Germanium Compounds: Chemistry and Applications

by Barry Arkles and Gerald L. Larson

Introduction

Germanium compounds have emerged as critically important materials in the fabrication of microelectronics, optics and sensors. Potential new applications in organic transformations and polymer synthesis have also been reported. This article highlights some of the chemistry associated with these applications. It also compares and contrasts the chemistry of germanium with the more widely understood chemistry of silicon. For readers with a deeper interest in the chemistry of germanium, comprehensive reviews provide a detailed description.[1-5]

Metallic Germanium and Metallization Chemistry

Germanium is a semiconductor. In fact, germanium was the first material to be fabricated into practical semiconductor devices, diodes. As a consequence, a significant body of literature relating to the electrical properties of germanium has developed. The mobility of holes in germanium is greater than that in silicon and that of any other semiconductor, particularly at low temperatures. This has made germanium an attractive candidate for high performance Complementary Metal-Oxide Semiconductor (CMOS) technology. In high speed digital communications associated with broad-band and cell phones, SiGe films are used to fabricate heterojunction bipolar transistors (HBTs). In other high speed applications SiGe films are deposited as molecular films, which act as templates for the epitaxial deposition of silicon. The resulting lattice mismatch creates a strained silicon layer, which exhibits enhanced electron mobility, providing improved device performance. SiGe technology has the potential to replace gallium arsenide, GaAs, in many applications. Other electronic applications of metallic germanium and its alloys include quantum dots, amorphous films for solar energy and LEDs.[6,7] Germane, GeH_4, in combination with silane, SiH_4, is the most widely used germanium precursor for chemical vapor deposition (CVD) of SiGe films. Other precursors include methylgermane, *n*-butylgermane, *t*-butylgermane and diethylgermane.[8]

A broader range of germanium compounds has been used to synthesize germanium nanowires including diphenylgermane[9,10] and germanium tetraiodide.[11] Amorphous a-GeCO:H films have been deposited from tetramethylgermane by Plasma-Enhanced Chemical Vapor Deposition (PECVD).[12]

Bulk germanium metal, fabricated from wafers, is currently of interest in the fabrication of monolithic fiber-optic receivers, since germanium photodiodes perform well at 1.3-1.5 micron wavelengths.
Germanium metal is also of utility in infrared detectors, which comprise the metal's largest current use.

Inorganic Germanium Chemistry

Bond energies of Ge-X bonds are generally found to be about 10% less than the corresponding Si-X bond energies. This is a reflection in the somewhat lower thermal stability of germanium compounds. The Pauling scale electronegativities of germanium and silicon are 2.01 and 1.90, respectively, their configuration energies are 11.80 eV and 11.33 eV, respectively. While silicon is apparently more electropositive than germanium, reactivity data indicate that polarization parameters may be more equivalent. Valence states of +2 are readily accessible for germanium and $GeCl_2$, $GeBr_2$ and GeI_2 are isolable divalent germanium compounds. In contrast, silicon dihalides are known as reactive intermediates as ascertained from studies of emission bands or trapping experiments. The chemistry of both elements proceeds primarily in the +4 oxidation state, although hyper-coordinate states, particularly for fluorinated derivative, are known.

Both silicon and germanium metal react with halogens and hydrogen halides to give analogous products. Halides of both elements react rapidly with water to give the respective metal oxide or hydroxide. Germanium oxides can be converted back to the halides by reaction with the appropriate acid. In the case of silicon, only hydrofluoric acid reacts with the oxides to form the fluorosilanes. This is a reflection of the strong Si-F bond.

Germanium compounds have higher optical densities than do silicon compounds. This leads to the second major application of germanium compounds: the controlled combustion of germanium tetrachloride with silicon tetrachloride in a hydrogen-oxygen flame in the chemical vapor axial deposition (CVAD) formation of ingots from which step-index fiber optics are drawn.[14,15]

Tetraethoxygermane is a liquid metal-organic precursor with a high vapor pressure that is well-suited for CVD of germanium oxide in optical and dielectric applications.[16,17] Sol-gel processing has also been employed as a method of preparing mixed germanium oxides. Again, tetraethoxygermane is the most widely used metal-organic perecursor, but other germanium alkoxides containing methoxy and isopropoxy groups are also used.[18]

