Communication

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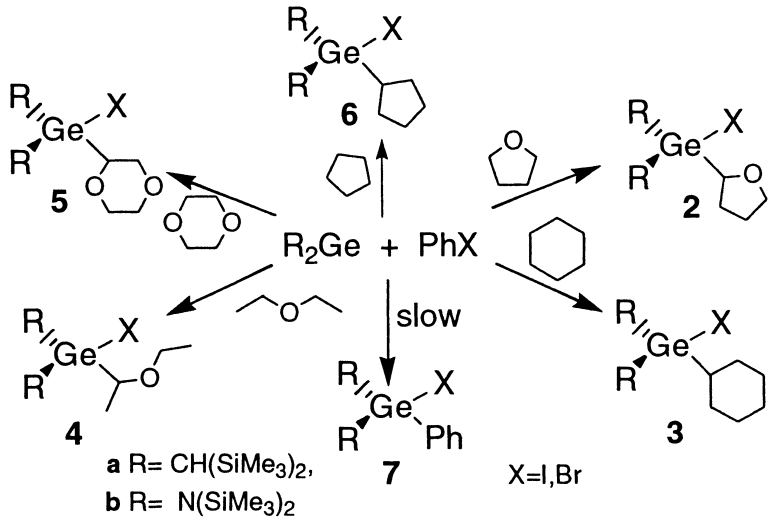

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C−H Activation of Ethers and Alkanes by Germylene−Aryl Halide Complexes

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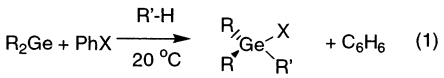
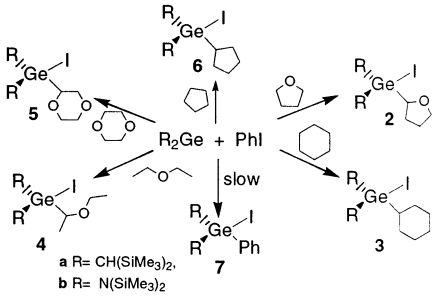
Selective intermolecular C−H activations and insertions have been the focus of much research both in academia and industry.[1−3] Main group radical-based C−H activations of alkanes have focused on halogenation, sometimes under phase-transfer conditions.[4,5] Although these reactions are selective for tertiary and secondary C−H bonds, most of the tertiary activation products are unstable to the reaction conditions and are observed only in trace amounts.

We have recently discovered a novel C−H activation of ethers and alkanes using $Ge[CH(SiMe_3)_2]_2$ (**1a**) or $Ge[N(SiMe_3)_2]_2$[6] (**1b**) and PhX (X = I, Br, Cl) (eq 1).



For ethers such as tetrahydrofuran (THF) (α-C−H 92 (kcal/mol), β-C−H 97.6),[7,8] and Et_2O (α-C−H 89, β-C−H 112)[9] the weakest C−H bonds are selectively activated. Activation of the C−H bonds in 1,4-dioxane (96),[7] cyclohexane (97),[7] cyclopentane (93),[10] and butane (97, 98)[11] have also been observed (Scheme 1). Benzene,

Scheme 1. Activation of Alkanes and Ethers by GeR_2 and PhI



derived from the phenyl halide, is produced along with the C−H activation product. Labeling studies with deuterated solvents and PhI or 2-bromotoluene, show monodeuterio arene by GC/MS. No trace of radical coupling products was observed by ^1H NMR spectroscopy or GC/MS for the reactions shown in Scheme 1.

The CH-activation products are synthesized by slow, room-temperature addition of **1a** or **1b** (0.02 M) dissolved in the alkane or ether of interest to an equimolar solution of PhI dissolved in the same alkane or ether. For **1a**, the optimal rate of addition can be judged by noting that the yellow-orange germylene color quickly fades to give a colorless solution before the next drop of germylene is added. The products in Scheme 1 have been characterized by ^1H and ^{13}C NMR spectroscopies, elemental analysis, and in the case of **3a**, X-ray crystallography (Figure 1a).

