Attempted Proof of Procedure for the Preparation of Cyclic Perarylated Oligogermanes $(GeAr_2)_4$ with various Aryl Groups.

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ABSTRACT

The focus of this study was the proof of procedure for the preparation of 2,5-xylyl ($C_6H_3(CH_3)_2$-) substituted tri- Ar_3GeCl, di- Ar_2GeCl_2 and mono-aryl $ArGeCl_3$ germanes as well as slightly modifying the synthesis to produce 2,4-xylyl substituted tri-, di- and mono-aryl germanes first reported by Komanduri. These substituted germanes could then further be used for preparing perarylated cyclic oligogermanes. These cyclic oligogermanes would then have the potential to be ring-opened, thus synthesizing a new series of discrete linear oligomers containing extended Ge-Ge chains. The production of relatively pure arylgermanes was successful, though provided significant challenges in purification. Difficulty in the long work up procedures gave way to product loss, and thus was difficult to reproduce. The generalization of this process with other xylene aryl groups was shown to be possible, but further investigation is needed to confirm. The use of the di-arylgermanes in the cyclization reactions involving sodium have not yet been reproducible.

Introduction

The first organic derivative of germanium (tetra-ethylgermanium, Et_4Ge) was synthesized in 1887.[1] For several years this was the only organogermanium compound until the synthesis of tetraphenylgermanium, Ph_4Ge, by Drew and Morgan, which brought quaternary organic germanium species into focus.[2] Since methods for the preparation of arylgermanes have involved the treatment of germanium tetrachloride $GeCl_4$ with an aryl Grignard, a Wurtz-Fittig reaction, or arylithium reagents. These methods were not efficient of selective, producing mixtures and resulting in low yields.[3]

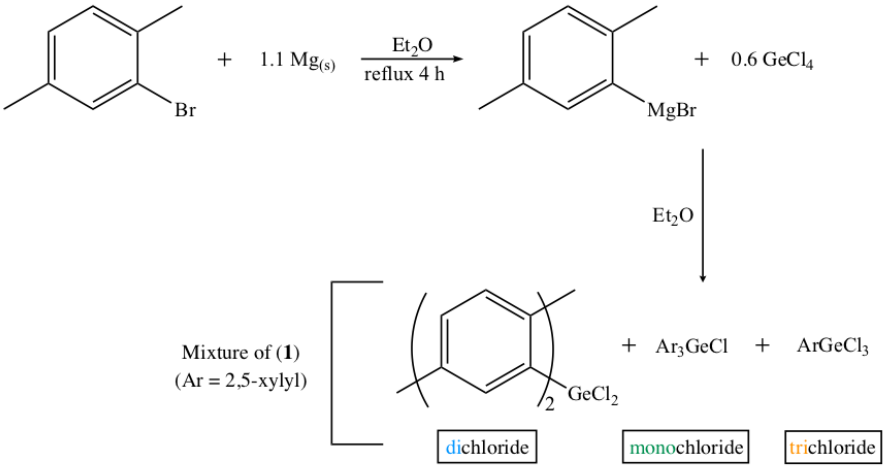
Many investigations have been conducted of the synthesis of cyclic group 14 compounds. Perphynylated cyclosilanes have been prepared via the addition of dichlorodiphenylsilane Ph_2SiCl_2 with either sodium, lithium, or magnesium [4-6] After isolation compounds corresponding to $(Ph_2Si)_n$ where n = 4, 5, and 6 respectively were reported.[7-9] Cyclic germanium compounds have been prepared following a similar method using dichlorodiphenylgermane Ph_2GeCl_2 and sodium metal. The resulting homocyclic germanium compounds of the formula $(Ph_2Ge)_n$ where n = 4, 5, and 6 were formed in various ratios. [10-12]

These compounds have again become of interest for their role as precursors in ring opening reactions that allow for the preparation of long linear oliogogermanes. The Weinert group reported on the ring opening of $(GePh_2)_4$ using molecular bromine to yield $Br(GePh_2)_4Br$.[13] The ring strain involved in the cyclogermane compound enabled the process to occur favorably and quickly.[14] Similar methods have been investigated by the Weinert group to ring open decaphenylcyclopentagermane $(GePh_2)_5$ but have shown uncontrolled ring opening when reacted with lithium metal under argon. In an attempt to control the ring breaking reactions, cyclogermanes using various aryl ligands are under examination.

