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# Germylene-Induced Hydrogenation of Benzophenone

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*Summary: $Ge[CH(SiMe_3)_2]_2$ reacts with benzophenone to form a conjugated triene. Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, is an effective precatalyst for the isomerization of one double bond and hydrogenation of a second double bond of this triene. This reaction demonstrates that germylene activation of the phenone moiety yields reactive double bonds amenable to catalytic transformation, even with bulky catalysts such as the presumed active form of Wilkinson's catalyst, $Rh(PPh_3)_2Cl$.*

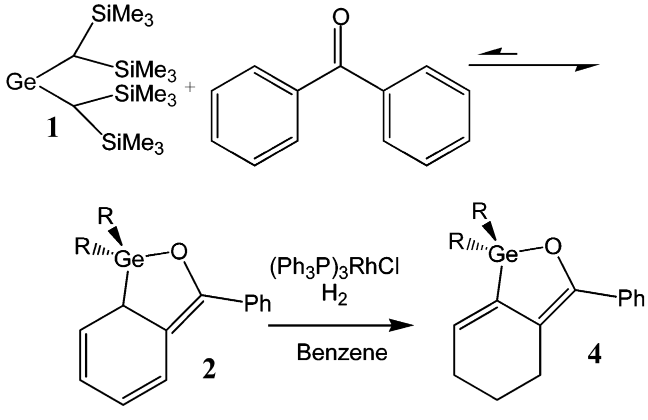
## Introduction

Aromatic double bonds exhibit a greater degree of stability than standard double bonds, even when two or three such bonds are in conjugation. Thus, a number of interesting organic reactions either are more difficult when applied to an aromatic system (for example, hydrogenation) or have met with only limited success (such as the Diels−Alder reaction).[1−3] Activation of aromatic rings for a wider range of reactivity could take a number of forms, including (1) allowing the reaction of interest to occur, (2) controlling the number and/or location of the reactive double bonds on the ring, and (3) differentiation of multiple aromatic rings.

We have recently reported the activation of a variety of phenones using $Ge[CH(SiMe_3)_2]_2$ (**1**) to give the conjugated triene **2** (Scheme 1).[4] This activated phenone is structurally prepared to undergo a variety of standard organic reactions. However, the presence of an equilibrium between **2**, free benzophenone, and **1** complicates reaction design.[4,5] Although the equilibrium heavily favors **2** (it is the only species observed in the $^1H$ NMR and UV/vis spectra), reaction with free germylene occurs over several hours upon the addition of typical germylene traps (benzil, dienes, alkynes) to a solution of **2**. For example, addition of 1.05 equiv of benzil to a 0.04 M solution of **2** in benzene resulted in quantitative formation of benzophenone and benzil-trapped germylene in 4 h. Therefore, a successful reaction design must include reagents that are inert toward **1** or undergo reaction with one or more double bonds of **2** more quickly than formation of free **1** from the equilibrium shown in Scheme 1.

## Results and Discussion

**Scheme 1. Activation of Benzophenone to Form a Conjugated Triene Followed by Catalytic Hydrogenation of One of the Double Bonds**



Addition of 1 equiv of benzophenone to a solution of **1** in benzene at 20 °C results in the orange color of the germylene fading within 2 min to generate a yellow color indicative of the quantitative formation of **2**. Addition of 8 mol % of Wilkinson's catalyst, $Rh(PPh_3)_3Cl$ (**3**), and 3 atm of hydrogen gas results in a partial hydrogenation to give **4** (Scheme 1). The $^1H$ NMR and $^{13}C$ NMR spectra of **4** suggest hydrogenation of a single double bond of the activated phenyl ring along with an internal isomerization. A single-crystal X-ray diffraction study supports this assignment (Figure 1.) The bond lengths of the activated ring indicate single bonds of 1.503−1.538 Å along with two remaining double bonds of 1.338(2) Å (C1−C2) and 1.356(2) Å (C6−C7). Further hydrogenation of the two remaining double bonds is likely prevented by steric constraints of the germylene. The unactivated phenyl group is not hydrogenated, as **3** is incapable of directly hydrogenating aromatic rings. Unlike **2**, compound **4** is not in equilibrium with **1** and the corresponding ketone.

