TRANSACTIONS, ILL. STATE ACAD. SCI.
Vol. 71, No. 1 (1978)

PRODUCT DISTRIBUTIONS IN THE ETHYLLITHIUM-GERMANIUM TETRACHLORIDE REACTION

Blaise J. Arena and P. S. Poskozim

Chemistry Department
Northeastern Illinois University
Chicago, Illinois 60625

ABSTRACT

Results are presented of a gas chromatographic product distribution analysis of the reaction between ethyllithium and germanium tetrachloride. These results indicate that the reaction does not proceed in a stepwise manner. An alternate rationalization involving "concerted" reaction between germanium tetrachloride and ethyllithium hexamer is offered.

The use of organolithium reagents is common in chemistry. However, there seems to be a general lack of quantitative data regarding product distributions in RLi substitution reactions, especially at low reactant ratios. The reaction between ethyllithium (EtLi) and germanium tetrachloride ($GeCl_4$) produces a wide range of organo and organochloro-germanes (eq.1).

$$GeCl_4 + EtLi \longrightarrow EtGeCl_3 + Et_2GeCl_2 + Et_3GeCl + Et_4Ge + Et_6Ge_2 + LiCl \qquad (1)$$

Any discussion of this reaction has generally assumed a stepwise mechanism (eq.2).

$$GeCl_4 \xrightarrow[k_1]{EtLi} EtGeCl_3 \xrightarrow[k_2]{EtLi} Et_2GeCl_2 \xrightarrow[k_3]{EtLi} Et_3GeCl \xrightarrow[k_4]{EtLi} Et_4Ge \qquad (2)$$

However, there seems to be no experimental evidence to support this assumption. In hopes of providing some clarification of this situation, we wish to report product distribution data for this reaction.

A series of reactions between EtLi and $GeCl_4$ in benzene was run. A solution of EtLi in benzene was added dropwise at a constant temperature of 28°C to a vigorously agitated benzene solution of $GeCl_4$. Reaction time was one hour. The degree of agitation was more than sufficient to cause immediate dispersal of each EtLi solution drop. Experimental conditions were constant for the series except for reactant ratio which was varied from 0.5:1 EtLi:$GeCl_4$ to 7:1 mole ratio. The product distribution analysis was done for each reaction using a gas chromatographic method. Due to the highly reactive nature of $EtGeCl_3$, difficulties were experienced in its analysis and only rough estimates were possible. These estimates indicate that the yield of $EtGeCl_3$ did not exceed that of Et_2GeCl_2. The product distributions for the series of reactions between EtLi and $GeCl_4$ in benzene are presented in Fig. 1.

All experimental parameters, solution concentration, degree of agitation, rate of EtLi addition, were aimed at facilitating the formation of the least substituted products. Reaction conditions were such as to create a very high degree of competition between molecules of $GeCl_4$ for available EtLi. In light of this, it is notable that in benzene, Et_3GeCl is the preferred reaction product at all reactant ratios of less than 3:1, even as low as 0.5:1. At higher ratios as expected Et_4Ge becomes the major product.

Assuming that the reaction <u>does</u> proceed in a stepwise fashion (eq.2) then a possible explanation of these results might be that $k_3 \gg (k_1, k_2, k_4)$ or simply that stirring was insufficient to prevent formation of more highly substituted products.

In order to test these possibilities, EtLi was treated with $EtGeCl_3$ (rather than $GeCl_4$) under conditions identical to those described above. Reactions were carried out at three ratios: 0.7, 1.5 and 2.1:1. It was found that at all three ratios, Et_2GeCl_2 is the major product, and that yield of Et_3GeCl is far less than that observed in the $GeCl_4$-EtLi reaction. Thus, neither $EtGeCl_3$ or Et_2GeCl_2 are naturally predisposed to proceed further to Et_3GeCl. The idea of $k_3 \gg (k_1, k_2, k_4)$ is not consistent with these results. Also, experimental conditions (i.e., rate and order of EtLi addition, agitation) are demonstrated to be effective in preventing formation of more highly substituted products. This strongly suggests that a simple stepwise substitution mechanism with $EtGeCl_3$ and/or Et_2GeCl_2 as precursors to Et_3GeCl is not the predominant route to Et_3GeCl in the $GeCl_4$-EtLi reaction.

