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Silicon-Induced Phenanthrene Formation from Benzynes and Allenylsilanes

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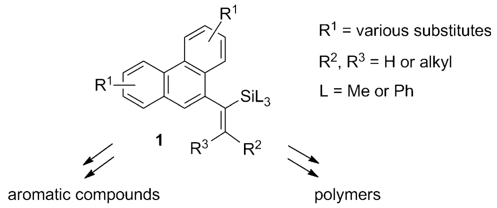
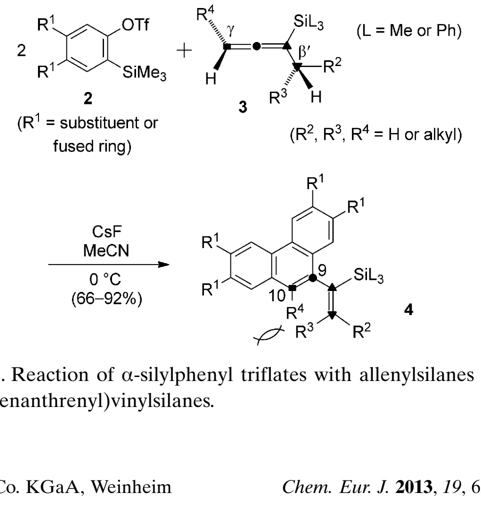
As an "angular" tricyclic aromatic hydrocarbon, phenanthrene appears as a white crystalline powder. Compounds in this family can be prepared by various methods that often require catalysts such as Pd and Ni salts.[1,2] For example, Cheng and co-workers[3] reported a new method for the synthesis of 10-methylene-9,10-dihydrophenanthrenes by Ni-catalyzed chemoselective cocyclization of arynes with allenes. Applicability of these metal-catalyzed reactions may be retarded by many disadvantages, such as the high cost of catalysts,[4] necessary prevention of air[5] or moisture,[6] requirement of multiple steps,[7,8] the resulting environmental issues, or the production of mixtures.[9] Compounds containing a phenanthrene moiety are found to play an essential role in the development of new materials. Examples include the use of a (phenanthrenyl)indole as a fluorescent probe for peptides and lipid membranes, as reported by Castanheira and co-workers;[10] tetraalkoxyphenanthrenes as precursors for luminescent conjugated polymers, as reported by MacLachlan and co-workers;[11] copolymers containing a phenanthrene group inserted along a polymer backbone with photoluminescence properties, as reported by Akcelrud and co-workers;[12] poly(phenanthrylene vinylene) as a light-emitting material for applications in electroluminescent devices, as reported by Bazan and co-workers;[13,14] and phenanthrene-based conjugated oligomers used as p-channel semiconductors in field-effect transistors, as reported by Geng and co-workers.[15] On the other hand, vinylsilanes react readily with a wide range of electrophiles to give products of addition or substitution.[16] The regiochemical outcome is normally unambiguous.[17] The combination of these two moieties working together (i.e., **1** in Scheme 1) would provide new avenues for the synthesis of aromatic compounds and polymers. Herein, we report the development of a new reaction that is induced by silicon and its application to the synthesis of (α-phenanthrenyl)vinylsilanes (**1**) with efficiency.



Scheme 1. Valuable-entity-containing moieties of phenanthrene and vinylsilane.

Our research group has been able to use the electronic effect of silicon to control different types of reactions. In 2001, a silicon-directed hydroxymethylation of β-silylcycloalkanone enol acetates by an electrochemical method was reported.[18] Silicon also directs the fragmentation of β-silylcycloalkanone radical cations by its β-stabilizing effect.[19] Moreover, silicon induces an ene-type reaction in the thermal conversion of enolates to β-silyl enones with molecular dioxygen.[20] By insertion into the backbone of polymers, silicon can induce photo-degradation of polyureas.[21]

