# Allenes from ynals

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**Abstract**—Hydrosilylation of ynals with triethylsilane is catalyzed by $RhCl(PPh_3)_3$ and leads to $\alpha$-triethylsilyl enals. Addition of aryl Grignard reagents takes place to give secondary allylic alcohols which are easily converted to 1,3-disubstituted allenes. © 2001 Elsevier Science Ltd. All rights reserved.

An interest in the chemistry and synthesis of allenes[1] led us to consider the approach which is summarized in Scheme 1. If the catalytic hydrosilylation reaction of ynal **1** produced isomeric $\alpha$-silyl enals **2** or **3**, both geometrical isomers could be converted to the same allene **5** through intermediate **4**, the product of Grignard addition to the aldehyde carbonyl group. A number of elimination processes could then be considered for the conversion of **4** to 1,3-disubstituted allenes **5**. The proposed approach is a member of a general family of reactions in which elimination of X and Y from vinylic precursor **6** leads to allene **5**. The most common mechanism for the allene-forming step is either a reductive elimination of X–Y,[2] or a nucleophilic addition to X, followed by elimination of $Y^-$.[3] Where X is halogen, metal–halogen exchange to form a vinyl metal intermediate, followed by expulsion of $Y^-$, also has been used to produce allenes.[4,5]

In early work, Chan and co-workers described a synthesis of *terminal* allenes from the adducts of $\alpha$-triphenylsilylvinyllithium with aldehydes and ketones.[3d,e] In a conceptually related study, Konoike and Araki described a synthesis of chiral, non-racemic allenes from $\alpha$-tri-*n*-butylstannyl allylic alcohols.[3b] Our goals were to develop a convenient means to access a series of 1,3-disubstituted allenes, and to avoid the use of tin-containing intermediates. Our results are discussed in what follows.

Journet's excellent method furnished products **1** in high yield.[6] Although the catalytic hydrosilylation of enones and enoates is very well developed, we were not aware of a specific example of the hydrosilylation of an $\alpha,\beta$-acetylenic aldehyde.[7] In the event, hydrosilylation of 3-cyclohexylprop-2-ynal (**1**, $R^1$ = cyclohexyl) took place during 4 h at 45°C in the presence of 1 mol%
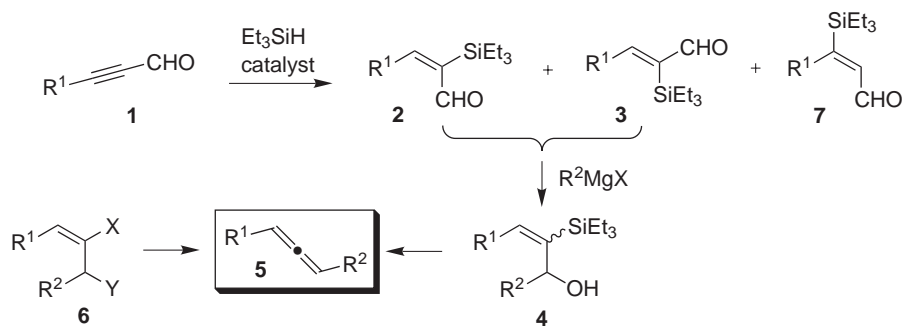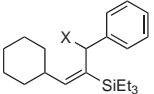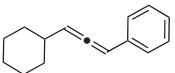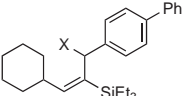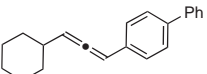


**Scheme 1.**
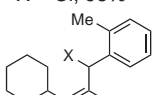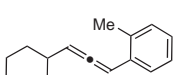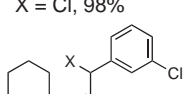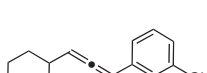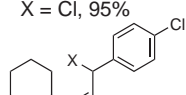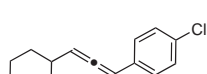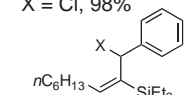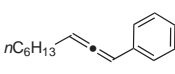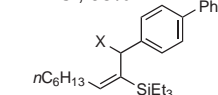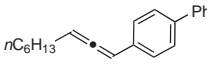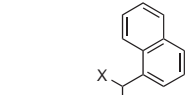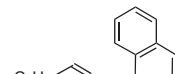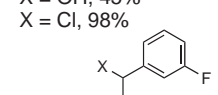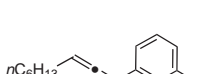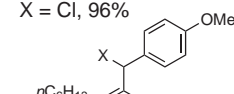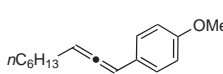
RhCl(PPh$_3$)$_3$ (Wilkinson's catalyst) in neat triethylsilane to give **2** (R$^1$=cyclohexyl) as the only product detected by $^1$H NMR at 300 MHz, after filtration through Celite followed by concentration. On the other hand, hydro-

