

Oxidation

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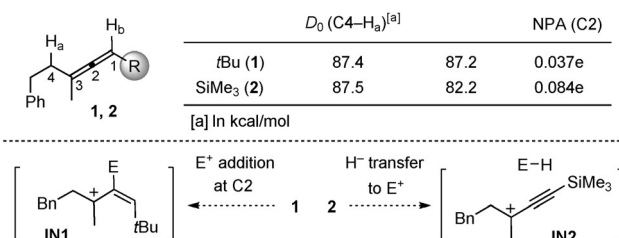
Complementary Iron(II)-Catalyzed Oxidative Transformations of Allenes with Different Oxidants

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Abstract: Substituent- and oxidant-dependent transformations of allenes are described. Given the profound influence of the substituent on the reactivity of allenes, the subtle differences in allene structures are manifested in the formation of diverse products when reacted with different electrophiles/oxidants. In general, reactions of nonsilylated allenes involve an allylic cation intermediate by forming a C–O bond, at the *sp*-hybridized C2, with either DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) or TBHP (tert-butyl hydroperoxide), along with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (10 mol %). In contrast, silylated allenes favor the formation of propargylic cation intermediates by transferring the allenic hydride to the oxidant, thus generating 1,3-enynes (E1 product) or propargylic THBP ethers (S_N1 product). The formation of these different putative cationic intermediates from nonsilylated and silylated allenes is strongly supported by DFT calculations.

Our recent investigations on new reactivity of allenes revealed that the silyl substituent has profound influence on their reaction course.^[1,2] For example, in the Alder ene reaction, the allenic $\text{C}(\text{sp}^2)\text{--H}$ bond is more active than allylic $\text{C}(\text{sp}^3)\text{--H}$ bonds.^[2] Density-functional theory (DFT) calculations revealed that the main source of this unexpected reactivity is the weakening of the allenic $\text{C}(\text{sp}^2)\text{--H}$ bond (Scheme 1). Compared to the nonsilylated allene **1**, the corresponding silylated counterpart **2** has an unusually weak $\text{C}(\text{sp}^2)\text{--H}$ bond ($82.2 \text{ kcal mol}^{-1}$), which is even lower than that of a typical allylic $\text{C}(\text{sp}^3)\text{--H}$ bond by 5 kcal mol^{-1} . In addition, the natural population analysis (NPA) indicates that the *sp*-hybridized C2 in **2** imparts significantly less positive charge relative to that of **1** and may cause the formation of complementary cationic intermediates such as **IN1** and **IN2** by different reagents.^[3,4] Therefore, depending on the choice of electrophiles or oxidants, the subtle difference in reactivity of structurally different allenes can be manifested to generate different final products.

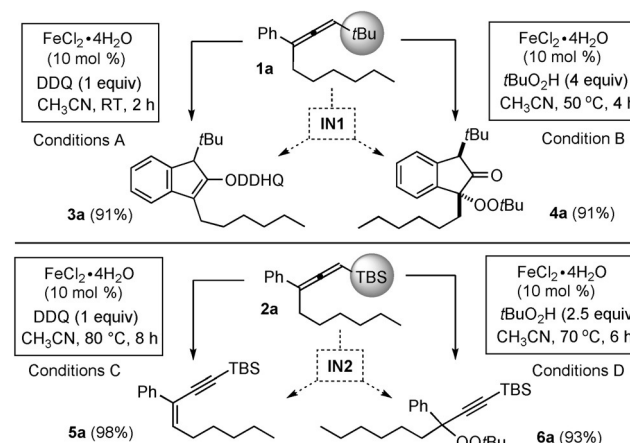
Described herein are clear demonstrations of novel complementary reactivity of allenes under different reaction



Scheme 1. Polar reaction versus single-electron-transfer processes of electron-rich allenes.

conditions to generate structurally diverse oxidation products. In general, nonsilylated allenes provided products by traditional reaction pathways involving the cation intermediate **IN1**, whereas the corresponding silylated counterparts lead to either E1 or S_N1 products by unprecedented oxidation pathways involving the propargylic cation intermediate **IN2**. The mechanistic aspects of these two different modes of reactions were further verified by DFT calculations.

Differentiation of the reactivity between **1a** and **2a** was investigated with two different oxidants, DDQ and TBHP, under iron-catalyzed reaction conditions (Scheme 2).^[5–7]



Scheme 2. Initial proof of complementary reactivity of nonsilylated and silylated allenes with DDQ. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, TBS = *tert*-butyldimethylsilyl.