Arylgermanium halides $Ar_nGeX_{(4-n)}$ and hydrides $Ar_nGeH_{(4-n)}$ (n = 1-3) have recently become of interest for their potential as starting materials for the aforementioned production of cyclic oligogermanes. However, these investigations have been hindered because of the lack consistent and efficient synthetic pathways for germanium polymer compounds.[15-16] Synthetic pathways that are used in the group are not applicable for organogermanium compound synthesis, thus requiring investigation into different preparatory routes. [15,17] Synthetic routes using organometallics compounds have included organolitihum or organomagensium compounds (RLi, RMgX), comproportionation reactions, or halogenation reactions starting from organogermanes.[18-23]However, a versatile and reliable pathway to prepare arylgermanium compounds had until recently been elusive.[24-26] Recently, work was done on a series of novel tetraarylgermanes Ar_4Ge (aryl = tolyl, xylyl, naphthyl, and mesityl derivatives) and triarylgermanium halides Ar_3GeX (X = Cl, Br).[27] The focus of this study was the proof of procedure for the preparation of 2,5-xylyl ($C_6H_3(CH_3)_2$-) substituted tri- Ar_3GeCl, di- Ar_2GeCl_2 and mono-aryl $ArGeCl_3$ germanes as well as slightly modifying the synthesis to produce 2,4-xylyl substituted tri-, di- and mono-aryl germanes first reported by Komanduri. These substituted germanes could then further be used for preparing perarylated cyclic oligogermanes. These cyclic oligogermanes would then have the potential to be ring-opened, thus synthesizing a new series of discrete linear oligomers containing extended Ge-Ge chains.

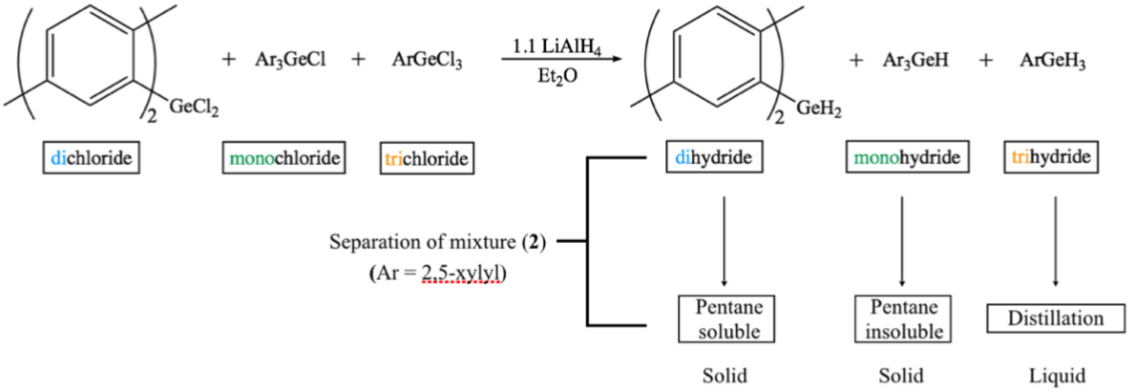
Experimental Details

The aryl substituted germanium compounds ArMg-Cl were prepared using the Grignard method described in Scheme 1. Magnesium was reacted with the desired arylhalide (2,5-xylyl-Cl or 2,4-xylyl-Cl) for a minimum of four hours and filtered to remove excess magnesium, a step crucial to preventing hexa-aryldigermanes (Ar_6Ge_2) from forming.[28] The Grignard solution was then added dropwise to the solution of $GeCl_4$ in Et_2O at 0°C and stirred for 4 hours. Following the reaction was quenched using 10% degassed HCl and the organic layer separated. After filtering and drying the organic layer to produce a white/yellow solid GC-MS was used to classify products. One complication in preparing pure triarylgermanium halides, also seen with other group 14 analogs, is the occurrence of subsequent products could be separated and all utilized as starting materials for varying reactions.