Organic Chemistry

In contrast to silicon, sterically hindered organogermanium compounds in the +2 state are readily isolated. Examples include dicyclopentadienylgermanium, di[bis(trimethylsilyl)methyl]germanium and bis[bis(trimethylsilyl)amino]germanium.
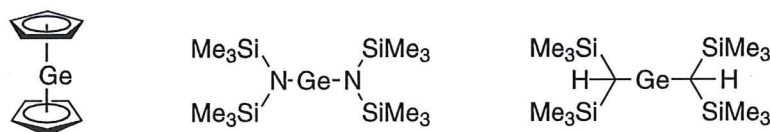

The bis[bis(trimethylsilyl)amino]germanium forms poly(germanium enolates) upon reaction with α,β-unsaturated ketones.[19]
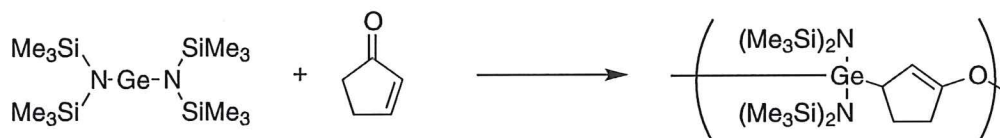
Di[bis(trimethylsilyl)amino]germanium also reversibly binds dihydrogen and carbon dioxide in 3-coordinate complexes.

Germanium dihalides, GeI_2 and $GeCl_2$ and its readily-prepared complexes with diethyl ether and 1,4-dioxane react with alkyl and aryl halides to yield alkyl and aryl germanium trihalides.[20]

$$CH_3CH_2CH_2CH_2Cl + GeCl_2 \longrightarrow CH_3CH_2CH_2CH_2GeCl_3$$
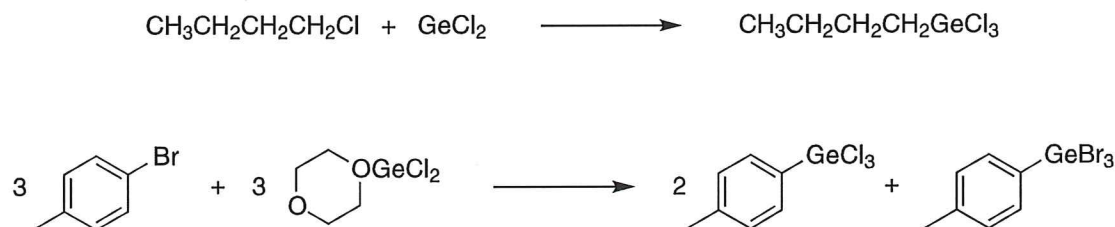
Most germanium reactions proceed in the +4 oxidation state. The following enumerations, though admittedly incomplete, provide examples.