It is well established that ethyllithium exists as a hexamer in benzene with slight dissociation to the monomer (Brown, Dickerhoof, and Bafus, 1962). Examination of the EtLi hexamer shows two sets of three ethyl groups with each set in a trigonal arrangement. The possibility of three ethyl groups from the hexamer simultaneously (in effect) exchanging with three chlorines from $GeCl_4$ presents itself. This idea is structurally reasonable (i.e., the arrangement of ethyl groups and chlorines is similar as are the dimensions of the EtLi hexamer and the $GeCl_4$ tetrahedron) and is consistent with the observed preferential formation of Et_3GeCl at low reactant ratios (see fig.2).

If the idea of reaction with EtLi oligomer (rather than monomer) is assumed to be valid, then changing the nature of EtLi from hexamer to tetramer should effect some change in preferred reaction product. This is found to be true.

EtLi is tetrameric in tetrahydrofuran (THF) (Brown, 1965). Using the previously described procedure, reactions between EtLi in benzene/THF and $GeCl_4$ in THF were run at 0.5, 1.5 and 2.5:1 ratios. Although lower overall yields were observed, Et_2GeCl_2 was found to be the preferred product at all three ratios.

The EtLi tetramer is a cube with ethyl groups at opposing corners (Brown, 1965). Again, if the idea of a "concerted" reaction is acceptable here, then exchange of two ethyl groups is the most structurally reasonable possibility.*

Experimental data have been presented which strongly indicate that the $GeCl_4$-EtLi reaction in benzene does not adhere to its traditional conception as a classical stepwise substitution reaction. Thus alternate rationalization seems to be warranted. We submit that "concerted" reaction between $GeCl_4$ and EtLi oligomer, although provocative, is a statistically (i.e. $GeCl_4$ collision with EtLi hexamer is more likely than collision with monomer) and structurally reasonable hypothesis which is consistent with the results described here.

---

*Following this hypothesis, one referee questioned why Et_4Ge was not the major product in the reactions of $EtGeCl_3$ and EtLi hexamer listed above. For Et_4Ge to form, the $EtGeCl_3$ tetrahedron must be oriented with ethyl group pointing away from the EtLi hexamer, statistically only a one-in-four possibility.

ACKNOWLEDGEMENT

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Office of Organized Research at Northeastern Illinois University for support of this research. We also wish to thank Mr. J. Ryan and Ms. D. Hockman for their technical assistance and Dr. D. Quane and Laramie Chemical Company for samples of Ge_2Et_6.

LITERATURE CITED

BROWN, T. L., 1965. The Structures of Organolithium Compounds. Adv. Organometal. Chem., 3: 365-395.

BROWN, T. L., Dickerhoof, D. N., and Bafus, D. A., 1962. The Infrared and Nuclear Magnetic Resonance Spectra of Ethyllithium. J. Amer. Chem. Soc., 84: 1371-1376.