Scheme 1: Grignard synthesis for preparing chloride mixture $Ar_nGeCl_{(4-n)}$ (n = 1-3)

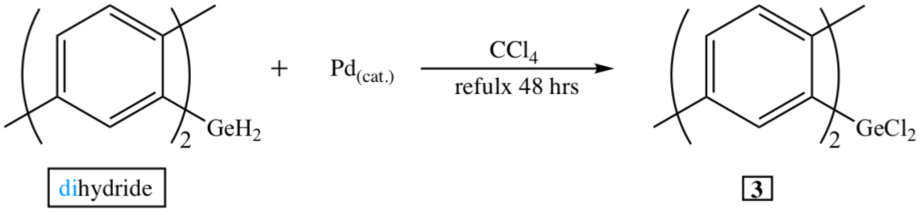
The chloride mixture was then reacted with $LiAlH_4$ over night. After quenching with a dilute sulfuric acid solution, the product was then filtered and stirred with potassium tartrate hydrate to balance pH. The solution was then filtered again and stirred in $MgSO_4$ for 30 minutes. After filtering off the $MgSO_4$ the solution was dried via vacuum in an ice bath to ensure none of the volatile $ArGH_3$ evaporated off. The mixture of halides was then separated, detailed in Scheme 2.



Scheme 2: Synthetic preparation of $Ar_nGeH_{(4-n)}$ (n = 1-3) mixture and separation.

Separation by short path distillation condensed a clear liquid solution of $ArGeH_4$. The remaining yellow solution contained Ar_2GeH_2 and Ar_3GeH and was dried via vacuum. The remaining solid was washed with pentane to separate the soluble Ar_2GeH_2 from the Ar_3GeH via filter cannulation. After separation, the pentane dissolved Ar_2GeH_2 was thoroughly dried.

A 3-neck flask was charged with pure Ar_2GeH_2 and dissolved CCl_4. A Catalytic amount of Palladium was added to the reaction and refluxed for 48 hours (Scheme 3). The resulting solution was filter cannulated and dried in warm water bath. Solids were washed multiple times with pentane to remove soluble impurities, then dried, resulting in a white powder.



Scheme 3: Synthetic preparation of pure (2,5-xylyl)$_2$GeCl$_2$

The prepared white powder, Ar$_2$GeCl$_2$, was then dissolved in toluene and added dropwise to a refluxing sodium and toluene solution. This was allowed to react for a minimum of 8 hours. The final black solution was then hot filtered and dried to produce an off-white powder. The solid was washed and filtered with both Et$_2$O and toluene to removes salts. The final solution was then dissolved in minimal toluene to create a supersaturated solution. After portioning off several small vials of this super saturated solution, it was then super-heated and immediately capped and left completely still for several days to form crystals. The crystals were then analyzed.

Results

	m/z	Assignment
2,5-$(CH_3)_2(C_6H_3)$	105	$(CH_3)_2C_6H_3^+$
(t_r=11.79 min)		
$ArGeCl_3$	284	$((CH_3)_2C_6H_2)GeCl_3^+$
(t_r=18.02 min)	248	$((CH_3)_2C_6H_2)GeCl^+$
	179	$((CH_3)_2C_6H_2)GeH_2^+$
	104	$((CH_3)_2C_6H_2)^+$
	77	$(C_6H_5)^+$
Ar_2GeCl_2	354	$((CH_3)_2C_6H_2)_2GeCl_2H^+$

(t_r=24.26 min)	248	$((CH_3)_2C_6H_2)_2GeCl_2^+$
	179	$((CH_3)_2C_6H_2)_2GeH_2^+$
	104	$((CH_3)_2C_6H_2)^+$
	77	$(C_6H_5)^+$
Ar_3GeCl	424	$((CH_3)_2C_6H_3)_3GeClH^+$
(t_r=27.62 min)	387	$((CH_3)_2C_6H_3)_3Ge^+$
	318	$((CH_3)_2C_6H_3)_2GeCl^+$
	283	$((CH_3)_2C_6H_3)_2GeH^+$
	209	$((CH_3)_2C_6H_3)_2^+$
	177	$((CH_3)_2C_6H_3)Ge^+$
	105	$((CH_3)_2C_6H_2)^+$

