial mass of the compound prior to fragmentation.

Proposed Mechanism:



Scheme 1: Proposed mechanism of the ligand coordination between palladium and an alkyne

Verification of Disylation:

1. 5 mmol hexamethyldisilane, 2.5 mmol of diphenylacetylene, and 0.025 mmol of triphenylphosphine were combined in a 50 mL round bottom flask.
2. 0.025 mmol palladium chloride and 50 microliters of triethylamine were added to the mixture
3. Round bottom flask was heated overnight at 80 C.

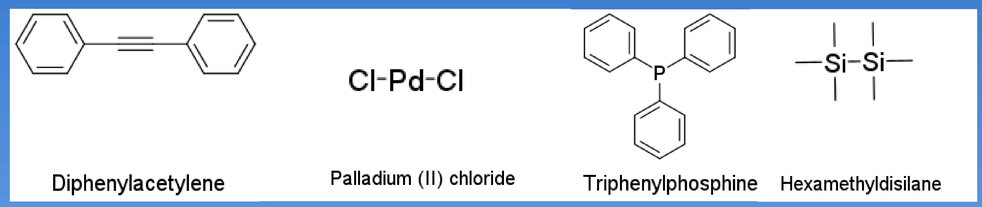


Figure 1: Structures of reagents used, left to right: hexamethyldisilane, diphenylacetylene, triphenylphosphine, palladium (II) chloride.

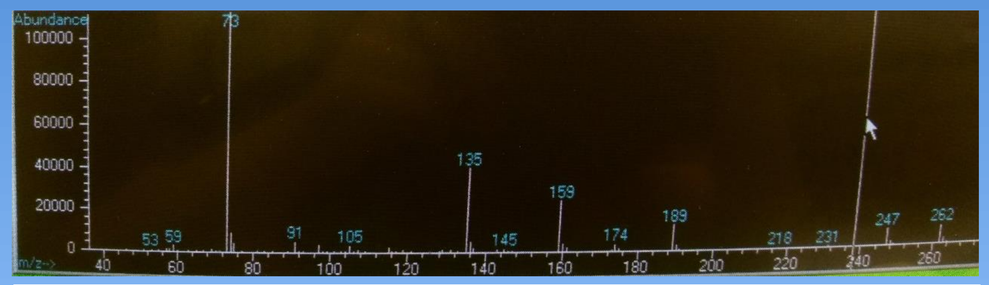
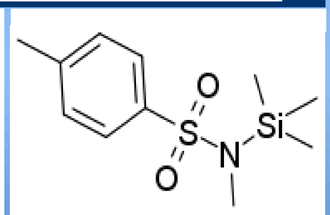


Figure 2: GCMS chromatogram of replication product- right-most peak at 262 matches the molar mass of expected product

Synthesis of N,4-dimethyl-N-(trimethylsilyl)benzenesulfonamide

1. 10.2 mmol N-methyl-p-tolylsulfonamide was combined with 20 mL toluene, 20 ml acetonitrile, and 48. 5 mmol chlorotrimethylsilane.
2. Solution was cooled to 0 C, solution of 12 mmol triethylamine in 5 mL toluene was added slowly.
3. Reaction was allowed to return to room temperature and stirred and heated overnight.
4. Slurry was washed with toluene and slurried in ether, then evaporated until solid in form.



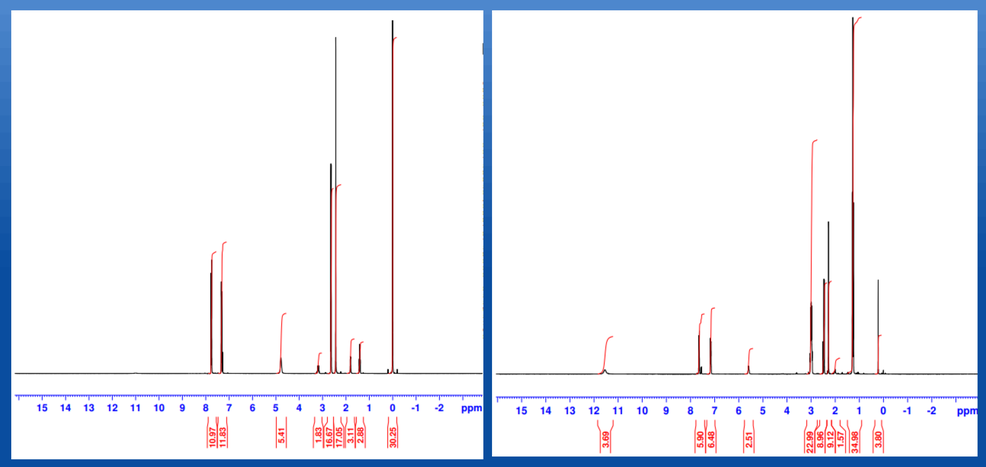


Figure 3: NMR spectra of synthesis of n-sulfonamide compound

Discussion:

For the verification of the disylation, the GCMS spectra showed that there were peaks that were comparative to that of a double bond, so we knew the triple bond had effectively been converted to a double bond. We also saw a set of peaks confirming the attachment of a silicon atom on each side of the double bond. Additionally, the chromatograph showed that the molar mass of the compound was 262, which was the same of the expected compound, and the fragment peaks corresponded to the functional groups in the compound as well.

Synthesizing the the n-sulfonamide compound created a large hurdle in our process. Multiple batches had to be made for repeated use for further experimentation, but over 10 replication rounds, only 2 resulted in the formation of the correct product. All other replications resulted in some sort of impurity in the product, most likely from triethylamine hydrochloride, present solvent that hadn't evaporated, or another impurity. Synthesis of the compound under nitrogen proved to be most effective, and ensuring solvents such as toluene and acetonitrile were dry also created positive results.

Overall, our research is in the beginning stages, and consists of multiple levels of trial and error, with numerous factors to take into account. We have set a foundation for forming our own experimental methods by creating some new reagents, while also using different solvents, catalysts, ligands or conditions to obtain our compound of interest. We are continuing to explore different silicon sources. To ensure the vinylmetal intermediate is the only one experiencing oxidation, we would switch the catalysts, oxidants and solvents to see which present the best results.

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