1. Grignard and alkali metal reagents will displace halides bound to germanium and silicon to provide the corresponding organogermane or organosilane.
2. Germanium forms Ge-Ge bonds readily through Grignard chemistry in addition to the alkyl-metal coupling. This is in contrast to the reactions with silicon halides where substitution at Si occurs and the formation of Si-Si bonds is not observed.
3. While Si-Si bonds are readily cleaved by Na/K in ether, Ge-Ge bonds are only cleaved under more rigorous conditions such as the use of higher boiling solvents like tetrahydrofuran. In both cases when multiple metal-metal bonds are present they give photoreactive compounds.
4. Organogermanium and organosilicon compounds can both be prepared by the copper catalyzed direct reaction of alkyl and aryl halides with the metal.
5. Silicon undergoes migration from carbon to oxygen in the Brook rearrangement of α-silyl ketones and in certain metal alkoxide substituted organosilanes.[21] Germanium does not undergo similar rearrangements.
6. Numerous doubly bonded Si=Si and Ge=Ge compounds have been prepared and studied, but represent a small class of chemistry for these elements.
7. Perfluorinated methyl and ethylgermanes are isolable and stable. Simple trifluoromethyl(methyl)silanes have been prepared and used synthetically in numerous synthetic organic transformations. Other perfluorinated methyl and ethylsilanes are thermally unstable, decomposing above 80°C.
8. Repeating Si-O bonds tend to form extended linear polymers in preference to cyclic structures, whereas repeating Ge-O bonds tend towards the cyclic structures.
9. In contrast to silicon hydrides, germanium hydrides readily undergo metallation. For example, the reaction of triphenylgermane with *n*-butyllithium followed by carbonation yields triphenylgermane carboxylic acid.
10. Like organosilanes, organogermanes can be fluorodemetallated. Additionally, organogermanes can be demetallated with bromine.
11. Germanium hydrides and silicon hydrides react with olefins in hydrogermylation and hydrosilylation processes. Both are catalyzed by platinum complexes, but catalysis in not a requirement for hydrogermylation. Trichlorogermane is particularly reactive and the reaction products are associated with both hydrogermylation and dichlorogermene insertion.[22]
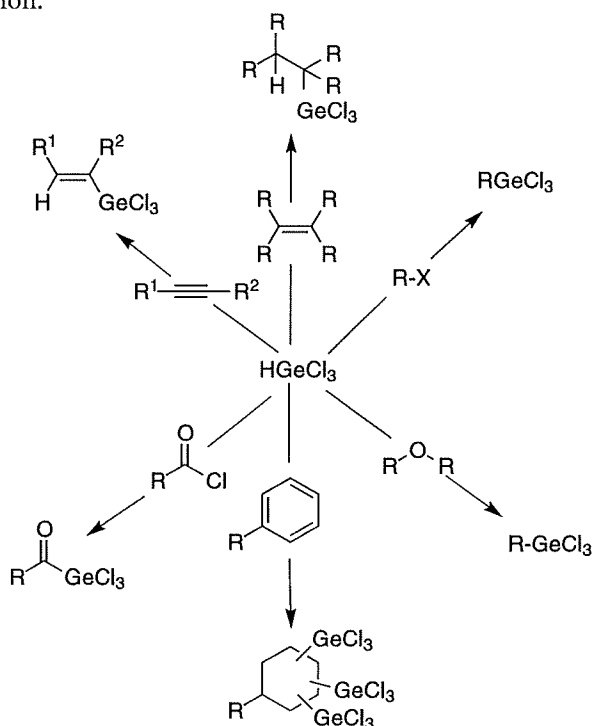
Germanium in Organic Synthesis

For a variety of reasons applications of organogermanes in organic synthesis are limited, while applications of organosilanes in this area have been and continue to be extensively utilized. Until recently organogermanes have had relatively poor availability compared to the organosilanes. Also, the Ge-O bond is somewhat more susceptible to hydrolysis compared to the Si-O bond. Beyond these facts, the single largest deterrent for these differences is the higher cost of the organogermanes versus the organosilanes. Consequently, only unique applications of organogermanium compounds in organic synthesis are likely to be of importance. Potential applications include trimethylgermylacetonitrile as an acetonitrile carbanion source, trimethylbromogermane and trimethylchlorogermane employed in the preparation of masked dienolates, trichlorogermane for ether cleavage, and germanium diiodide and cesium trichlorogermanate for conversion of alkyl halides to alkylgermyltrihalides. A review of the synthetic utility of organogermanium compounds along with the synthesis of various organofunctional germanium compounds has been reported.[23]

The cross-coupling of arylgermanium compounds have been reported. Although the reactivities are good and compare well with the organosilicon (Hiyama-Denmark) cross-coupling protocols they do suffer from cost when compared with the organosilanes. Tris(2-furyl)arylgermanes were successfully cross-coupled with aryl halides making use of the inert nature of the 2-furyl ligand. The tris(2-furyl)arylgermanes were nicely prepared by a Pd-catalyzed arylation of tris(furyl)germane.[24]
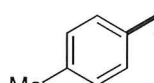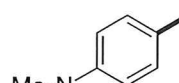
13 examples: 52 - 100%
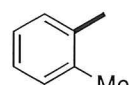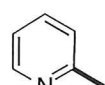