To continue the study of silicon-directed, -induced, and -promoted reactions,[22] we found a way to directly obtain (phenanthrenyl)vinylsilanes **4** by reacting two equivalents of 2-(trimethylsilyl)phenyl triflates **2** with allenylsilanes **3**[23] in the presence of CsF and dry air at 0 °C for 8.0–10 h (Scheme 2). Various reactants were employed for the examination of the nature and character of the reaction (Table 1). The benzene nuclei of silylphenyl triflates **2** were attached to methyl groups or fused with 1,3-dioxole and cyclopentene rings (i.e., **2b–d**); the allenylsilanes[24] were attached with a methyl, ethyl, *n*-propyl, isopropyl, and *n*-butyl group at the



Scheme 2. Reaction of α-silylphenyl triflates with allenylsilanes to generate (α-phenanthrenyl)vinylsilanes.

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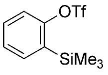
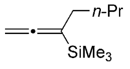
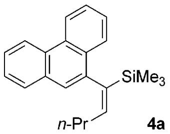
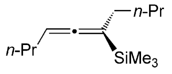
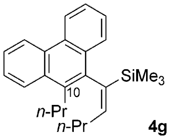
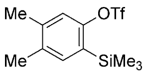
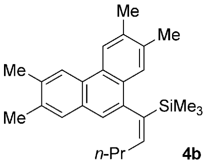
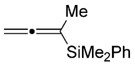
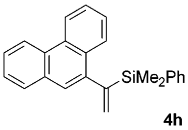
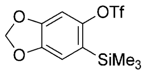
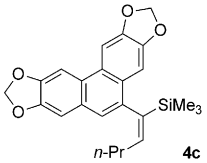
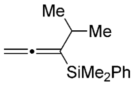
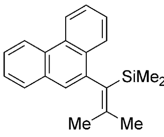
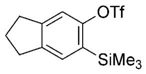
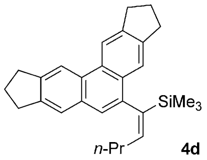
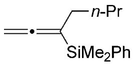
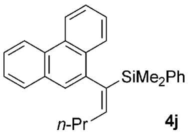
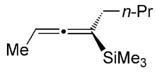
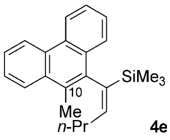
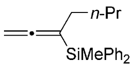
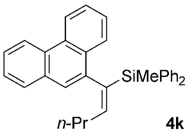
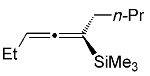
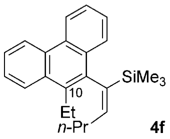
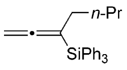
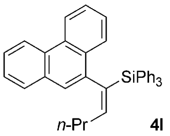
Table 1. Reactants **2** and **3**, products **4**, and the isolated yields of the new reaction.[a]

2	3	4	Yield [%]	Time [h]	2	3	4	Yield [%]	Time [h]
 **2a**	 **3a**	 **4a**	92	8	**2a**	 **3d**	 **4g**	78	8
 **2b**	**3a**	 **4b**	90	10	**2a**	 **3e**	 **4h**	82	8
 **2c**	**3a**	 **4c**	82	10	**2a**	 **3f**	 **4i**	81	8
 **2d**	**3a**	 **4d**	85	10	**2a**	 **3g**	 **4j**	92	8
 **2a**	 **3b**	 **4e**	83	8	**2a**	 **3h**	 **4k**	73	8
2a	 **3c**	 **4f**	80	8	**2a**	 **3i**	 **4l**	66	8