Table 1: GC-MS data for product mixture of chlorides

	m/z	Assignment
$ArGeH_3$	180	$((CH_3)_2C_6H_3)GeH_3^+$
(t_r=10.06 min)	165	$(CH_3(C_6H_3))Ge^+$
	151	$(C_6H_3)GeH_4^+$
	107	$((CH_3)_2C_6H_3)H_2^+$
	91	$(CH_3(C_6H_3))H^+$
	78	C_6H_3+
Ar_2GeH_2	284	$((CH_3)C_6H_3)_2GeH_2^+$
(t_r=20.28 min)	180	$((CH_3)_2C_6H_3)GeH_3^+$
	165	$((CH_3)C_6H_3)GeH_3^+$
	151	$(C_6H_3)GeH_4^+$
	105	$((CH_3)_2C_6H_3)^+$
	77	$C_6H_4^+$
Ar_3GeH	284	$((CH_3)_4C_6H_3)GeH^+$
(t_r=26.41 min)	269	$((CH_3)_3(C_6H_3))Ge^+$

	207	$((CH_3)_2(C_6H_3))_2^+$
	192	$(CH_3)_3(C_6H_3)_2^+$
	179	$((CH_3)_2(C_6H_3))GeH^+$

Table 2: GC-MS data for product mixture of halides

	m/z	Assignment
$ArGeCl_3$	284	$((CH_3)_2C_6H_2)GeCl_3^+$
(t_r=18.13 min)	248	$((CH_3)_2C_6H_2)GeCl^+$
	179	$((CH_3)_2C_6H_2)GeH_2^+$
	104	$((CH_3)_2C_6H_2)^+$
	77	$(C_6H_5)^+$
Ar_2GeCl_2	354	$((CH_3)_2C_6H_2)_2GeCl_2H^+$
(t_r=23.96 min)	248	$((CH_3)_2C_6H_2)_2GeCl_2^+$
	179	$((CH_3)_2C_6H_2)_2GeH_2^+$
	104	$((CH_3)_2C_6H_2)^+$
	77	$(C_6H_5)^+$
Ar_3GeCl	424	$((CH_3)_2C_6H_3)_3GeClH^+$
(t_r=27.28 min)	387	$((CH_3)_2C_6H_3)_3Ge^+$
	318	$((CH_3)_2C_6H_3)_2GeCl^+$
	283	$((CH_3)_2C_6H_3)_2GeH^+$
	209	$((CH_3)_2C_6H_3)_2^+$
	177	$((CH_3)_2C_6H_3)Ge^+$
	105	$((CH_3)_2C_6H_2)^+$
2,5-$(CH_3)_2(C_6H_3)$	105	$(CH_3)_2C_6H_3^+$
(t_r=24.64 min)	209	$((CH_3)_2C_6H_3)_2^+$
	77	$(C_6H_5)^+$

Table 3: GC-MS data for product mixture after attempted cyclization

Discussion

After the reaction with $GeCl_4$ the resulting sample was analyzed by GC-MS with four main components in the product mixture with retention times at 11.79, 18.02, 24.26, and 27.62 minutes (**Table:1**). The peak at t_r=11.79 minutes is a small peak of xylene with features at *m/z*= 105. The second compound eluted off the column with t_r = 18.02 minutes is the trichloride $ArGeCl_3$ with a MS having peaks at m/z = 284, 248, 179, 104, and 77 amu, which correspond to the parent ion ($ArGeCl_3^+$), and ($ArGeCl^+$), ($ArGeH_2^+$), ($C_6H_2(CH_3)_2^+$), and ($C_6H_5^+$), respectively. The main peak eluting third off the column is dichloride Ar_2GeCl_2 with t_r = 24.26 minutes as its MS has peaks at m/z = 354, 248, 179, 104, and 77 amu, corresponding to the parent ion ($Ar_2GeCl_2H^+$) and ($ArGeCl_2^+$), ($ArGeH_2^+$), ($C_6H_2(CH_3)_2^+$), and ($C_6H_5^+$), respectively. The final eluted compound with t_r = 27.62 minutes matches the fragmentation of monochloride Ar_3GeCl, with MS features at m/z = 424, 387, 318, 283, 209, 177, 105, and 79 amu, indicating the presence of (Ar_3GeClH^+), (Ar_3Ge^+), (Ar_2GeCl^+), (Ar_2GeH^+), (Ar_2^+), ($ArGe^+$), and (Ar^+).