X = I; 90%   X = Br; 90%   X = Br; 80%   X = I; 59%
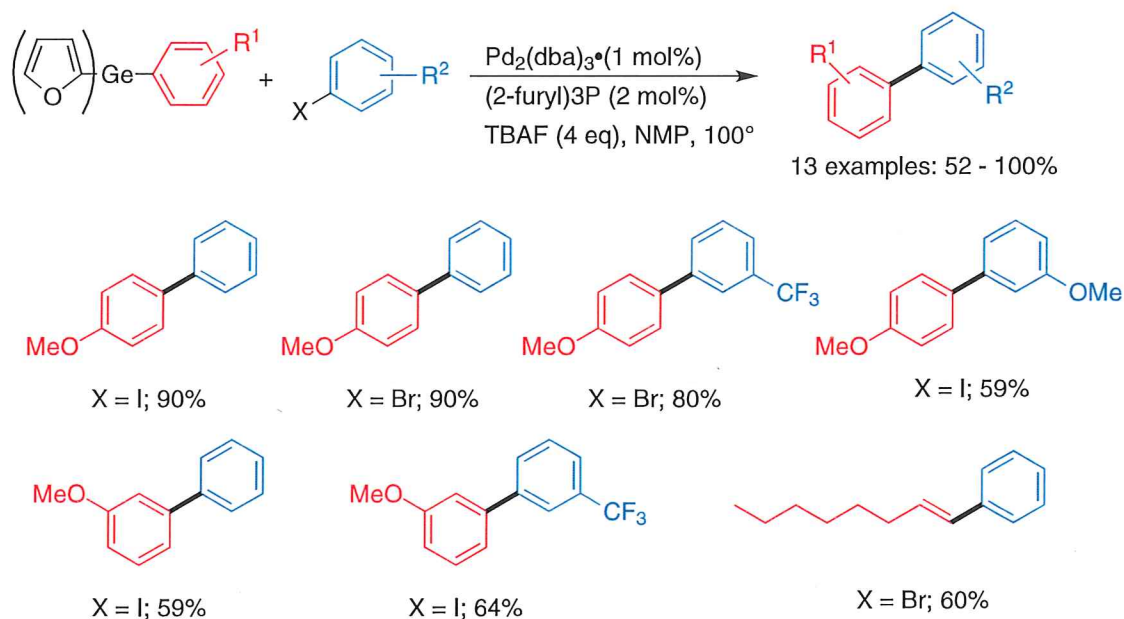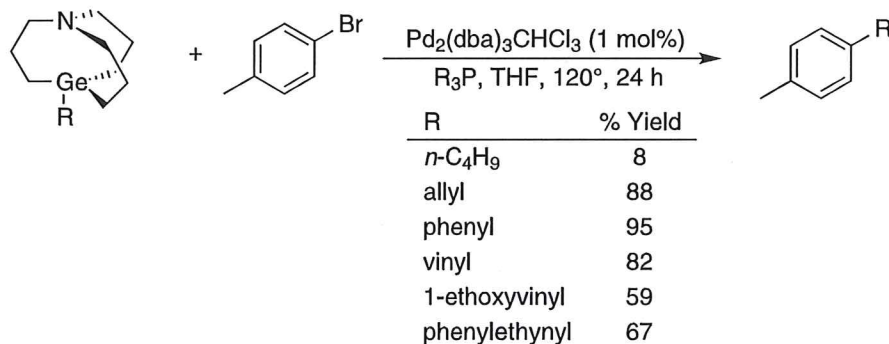

X = I; 59%   X = I; 64%   X = Br; 60%
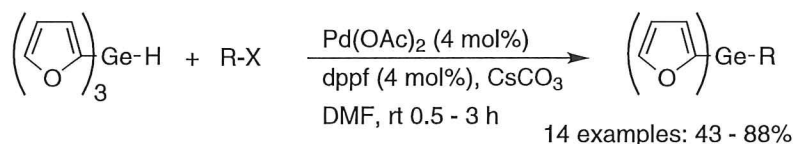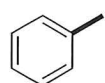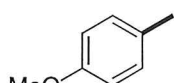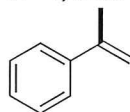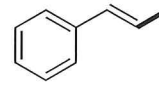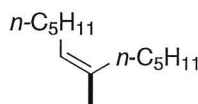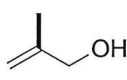
It was shown that the 5-substituted 1-aza-5-germabicyclo[3.3.3]undecanes would cross-couple with aryl bromides. Not surprisingly, the *n*-butyl group did not cross-couple well, although the allyl, phenyl and alkynyl groups did so quite well.[25]

R	% Yield
n-C$_4$H$_9$	8
allyl	88
phenyl	95
vinyl	82
1-ethoxyvinyl	59
phenylethynyl	67