Through brief optimization (see the Supporting Information), it was found that treating **1a** with DDQ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ as the catalyst (Conditions A) generated the indene derivative **3a** (91%).^[8,9] In contrast, by replacing DDQ with TBHP and using a slightly higher temperature (Conditions B), a single

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diastereomer of the α -peroxy indanone **4a** was obtained (91 %). Under similar reaction conditions, the silylated allene **2a** afforded 1,3-enyne **5a** as a single isomer (98 %) with DDQ (Conditions C),^[10] whereas with TBHP (Conditions D), the corresponding propargylic peroxy ether **6a** was obtained (93 %).

On the basis of these diverse reactivities, we further explored a series of phenyl-group-containing trisubstituted allenes^[11] under Conditions A (Table 1). Both *gem*-phenyl,-

Table 1: Iron-catalyzed reaction of alkyl,aryl-substituted allenes with DDQ.

$\text{Ph}-\text{C}(\text{R}^1)=\text{C}(\text{R}^2)=\text{CH}_2 \xrightarrow[\text{CH}_3\text{CN, RT, 2 h}]{\text{Conditions A: FeCl}_2 \cdot 4\text{H}_2\text{O (10 mol \%), DDQ (1 equiv)}} \text{Product}$			
Entry	Allene	Product	Yield [%] ^[a]
1	1b , R = H	3b	76
2	1c , R = Ph	3c	88
3	1d , R = CH ₂ CH ₂ OTBS	3d	81
4	1e	3e and 3e'	84
5	1f , R = <i>t</i> Bu; 1g , R = Ph	3f , 3g (not observed) ^[c]	—
6	1h	3h and 3h' ^[d]	78
7	1i , R = <i>t</i> Bu	3i	85
8	1j , R = Et	3j	93
9	1k , Ar = 4-FC ₆ H ₄	3k and 3k'	92
10	1l , Ar = 4-MeOC ₆ H ₄	3l and 3l'	78
11	1m	3m	92

[a] Yield of isolated product. [b] The ratio was determined by ¹H NMR analysis. [c] Recovered starting material. [d] During purification **3h** was further oxidized to the corresponding naphthalene derivative **3h'** (ca. 10%).

methyl- (**1b**) and *gem*-phenyl,benzyl-substituted (**1c**) allenes provided **3b'** and **3c'**, respectively, as a minor component together with the major products **3b** and **3c** (entries 1 and 2), whereas **1d**, containing a ω -silyloxypropyl group, provided **3d** exclusively (entry 3). When a competing nucleophile such as a hydroxy group exists on the allene, it participated preferentially over the phenyl group, thus generating a mixture of **3e** and **3e'** in a 1:6.5 ratio (entry 4). The disubstituted allenes **1f** and **1g** having a *tert*-butyl and phenyl group, respectively,

did not afford the corresponding products **3f** and **3g**; instead the starting material was recovered (entry 5). The cycloalkyl-based allene **1h** afforded the DDQ-incorporated 1,3-diene **3h** (entry 6). The *gem*-diphenyl-substituted allenes **1i** and **1j**, bearing *tert*-butyl and ethyl groups, respectively, behaved similarly, thus generating the corresponding **3i** (85 %) and **3j** (93%; entries 7 and 8). The unsymmetrical *gem*-diphenyl-substituted allenes **1k** and **1l**, carrying *p*-fluoro and *p*-methoxy substituent, respectively, provided the corresponding mixtures of **3k**/**3k'** (10:1) and **3l**/**3l'** (1:3.5), thus showing the preferential participation of the more electron-rich aryl group (entries 9 and 10). This preference was further demonstrated by the allene **1m**, having phenyl and 3,4,5-trimethoxyphenyl groups, and it exclusively afforded the indene derivative **3m** (entry 11).

We further examined the reactivity of these phenyl-substituted allenes^[11] under reaction Conditions B (Table 2).

Table 2: Reactions of alkyl,aryl-substituted allenes with TBHP.

$\text{Ph}-\text{C}(\text{R}^1)=\text{C}(\text{R}^2)=\text{CH}_2 \xrightarrow[\text{CH}_3\text{CN, 50 }^\circ\text{C, 4 h}]{\text{Conditions B: FeCl}_2 \cdot 4\text{H}_2\text{O (10 mol \%), tBuO}_2\text{H (4 equiv)}} \text{Product}$			
Entry	Allene	Product	Yield [%] ^[a,b]
1	1b , R = CH ₃	4b	83
2	1i , R = Ph	4i (X-ray)	91
3	1m	4m	89
4	1k	4k and 4k'	80
5	1n , R ¹ = Me, R ² = H	4n	58
6	1o , R ¹ = H, R ² = H	4o	52
7	1p , R ¹ = Me, R ² = OMe	4p	56

[a] Yield of product after purification. [b] Single diastereomer was observed.