Oxidative addition (OA) of aryl halide to germylene is a concentration-dependent side reaction. At high concentration of

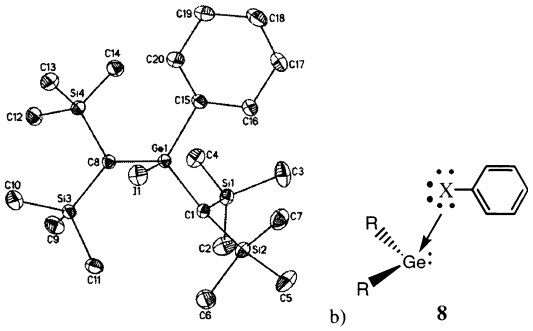
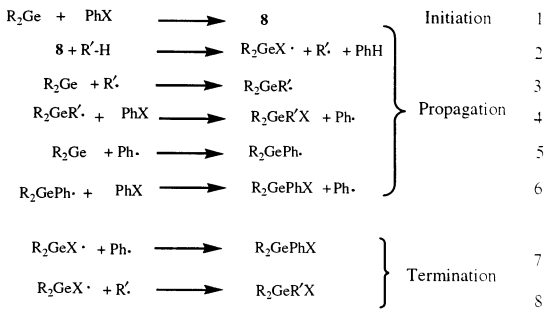


Figure 1. (a) ORTEP of **3a**. Selected bond lengths (Å) and angles (deg): Ge−I, 2.5946(4); Ge−C15, 1.9866(13); C1−Ge−C8, 107.10(5); C8−Ge−C15, 117.51(5); C8−Ge−I, 106.52(4); C15−Ge−I, 102.40(4). (b) Proposed intermediate.

Scheme 2. A Proposed Mechanism for C−H Activation Invoking Free Phenyl Radical



reactants (0.2 M), the OA product, **7a**, is formed in up to 40% yield, and **7b**, in 82% yield. At low concentration of PhI (0.02 M) and **1a** (<0.03 mM) the C−H activation product is produced almost exclusively, with less than 1% of **7a** formed (as determined by ^1H NMR spectroscopy). Related oxidative addition products have been reported for Sn and Si analogues. Lappert has investigated the reaction chemistry of the analogous stannylene $Sn[N(SiMe_3)_2]_2$ toward alkyl and aryl halides and reported that the reaction of $Sn[N(SiMe_3)_2]_2$ with PhBr in THF gives a 9:1 ratio of $[(Me_3Si)_2N]_2Sn(Ph)Br$:$[(Me_3Si)_2N]_2SnBr_2$.[12] Similarly, West reported that reaction of a stable silylene with PhBr in hexanes results in oxidative addition and disilane formation.[13] In neither case were the analogous CH-activation products reported.

A proposed mechanism is presented in Scheme 2. Abstraction of a hydrogen radical by free phenyl radical is not supported by key experiments reported herein. Instead, we propose that the hydrogen radical abstraction occurs at the *ipso*-carbon of species **8** as the Ge−X bond and an incipient phenyl radical form and the C−X bond breaks. This is consistent with a recent theoretical analysis of the related West silylene chemistry.[14]

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The regioselectivity of this reaction has been studied using **1a** and PhI. Reaction with butane at −30 °C results in a 1°:2° ratio of 0.08: 1 and reaction with methylcyclopentane at 20 °C gives a 2°:3° ratio of 1: 7.1. These ratios indicate a radical-like selectivity related to that observed for free phenyl radical generated by phenylazotriphenylmethane (PAT) at 60 °C (0.11−0.13:1.01; and 1:4.8 respectively).[15]

A difference in reactivity is observed when the halide is varied. Virtually all **1a** is consumed instantly upon addition to a PhI/THF solution. When PhBr is used, the reaction takes 3 days to go to completion. In the case of PhCl, the reaction is 33% complete after 12 days at room temperature, or complete after 2 days at reflux. This suggests that cleavage of the C−X bond is involved in the rate-limiting step.