Substituted germatranes have been shown to cross-couple. The organic groups on the germatrane can be aryl, vinyl, or ethynyl with ethynyl giving the best results. A significant amount of homo-coupling can occur under the reaction conditions.[26]

43%   34%

64%   +   16%

Pd(dba)$_2$ (5 mol%)
**1** (10 mol%), TBAF (1.5 eq.)
THF, reflux, 15 h

89%
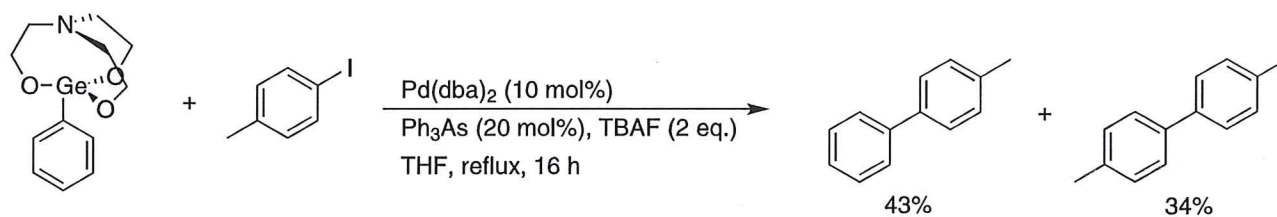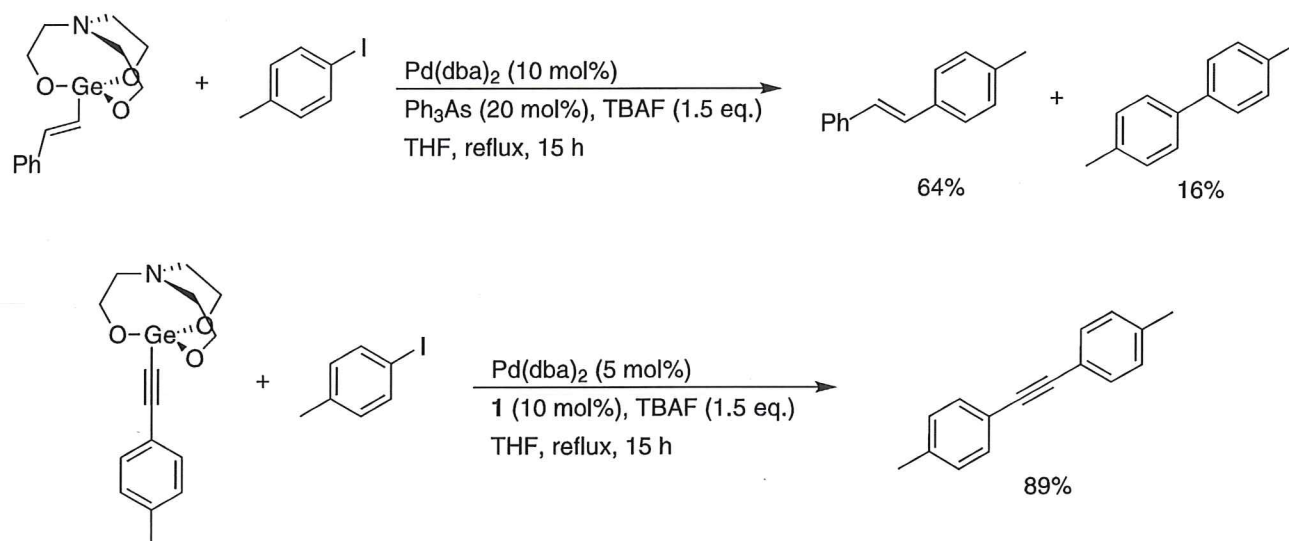
A comparison of the use of arylgermanium, arylsilicon and aryltin compounds in cross-coupling reactions was carried out. It was found that the tin derivatives were more reactive than the arylsilanes, which were more reactive than the arylgermanes. The presence of a chlorine on the silane or germanes was sufficient for the fluoride-promoted transfer of as many as three aryl groups from the germanium or silicon.[27] A pair of reviews of the cross-coupling chemistry of both organosilanes and organogermanes have appeared.[28,29]
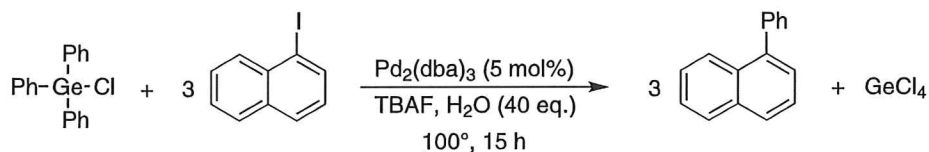
Tri-*n*-butylgermane is an effective reducing agent. It reduces benzylic chlorides 70 times faster than the hydridosilanes and reduces acyl chlorides to aldehydes in the presence of Pd (0).[30,31]
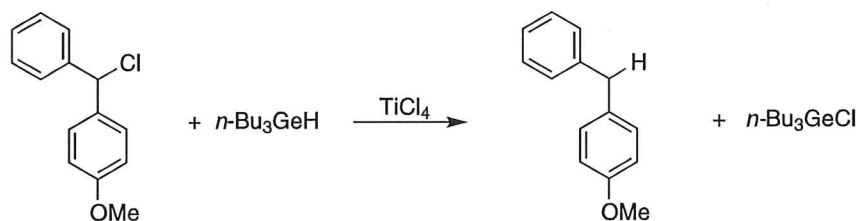
The cross-coupling of aryltrichlorogermanes with aryl bromides and iodides in a alkaline aqueous medium was shown to occur with good yields of the diaryl substrates.[32] In addition to the advantage of an aqueous, non-organic solvent medium, the reaction occurs best with $Pd(OAc)_2$ and does not require an organic ligand.