This hydrogenation reaction succeeds by having a substantially faster rate of reaction than the equilibrium liberating free **1**. In the absence of benzophenone, **1** is catalytically hydrogenated by **3** to the germane $H_2Ge[CH(SiMe_3)_2]_2$. In addition, the catalyst itself can react directly with **1** by undergoing ligand exchange to lose a phosphine, as reported by Lappert.[6] Neither of these other products is observed.

Catalytic deuteration of **2** with 3 atm of $D_2$ leads to incorporation of three deuterium atoms. One D is located on each of the newly formed methylene groups on the hydrogenated ring (C3−C5), as determined by both $^1H$ and $^{13}C$ NMR spectroscopy. The peaks in the

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10.1021/om034025t CCC: $25.00
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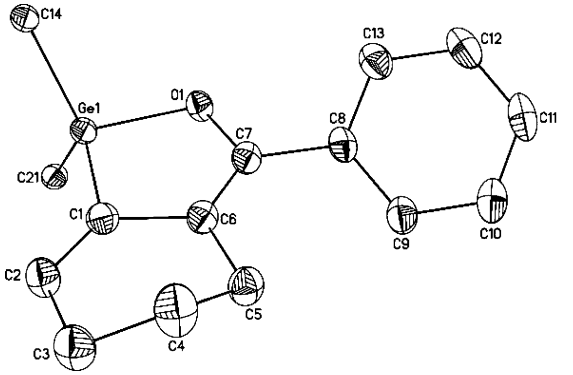
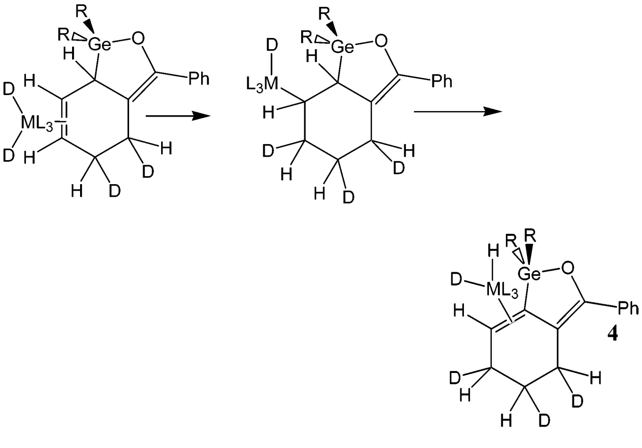


**Figure 1.** ORTEP structure of **4-$d_3$** with $Si(CH_3)_3$ omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1−O1 = 1.8441(10), Ge1−C1 = 1.9400(15), C1−C2 = 1.338(2), C2−C3 = 1.510(2), C4−C5 = 1.506(2), C1−C6 = 1.467(2), C6−C7 = 1.356(2); O1−Ge10−C1 = 89.76(6), C2−C1−C6 = 122.25(14). Thermal ellipsoids at 50% probability.

**Scheme 2. Proposed Stepwise Mechanism for Addition of a Third Deuterium Atom Combined with Double-Bond Isomerization**



$^1H$ NMR spectrum of the deuterated materials show a 50% intensity decrease for each of the methylene carbons. Additionally, an increase in the complexity of the splitting pattern is observed due to H−D coupling. The proton-decoupled $^{13}C$ NMR spectrum shows C−D coupling of 17−20 Hz for the three $CH_2$ peaks present. The IR spectrum indicated D incorporation with bands observed at 2170 and 2037 cm$^{-1}$ correlating to $\nu$(C−D).