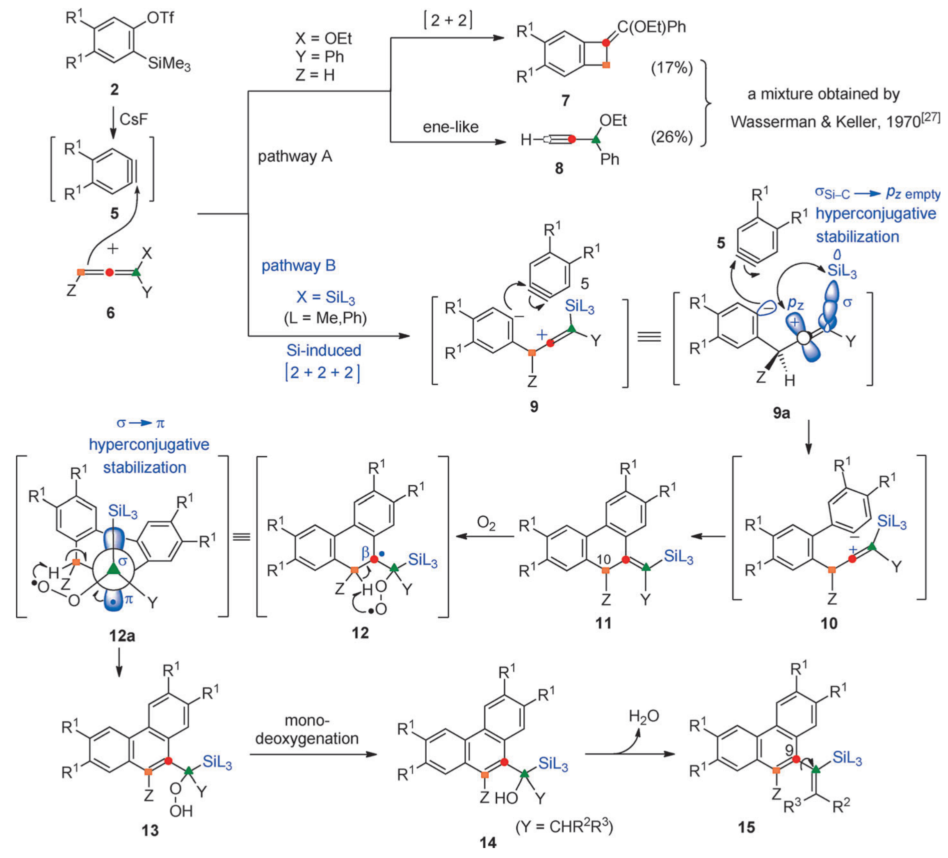
[a] A solution containing a sulfonate **2** (≈0.38 mmol, 1.0 equiv), an allenylsilane **3** (≈0.31 mmol, 0.8 equiv), and CsF (≈0.57 mmol, 1.5 equiv) in CH_3CN (2.5 mL) was stirred at 0 °C in the presence of dry air for 8.0–10 h.

α- or the γ-position (i.e., **3a**–**i**). Furthermore, the three ligands on the Si atom in **3** (i.e., $SiMe_3$, $SiMe_2Ph$, $SiMePh_2$, or $SiPh_3$) were altered. Sufficient yields between 66–92 % were obtained for all of these reactions. In contrast, when the triflate **2a** was treated with the norsilyl compound *n*-butylallene instead of an allenylsilane **3** under the same conditions, as shown in Scheme 2, a mixture containing three major fractions was produced. None of them was detected by GC-MS to have an exact mass around 246.14, which would correlate with the desired norsilyl phenanthrene.

The γ and β′ positions of allenylsilanes **3** must both contain a hydrogen atom to make the annulation possible. These two hydrogen atoms were sacrificed during the aromatization and the subsequent formation of the conjugated carbon–carbon double bond, respectively.

A plausible mechanism, illustrated in Scheme 3, takes into account the essential roles played by the Si atom in allenylsilanes. A benzyne (**5**) is first generated by 1,2-elimination of a silylphenyl triflate (**2**) with CsF.[25,26] Wasserman and Keller[27] reported that reaction of benzyne with allenes **6** (without a silyl group) gives a mixture of a cyclobutane derivative **7** through a [2+2] cycloaddition and an acetylene **8** through an ene-like reaction (see pathway A). Many novel metal free carbon–carbon bond forming methods involving aryne chemistry have also been developed and applied in organic syntheses.[28]