Y = H, Me, F, OMe   X = Br, I   15 examples: 48 - 96%

X = I; 70%   X = Br; 66%   X = Br; 71%   X = Br; 59%   X = Br; 72%
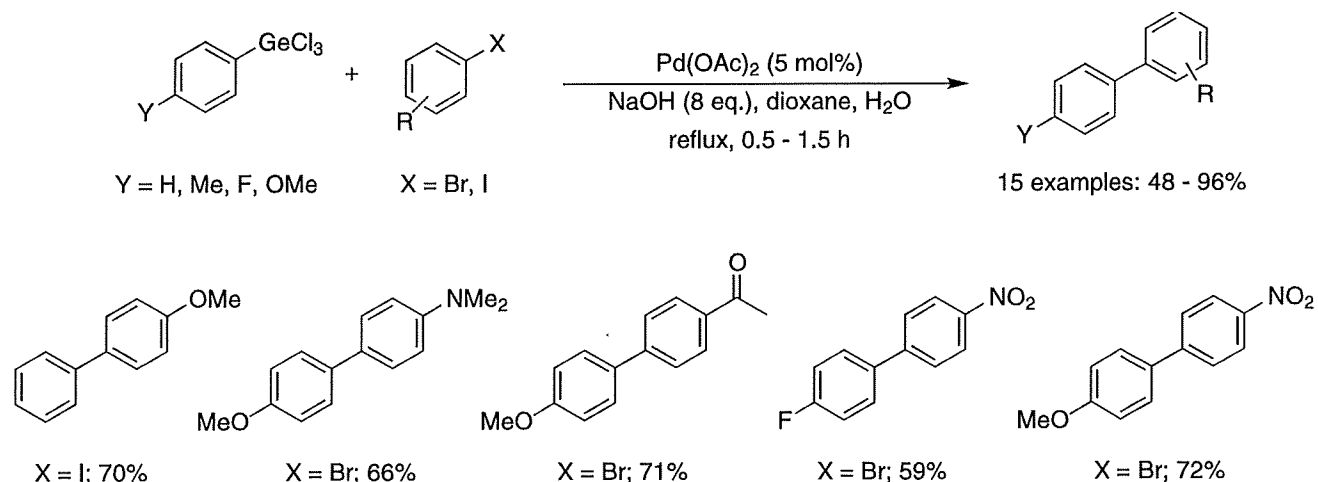
Polymers and Polymerization

The most commercially important application of germanium compounds is as catalysts in synthesis of polyester. Non-yellowing polyester fibers and clear polyester beverage bottles are produced by germanium dioxide and hydroxygermatrane-catalyzed condensation of dimethyl terephthalate and selected diols. Copolymers have been prepared from organogermanes with polymerizable functionality, including allyl, vinyl and methacrylate groups.[33,34]

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