Literature precedence suggests the isomerization step occurs via a migratory insertion followed by $\beta$-hydride elimination (Scheme 2).[7,8] This mechanism of isomerization ensures that deuterium is incorporated from the added $D_2$ gas. Equilibrium geometry calculations (B3LYP DFT, 6-31G*)[9] indicate a decrease in energy of 27 kJ/mol for such an isomerization. Scheme 2 illustrates the addition of the third deuterium and the isomerization after the double-bond hydrogenation step. However, it is also possible that the isomerization precedes the hydrogenation step. Although $\beta$-hydride elimination may occur during typical hydrogenations catalyzed by **3**, the double bond would usually be subsequently hydrogenated. In the case of **4**, further hydrogenation is not observed, possibly inhibited by the steric bulk of the bis(trimethylsilyl)methyl groups on the germanium.

The partial hydrogenation, catalyzed by Wilkinson's catalyst, of a triene generated from benzophenone is novel. However, the partial hydrogenation of aromatic and substituted aromatic compounds is well-documented. Hydrogenation of aromatic rings has been successfully accomplished,[10,11] even in the presence of a variety of functional groups.[12−14] Benzene can also be selectively hydrogenated to cyclohexene using a variety of rhodium catalysts with minimal functional group tolerance.[15] Selective hydrogenation of specific double bonds or the hydrogenation of only one aromatic ring when several are present has been far less successful. Hydrogenation of only one ring of multicyclic aromatics and selective hydrogenation of a single double bond of perinaphthylene or perianthracene have been accomplished using a rhodium cluster catalyst.[16,17]

## Experimental Section

**General Procedures. 1** was synthesized via literature procedures.[18] All reactions were carried out using standard dry benzene under an argon atmosphere.

**1,1-Bis(bis(trimethylsilyl)methyl)-3-phenyl-1,4,5,6-tetrahydrobenzo[*c*][1,2]oxagermole (4).** A glass bomb was charged with **1** (100 mg, 0.256 mmol) and benzophenone (46 mg, 0.25 mmol) in benzene (4 mL). Within 2 min the orange color of **1** faded, leaving a yellow color indicative of triene formation. Chlorotris(triphenylphosphine)rhodium (20 mg, 0.022 mmol, 8 mol %) was added to the solution. The solution was frozen at −78 °C and the headspace in the bomb evacuated. The bomb was back-filled with 3 atm of $H_2$. The solution was thawed and stirred at room temperature for 16 h. The volatile components were removed in vacuo, leaving a red residue that was dissolved in hexane and filtered through Celite to remove the catalyst. The solvent was removed to yield 98 mg of crude hydrogenated material (67% crude yield). The crude material (35 mg) was recrystallized from propionitrile (1.5 mL) to give 10.6 mg of analytically pure **4** (30% yield on recrystallization). $^1H$ NMR (400 MHz, $C_6D_6$): $\delta$ 7.80 (d, $^3J$(H,H) = 8.0 Hz, 2 H; Ar *H*), 7.23 (t, $^3J$(H,H) = 8.0 Hz, 2 H; Ar *H*), 7.10 (t, $^3J$(H,H) = 8.0 Hz, 1 H; Ar *H*), 6.03 (t, $^3J$(H,H) = 4.4 Hz, 1 H; C═C*H*), 2.57 (t, $^3J$(H,H) = 6.0 Hz, 2 H; C$H_2$), 2.09 (td, $^3J$(H,H) = 6.0 Hz, $^3J$(H,H) = 4.4 Hz, 2 H; C$H_2$), 1.56 (pseudo quintet, $^3J$(H,H) = 6.0 Hz, 2 H; C$H_2$), 0.30 (s, 18 H; $SiMe_3$), 0.23 (s, 18 H; $SiMe_3$), 0.16 (s, 2 H; GeC*H*Si). $^{13}C$ NMR (100.5 MHz, $C_6D_6$): $\delta$ 154.37, 142.83, 137.20, 131.44, 128.53, 128.13, 127.67, and 114.71 (Ar *C*═C), 27.44, 26.44, and 22.47 ($CH_2$), 12.33 (Ge*C*HSi), 3.46 and 3.33 ($SiMe_3$). IR (neat): $\nu$ 1661 cm$^{-1}$ (C═C). Anal. Calcd for $C_{27}H_{50}GeOSi_4$: C, 56.34; H, 8.75. Found: C, 56.02; H, 8.83.