In contrast to the pathway A involving norsilylallenes, arylated zwitterionic adducts **9** are generated as intermediates through pathway B by use of allenes **6** that are attached directly to an SiL_3 group. The driving force is that the vinyl cationic intermediates **9a** can be stabilized by the β-silyl group through the "$\sigma_{SiC} \rightarrow p_{z\,\text{empty}}$ hyperconjugation."[29] As a result, it may offer a considerable length of time[30] for **9** (also **9a**) to react with the second molecule of benzynes **5**. Annulation then takes place on the resultant biphenyl intermediates **10** to form the tricycles **11**. Its formation is supported by the performance of the same reaction in a spinning NMR tube containing triflate **2a** and allenylsilane **3b** in deuterated acetonitrile without oxygen gas. A quartet with coupling of $J = 7.2$ Hz was detected at $\delta = 3.45$ ppm for the C(10) proton of the dihydrophenanthrene **11** and a doublet with coupling of $J = 7.2$ Hz at $\delta = 1.57$ ppm for three



Scheme 3. A plausible mechanism for the oxidative annulation to form phenanthrenes.

protons of the methyl group (i.e., Z) attached to the C(10) position in the ^{1}H NMR spectrum was also observed. These chemical shifts and the coupling constants are consistent with those of related compounds reported in the literature.[3]

The intermediates **11** then undergo an oxidative aromatization by reacting with molecular oxygen. Once again, the silyl group plays a stabilization role; it exerts the "σ→π hyperconjugation"[31] on the β-carboradical center in the intermediates **12** (cf. **12a**). Subsequently, an intramolecular hydrogen transfer takes place from a benzylic carbon atom to an oxygen atom through a six-membered ring transition state. Monodeoxygenation[32] occurs in the resultant peroxides **13** to afford benzylic alcohols **14**. Finally, compounds **14** undergo dehydration in situ to give the final products **15**. The intrinsic stabilizing ability of the silyl groups greatly contributes to the arene formation.

In a control experiment, the same arene formation reaction was performed under nitrogen gas. This reaction mixture was monitored by TLC, which showed several spots after 10 h. Further exposure of the reaction mixture to air gradually strengthened the spot associated with the desired products **4**. These results provide evidence to support the oxidative aromatization mechanism shown in Scheme 3, in which the O_2 gas was essential.

To confirm the structure and regiochemistry of (α-phenanthrenyl)vinylsilanes **4**, we unambiguously determined the molecular framework of compound **4c** by using single-crystal X-ray diffraction analysis (see Figure 1a). The monoclinic crystals (m.p. 191–192 °C, dichloromethane) possessed the space group $C2/c$ with $a = 36.560(12)$ Å, $b = 7.831(3)$ Å, $c = 15.907(5)$ Å, $\alpha = 90°$, $\beta = 103.960(6)°$, and $\gamma = 90°$. The X-ray data indicate that the $SiMe_3$ group therein was trans to the *n*-propyl group. In the ^{1}H NMR spectrum, a characteristic triplet with coupling of $J = 6.8$ Hz occurred at $\delta = 6.216$ ppm for the SiC=CH proton and a singlet at $\delta = 7.015$ ppm for the phenanthrene-C(10)H proton. Furthermore, the SiC=CH resonance was saturated in a Nuclear Overhauser Enhancement (NOE) experiment, which led to a 6.08 % enhancement of the $Si(CH_3)_3$ peak. Conversely, saturation of the $Si(CH_3)_3$ resonance led to a 0.85 % enhancement of SiC=CH peak. These NOE results confirmed the cis relationship between the vinylic proton and the $Si(CH_3)_3$ group in compound **4c**. Meanwhile, two sets of doublets of triplets (coupling of $J^2 = 4.8$ and $J^3 = 12.6$ Hz) were detected in the ^{1}H NMR spectrum of **4g** for the two protons of the CH_2 attached to the phenanthrene-C(10) position. As shown in Figure 1b, obtained by the consistent-valence force field (CVFF) computation of compound **4g**, steric congestion existed between the two propyl groups attached to the phenanthrenyl and the vinyl groups. Resulting from the vinyl-C(9) single bond rotation (cf. structure **15**), the dihedral angle was found 82.04° between the plane of phenanthrene and the plane defined by the SiC=CH moiety in **4g**. It might be the cause of the non-equivalency of these two protons.