The resulting product mixture after the lithium aluminum hydroxide reaction was analyzed by GC-MS to verify products, showing a chromatogram having three major compounds with retention times at 10.06, 20.28, and 26.41 minutes. (**Table:2**) The first eluted compound off the column was $ArGeH_3$ at t_r = 10.06 minutes, with its MS fragmentation patterning m/z = 180, 165, 151, 107, 91, and 78 amu matching parent ion (($C_6H_3(CH_3)_2GeH_3^+$, then successive loss of methyl groups giving (($C_6H_3(CH_3)Ge^+$) and ($C_6H_3GeH^+$), $(C_6H_3(CH_3)_2)H_2^+$, $(C_6H_3(CH_3))H^+$, and PhH^+, respectively. The second eluted compound at t_r = 20.28 minutes was Ar_2GeH_2, and has the following fragmentation: m/z = 284, 180, 165, 151, 105, and 77, these peaks correspond to $(C_6H_3(CH_3)_2)_2GeH_2^+$, $(C_6H_3(CH_3)_2)GeH_3^+$, $(C_6H_3(CH_3))GeH_{3+}$, $(C_6H_3)GeH_4^+$, $(C_6H_3(CH_3)_2^+$, and PhH^+ respectively. The last compound eluted off is Ar_3GeH at $t_r = 26.41$ minutes, and its MS has leaks at m/z = 284, 269, 207, 192, and 179 amu. These peaks correspond to the ions of $(C_6H_3(CH_3)_2)_2GeH^+$, followed by the loss of one methyl group, $(C_6H_3(CH_3)_2)_2^+$ with another loss of a methyl group, and $ArGeH^+$, respectively.

The side products generated from the LAH reaction, Ar_3GeH and $ArGeH_3$, and the major Ar_2GeH_2 species could all be used as starting materials a new series of linear oligomers, since these materials could be used in the hydrogermolysis reactions. After separation, the resulting insoluble white solid was identified by GC-MS as relatively pure dichlordiarylgermane Ar_2GeCl_2 with slight impurities of Ar_3GeCl and $ArGeCl_3$.

The attempted cyclotetragermane production resulted in an off-white/yellow product that upon analysis yielded predominately Ar_2GeCl_2 with slight impurities of Ar_3GeCl and $ArGeCl_3$. The sample was analyzed by GC-MS with four main components in the product mixture with retention times at 18.13, 23.96, 27.28, and 24.64 minutes (**Table:3**). The features at 18.13, 23.96, and 27.28 minutes correspond to $ArGeCl_3$, Ar_2GeCl_2, and Ar_3GeCl respectively as discussed before. The feature at 24.64 minutes, however showed *m/*z= 105, 209, and 77 indicating $((CH_3)_2C_6H_3)^+$, $((CH_3)_2C_6H_3)_2^+$, $(C_6H_5)^+$. This longer retention time suggests that an unaccounted-for reaction occurred at during the sodium reaction. The lack of cyclization indicates that the sodium reaction did not react as expected. This could be due to the impurities found in the final Ar_2GeCl_2 solution. Re-purification and reaction is underway; however, results will not be mentioned in this text. Both the para-xylene and meta-xylene reactions produced same results throughout, though the product for the reaction of the meta-xylene were ruined in a lab error that resulted in complete loss of product before the cyclization reaction with sodium. Further work is needed to reexamine the process of the production of product with the meta-xylene.

Conclusion

This study aimed to prove that reproducibility of a previously designed and executed synthetic pathway first outlined in the dissertation by Komanduri. The production of relatively pure arylgermanes was successful, though provided significant challenges in purification. Difficulty in the long work up procedures gave way to product loss, and thus was difficult to reproduce. The generalization of this process with other xylene aryl groups was shown to be possible, but further investigation is needed to confirm. The use of the di-arylgermanes in the cyclization reactions involving sodium have not been reproducible. Though, currently ongoing research preliminarily shows that the reaction is producible. Investigation into the variables that play apart into the cyclization need to be conducted to optimize the final procedure.

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