Differing, detailed reactivity is observed for germylenes **1a** and **1b**, and is attributed to their different Lewis acidities. Although both activate alkanes and ethers, **1b** reacts more slowly than **1a**. Parallel activations of methylcyclopentane run under identical conditions show that all of **1a** has been consumed, while up to 35% of **1b** is still observed via ^{1}H NMR spectroscopy. Reactions run with **1b** produce more **7**. For example, when the synthesis of **2b** is undertaken employing the optimized conditions for **2a**, **7b** is produced in 13% yield, whereas the yield for **7a** is <1%. When aromatic substrates, such as toluene, ethyl benzene, or cumene are used, the products from benzylic C−H activation are observed when **1a** is employed. However, reaction of aromatic substrates with **1b** results only in slow formation of **7b**.

Competition experiments were performed at 60 °C using a 50:50 mol:mol solution of cumene:THF-d_8. When **1a** and PhI are added to the solution, a 4.7 ± 0.4 ratio of C−H activation products is observed. When PAT is used to generate phenyl radical, the ratio of cumene/THF activation is 3.4 ± 0.3, suggesting that a species other than free phenyl radical is involved in the C−H activation initiated by **1a** and PhI. If this competition is performed using **1b** and PhI, only **7b** and the C−H activation product derived from THF-d_8 are observed; no trace cumene activation is observed. Free phenyl radical, generated by PAT, readily abstracts H radical from aromatic substrates such as cumene and toluene.[15] Hence, these results in which C−H activation of THF by **1b** and PhI occurs in the presence of cumene are inconsistent with formation of free phenyl radical. Had free phenyl radical formed, one would have expected to observe a ∼3.4:1 ratio of cumene/THF-d_8 C−H activation.

Competition experiments at 60 °C using a 1:1 ratio of THF:THF-d_8 with germylene **1a** and PhI gives a k_H/k_D of 5.0 ± 0.2 as determined by GC/MS; for **1b** the ratio is 4.1 ± 0.2; for phenyl radical generated by PAT the ratio is 4.2 ± 0.2. The different k_H/k_D values for **1a** and **1b** argue against a common intermediate, including free phenyl radical, being formed in reactions employing **1a** or **1b**. The different k_H/k_D values for **1a** and phenyl radical generated from PAT also argue against free phenyl radical being generated in the C−H activation. Although the k_H/k_D values for **1b** and PAT are not statistically different, the cumene/THF competition experiment above argues against free phenyl radical playing a role in the case of **1b**.

The competition experiments and the k_H/k_D ratio observed for **1a** are inconsistent with the formation of free phenyl radical. The experimental evidence is consistent with hydrogen abstraction occurring via an incipient radical present on the *ipso*-carbon of the phenyl ring in **8** (Figure 1b). The germyl-X radical may then combine with the solvent radical to yield the observed products (step 8). Fast recombination within the solvent cage is consistent with the absence of R′−R′ coupling products. Note that high dilution conditions minimize the likelihood of reaction between R′• and GeR_2, thus avoiding steps 3−7 and the manifold of reactions required to form OA product **7**. Species **8** is consistent with the different isotope effects observed for **1a** and **1b**, the differing isotope effect observed for **1a** and PAT, and the differing substrate reactivity observed. Steps 3−7 are similar to the mechanism proposed by Lappert for the reaction of stannylene chemistry and aryl halides.[11]

Single-electron transfer (SET) is not uncommon in germanium chemistry[16,17] and plays an important role in main group C−H activations as well. To test whether the reactions reported herein proceed by SET from PhI to Ge, forming a radical germyl anion, the radical anion of **1a** was generated using sodium metal in THF according to the method of Gaspar et al.[18,19] No trace of a C−H activation product was observed by ^{1}H NMR spectroscopy. Additionally, during the reaction of **1a** with PhI, UV−vis spectroscopy showed only loss of the germylene peak at 420 nm as the reaction progressed; the characteristic green color of the germyl radical anion (λ_{max} = 666 nm) was not observed. Thus, the reactions described in this communication likely do not involve radical anion species.

In summary, a new reaction for regioselective activation of C−H bonds using a germylene/aryl halide reagent has been discovered. The reaction works for both straight-chain and cyclic alkanes and a variety of ethers. In contrast to previously reported main group C−H activations that result in a carbon−halogen bond, these C−H activated products have a C−Ge bond. High yields of C−H activation products can be obtained through the use of high-dilution techniques.

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Supporting Information Available: Experimental details (PDF). An X-ray crystallographic file in CIF format for compound **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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