Four advantages are associated with this newly invented reaction: 1) The starting materials were versatile; benzynes and allenylsilanes with various substituents and ligands were adaptable to generation of the desired products; 2) (α-Phenanthrenyl)vinylsilanes were produced exclusively as the *E*-isomers; often the methods for the generation of vinylsilanes lead to a mixture of *E*- and *Z*-isomers;[33,34] 3) No catalysts were required in our reaction for the phenanthrenes formation; other examples usually need catalysts such as $CuBr_2$,[35] CuI,[36] $NiBr_2$(dppe),[3] and Pd with various ligands;[37,38] 4) The new reaction provided products in good yields (66–92 %), which were higher than those associated with the metal-catalyzed[3,39] cyclizations in the formation of phenanthrenes from benzynes and (norsilyl)allenes (29–77 %).

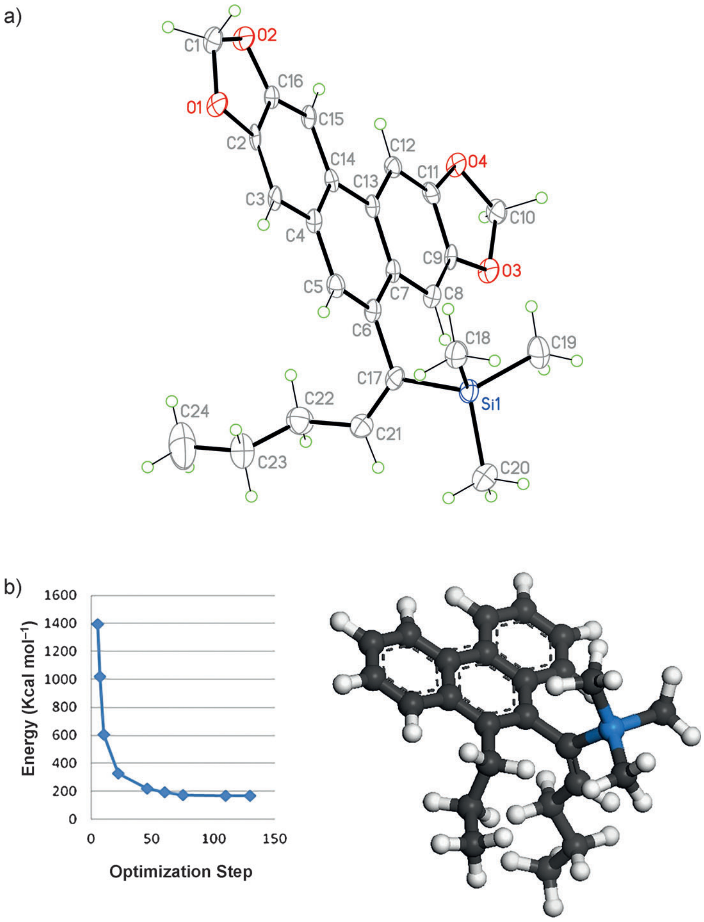


Figure 1. a) ORTEP diagram of **4c** obtained by X-ray analysis. b) Severe steric congestion existed in compound **4g**, of which the thermodynamically most stable conformation was obtained by the CVFF calculation. Its minimization process with quantified energy is shown in the left bottom corner. CCDC-884621 (**4c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.[a]

In conclusion, an efficient method for the direct synthesis of various phenanthrenes with a vinylsilane moiety starting from two equivalents of benzynes and one equivalent of allenylsilanes was developed. It involved a new silicon-induced reaction, which proceeded through a [2+2+2] pathway. The success was attributed to the stabilizing capability of a silicon on a β vinyl carbocation by the $\sigma_{\text{SiC}}\rightarrow p_{z\,\text{empty}}$ hyperconjugation and, subsequently, on a β carboradical by the σ→π hyperconjugation. Without the need for a catalyst, this reaction led to the desired products in good-to-excellent yields with high regioselectivity under mild conditions.

Acknowledgements

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Keywords: allenylsilanes · arenes · benzynes · phenanthrenes · silicon

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