The *gem*-phenyl,methyl- and *gem*-diphenyl-substituted allenes **1b**, **1j**, and **1m** afforded the corresponding propargylic peroxy ethers **4b**, **4i**, and **4m** in excellent yields (entries 1–3). For the allene **1k**, containing phenyl and 4-fluorophenyl groups, the isomeric products **4k** and **4k'** were generated in a 1:1 ratio (entry 4). The allenes **1n–p**, bearing a cinnamyl group, provided the cyclopentenone derivatives **4n–p** without incorporation of peroxy ether in marginal yields (entries 5–7). In all cases a single diastereomer was obtained. The relative stereochemistry of the

product **4i** was confirmed unambiguously by X-ray diffraction analysis.^[12]

Next, we investigated the reaction profiles of structurally diversified silylated allenes^[13] under reaction Conditions C (Table 3). Unsymmetrically substituted silylated allenes (**2b**–

Table 3: Iron-catalyzed oxidative transformation of silyl allenes with DDQ.

Entry	Silyllallene	Product	Yield [%] ^[a]
1	2b , SiR ₃ = SiEt ₃	5b (1 : 1) ^[b]	62
2	2c , SiR ₃ = SiMe ₂ tBu	5c (1.6 : 1) ^[b]	82
3	2d , SiR ₃ = Si <i>i</i> Pr ₃	5d (1.6 : 1) ^[b]	75
4	2e	5e	36 ^[c]
5	2f	5f	64
6	2g	5g	67
7	2h	5h	78
8	2i , <i>n</i> = 7	5i	73
9	2j , <i>n</i> = 12	5j	75
10	2k , <i>n</i> = 15	5k	74

[a] Yield of isolated product. [b] The ratio was determined by ¹H NMR analysis. [c] The low yield was due to its volatility.

e) afforded the regioisomeric 1,3-enynes **5b–e**, where different silyl groups (TES, TBS, TIPS) have little influence on the yields (entries 1–3). The cyclopropyl-substituted allene **2e** afforded the 1,3-enyne **5e** in low yield, which is mainly due to its volatility (entry 4). The symmetrical cyclic *gem*-dialkyl-substituted allenes **2f–k** provided the corresponding 1,3-enynes **5f–k** as the only products in good yield (entries 5–11).

The reactivity of these silylated allenes^[13] was further explored under the reaction Conditions D (Table 4). Different silylated allenes, **2b** (SiEt₃), **2c** (SiMe₂tBu), and **2d** (Si*i*Pr₃), reacted smoothly to provide the corresponding propargylic peroxides **6b**, **6c**, and **6d** in good yields (entries 1, 2 and 3). While the cyclopropyl allene **2e** delivered the *tert*-butyl propargylic peroxide **6e** in 70% yield (entry 4), the silyllallene **2l** led to the propargylic peroxide **6l** in excellent yields (entry 5). The silylated allene **2m**, with a prenyl group, formed only the corresponding propargylic peroxide product **6m** in moderate yield, without a change to the double bond in the prenyl group (entry 6). The silylated allenes **2f**, **2n**, **2i**, **2o**, **2j**, **2k**, and **2p** reacted smoothly to provide corresponding

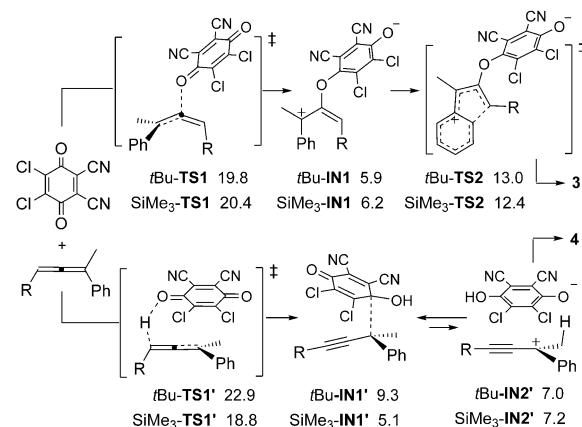
Table 4: Iron-catalyzed oxidative transformation of silyl allene and TBHP.