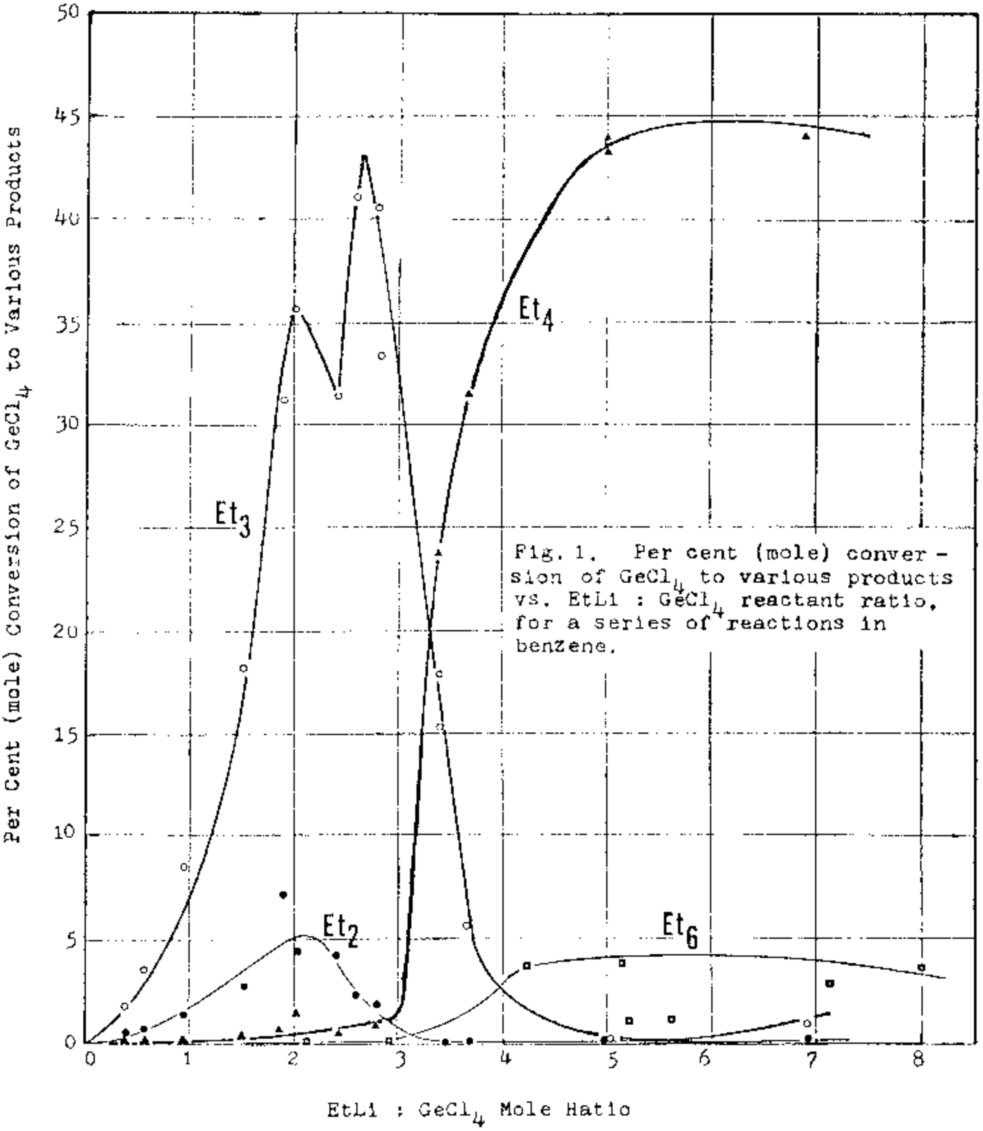

Fig. 1. Per cent (mole) conversion of $GeCl_4$ to various products vs. EtLi : $GeCl_4$ reactant ratio, for a series of reactions in benzene.

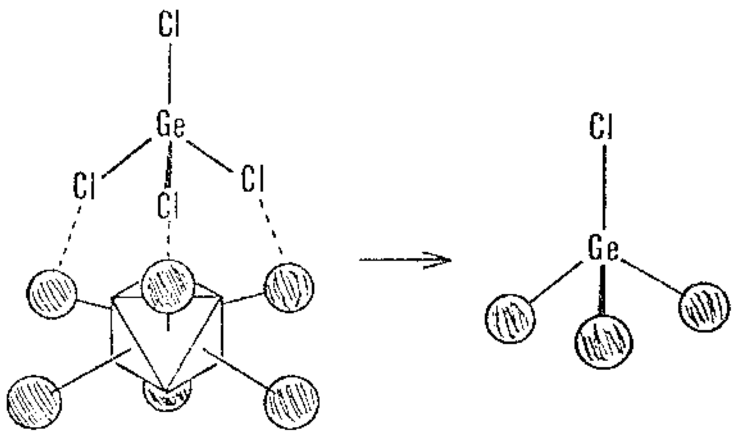

Fig. 2. Illustration of proposed mode of reaction between EtLi hexamer and $GeCl_4$ tetrahedron.