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**1,1-Bis(bis(trimethylsilyl)methyl)-3-phenyl-1,4,5,6-tetrahydrobenzo[*c*][1,2]oxagermole-4,5,6-$d_3$ (4-$d_3$).** The synthesis was identical with that above, except $D_2$ was used in place of $H_2$. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.80 (d, $^3J$(H,H) = 8.0 Hz, 2 H; Ar *H*), 7.23 (t, $^3J$(H,H) = 8.0 Hz, 2 H; Ar *H*), 7.10 (t, $^3J$(H,H) = 8.0 Hz, 1 H; Ar *H*), 6.03 (d, $^3J$(H,H) = 4.4 Hz, 1 H; C═C*H*), 2.52 (m, 1 H; C$H_2$), 2.06 (m, 1 H; C$H_2$), 1.53 (m, 1 H; C$H_2$), 0.30 (s, 18 H; $SiMe_3$), 0.23 (s, 18 H; $SiMe_3$), 0.16 (s, 2 H; GeC*H*Si). $^{13}$C NMR (100.5 MHz, $C_6D_6$): $\delta$ 154.37, 142.90, 137.26, 131.43, 128.33, 128.13, 127.65, and 114.70 (Ar *C*═C), 27.28 (t, $^1J$(C,D) = 18 Hz), 25.95 (t, $^1J$(C,D) = 17 Hz), and 21.87 (t, $^1J$(C,D) = 20 Hz) (*C*$H_2$), 12.36 (Ge*C*HSi), 3.40 and 3.29 ($SiMe_3$). IR (neat): $\nu$ 2170, 2037 cm$^{-1}$ (C−D), 1662 cm$^{-1}$ (C═C). EI/MS: $[M]^+$ 579.333 au. Anal. Calcd for $C_{27}H_{47}D_3GeOSi_4$: C, 56.05; H/D, 8.71. Found: C, 56.25; H/D, 8.76.

**Structural Determination of 4.** Colorless blocks of **4-$d_3$** were grown from a propionitrile solution at 22 °C. Crystal data for **4-$d_3$** ($C_{27}H_{47}D_3GeOSi_4$): $M_r = 578.64$, $T = 118(2)$ K, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.3590(16)$ Å, $b = 11.6647(19)$ Å, $c = 15.660(3)$ Å, $\alpha = 100.674(3)°$, $\beta = 103.803(3)°$, $\gamma = 91.311(3)°$, $V = 1627.5(5)$ Å$^3$, $Z = 2$, $d$(calcd) = 1.181 g cm$^{-3}$, $\mu$ = 1.105 mm$^{-1}$, $\lambda$ = 0.710 73 Å, $2\theta_{max}$ = 56.68°, 16 189 measured reflections, 7941 independent reflections, 7174 reflections greater than $2\sigma(I)$, 310 refined parameters, GOF = 1.031, R1 = 0.0281, wR2 = 0.0720 ($I > 2\sigma(I)$), R1 = 0.0329, wR2 = 0.0748 (for all data), largest difference peak and hole 0.607 and −0.292 e Å$^{-3}$. A crystal of dimensions 0.22 × 0.22 × 0.16 mm was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with an LT-2 low-temperature device and normal-focus Mo-target X-ray tube operated at 2000 W power (50 kV, 40 mA). The detector was placed at a distance 4.950 cm from the crystal. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS[19] and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL[20] software package by full-matrix least-squares procedures on $F^2$ for all reflections. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The file CCDC-208103 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax (+44) 1223-336-033; email deposit@ccdc.cam.ac.uk).

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**Supporting Information Available:** Tables giving X-ray crystallographic data for compound **4**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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