Entry	Silyllallene	Product	Yield [%] ^[a]
1	2b , Silyl = SiEt ₃	6b	73
2	2c , Silyl = SiMe ₂ tBu	6c	93
3	2d , Silyl = Si <i>i</i> Pr ₃	6d	82
4	2e , R =	6e	70
5	2l , R =	6l	93
6	2m , R =	6m	93
7	2f , <i>n</i> = 1	6f	72
8	2n , <i>n</i> = 2	6n	88
9	2i , <i>n</i> = 3	6i	85
10	2o , <i>n</i> = 4	6o	82
11	2j , <i>n</i> = 7	6j	73
12	2k , <i>n</i> = 10	6k	89
13	2p	6p (X-ray)	56

[a] Yield of isolated product.

propargylic *tert*-butyl propargylic peroxides **6f**, **6n**, **6i**, **6o**, **6j**, **6k**, and **6p**^[12] in excellent yields (entries 7–13).

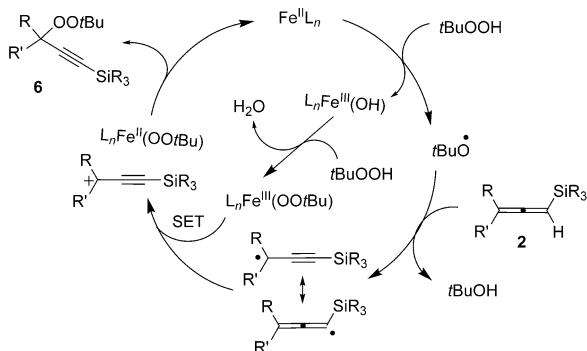
To gain insight into the reactivity and selectivity of these allene-based transformations, DFT calculations were carried out (Scheme 3). For nonsilylated allenes, clearly the *t*Bu-TS1



Scheme 3. Mechanisms for the transformations of alkyl- and silyl-substituted allenes with DDQ (relative free energies (in kcal mol^{−1}) were calculated at the M06-2X/6-31 + G* level of theory; details are given in the Supporting Information).

(19.8 kcal mol⁻¹), with DDQ interacting at C2 to generate an allylic cation,^[11] *t*Bu-**IN1** (5.9 kcal mol⁻¹), is significantly more favorable than its reaction via *t*Bu-**TS1'** (22.9 kcal mol⁻¹) by a hydride transfer to generate *t*Bu-**IN1'** (9.3 kcal mol⁻¹). In contrast, silylated allenes show the opposite preference. The transition-state SiMe₃-**TS1'** (18.8 kcal mol⁻¹), resulting from a hydride transfer to generate SiMe₃-**IN1'** (5.1 kcal mol⁻¹), is lower in energy by 1.6 kcal mol⁻¹ than that of SiMe₃-**TS1** (20.4 kcal mol⁻¹), where DDQ interacts at C2 to generate SiMe₃-**IN1** (6.2 kcal mol⁻¹).^[14] These energy profiles of the initial bond-forming step leading to different products clearly support the observed mode-selective reactions of nonsilylated allenes.^[15,16]

A plausible mechanism for this iron-catalyzed propargylic peroxide formation is proposed in Scheme 4. Initial Fe^{II}-promoted homolytic cleavage of the weak O–O bond would



Scheme 4. Mechanism of iron-catalyzed reaction of silyl allenes.

generate a *tert*-butoxyl radical,^[5] which abstracts the allenic C(sp²)-H hydrogen from the substrate **2** to generate a propargylic radical. The resulting carbon-centered propargylic radical then undergoes an electron-transfer process with Fe^{III}-OO*t*Bu to give the propargylic cation and [Fe^{II}-OO*t*Bu], which then form the observed *tert*-butyl propargylic peroxides^[7b] **6** and regenerate the Fe^{II} catalyst. However, formation of the –OO*t*Bu bond directly by the initially forming a carbon-centered propargyl radical and a either a free or metal-bound *tert*-butylperoxyl radical cannot be excluded.^[7f,g]

In conclusion, we have discovered efficient and mode-specific reactions of nonsilylated and silylated allenes with DDQ and/or *t*BuOOH in the presence of an iron catalyst. Trisubstituted allenes containing geminal aryl-aryl or aryl-alkyl substitution patterns provide indene/indanone derivatives. In contrast, silyl-substituted allenes, regardless of the nature of the other substituents, consistently generate 1,3-enynes as the major products with DDQ, and *tert*-butyl propargylic peroxides with *t*BuOOH. The DFT-calculated energy profiles associated the initial bond-forming step in each reaction pathway nicely justify the experimental observations.

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