**Table 1.** Allenes[a]

| | | | $^{13}$C NMR C(sp) | $^1$H NMR H-C(sp$^2$) | IR C=C=C |
|---|---|---|---|---|---|
| **1** | X = OH, 56%; X = Cl, 95% | 88% | 204.1 | 6.15 (dd, $J$ = 6.3, 2.9 Hz, 1H) 5.56 (dd, $J$ = 6.3, 6.3 Hz, 1H) | 1950 cm$^{-1}$ |
| **2** | X = OH, 55%; X = Cl, 98% | 85% | 204.4 | 6.21 (dd, $J$ = 6.3, 2.9 Hz, 1H) 5.61 (dd, $J$ = 6.3, 6.3 Hz, 1H) | 1950 cm$^{-1}$ |
| **3** | X = OH, 52%; X = Cl, 98% | 85% | 204.8 | 6.34 (dd, $J$ = 6.4, 3.1 Hz, 1H) 5.52 (dd, $J$ = 6.4, 6.4 Hz, 1H) | 1950 cm$^{-1}$ |
| **4** | X = OH, 50%; X = Cl, 95% | 83% | 204.5 | 6.10 (dd, $J$ = 6.3, 2.9 Hz, 1H) 5.60 (dd, $J$ = 6.3, 6.3 Hz, 1H) | 1950 cm$^{-1}$ |
| **5** | X = OH, 55%; X = Cl, 98% | 90% | 204.2 | 6.12 (dd, $J$ = 6.3, 3.1 Hz, 1H) 5.58 (dd, $J$ = 6.3, 6.3 Hz, 1H) | 1950 cm$^{-1}$ |
| **6** | X = OH, 50%; X = Cl, 98% | 86% | 205.2 | 6.12 (dt, $J$ = 6.4, 3.1 Hz, 1H) 5.57 (dt, $J$ = 6.4, 6.4 Hz, 1H) | 1945 cm$^{-1}$ |
| **7** | X = OH, 48%; X = Cl, 97% | 86% | 206.6 | 6.19 (dt, $J$ = 6.5, 2.9 Hz, 1H) 5.62 (dt, $J$ = 6.5, 6.5 Hz, 1H) | 1950 cm$^{-1}$ |
| **8** | X = OH, 45%; X = Cl, 98% | 82% | 205.6 | 6.83 (dt, $J$ = 6.6, 2.9 Hz, 1H) 5.61 (dt, $J$ = 6.6, 6.6 Hz, 1H) | 1945 cm$^{-1}$ |
| **9** | X = OH, 47%; X = Cl, 96% | 82% | 205.4 | 6.01 (dd, $J$ = 6.6, 2.9 Hz, 1H) 5.59 (dd, $J$ = 6.6, 6.6 Hz, 1H) | 1950 cm$^{-1}$ |
| **10** | X = OH, 48%; X = Cl, 75% | 55% | 204.4 | 6.08 (dd, $J$ = 6.5, 3.1 Hz, 1H) 5.53 (dd, $J$ = 6.5, 6.5 Hz, 1H) | 1950 cm$^{-1}$ |

[a] Percentages refer to isolated yields. Alcohols and allenes were characterized by $^1$H and $^{13}$C NMR, IR and mass spectrometry.

$$(1)$$
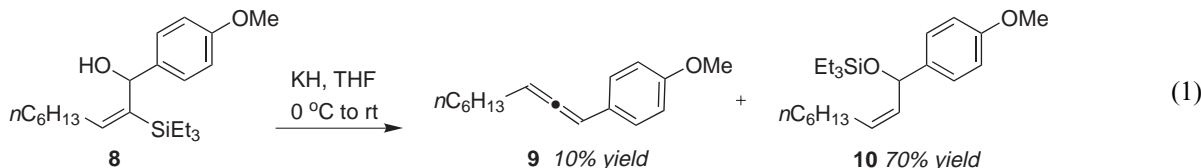
**silylation** of non-2-ynal (**1**, $R^1 = n$-hexyl) under the same conditions led in quantitative yield to an *E,Z* mixture of α-triethylsilyl enals **2** (67%) and **3** (10%), along with β-triethylsilyl product **7** (23%). The high degree of stereo- and regiospecificity of the first hydrosilylation is ascribed to the steric bias imparted on the first reaction by the cyclohexyl group. The regioselectivity is important, since β-triethylsilyl enal **7** does not lead to allene. Consequently, we initiated a limited study to determine conditions that would minimize the proportion of **7** in the product. Hexachloroplatinic acid, Karstedt's catalyst[7a] and two palladium pincer catalysts[8] were examined in combination with triethylsilane and **1** ($R^1 = n$-hexyl). Results in all cases were inferior to those obtained with $RhCl(PPh_3)_3$.

Addition of a series of Grignard reagents to the crude product mixtures led to allylic alcohols **4**, which were characterized, following purification by flash column chromatography (Table 1). A series of simple and substituted aromatic Grignard reagents were examined. The elimination step to form the allenes was carried out by analogy with Chan's pioneering work.[3d] Treatment of the allylic alcohols with thionyl chloride in $CCl_4$/pyridine at 0°C led in excellent yield to allylic chlorides. Exposure of the chlorides to 2 equiv. of tetra-*n*-butylammonium fluoride in DMSO at rt for 24 h led in high yield to the allenes shown in Table 1.

Several interesting observations were made during the execution of this work. Exposure of **2** ($R^1 = n$-hexyl) to excess triethylsilane and 1 mol% Wilkinson's catalyst for 8–9 h at 45°C led to the formation of the triethylsilyl ether of 2-triethylsilyl-2-nonen-1-ol. This reaction promises to be useful for the conversion of ynals to 2-triethylsilyl primary allylic alcohols. A single attempt to perform a KH-mediated Peterson olefination on **8** (Eq. (1)) led in low yield to the desired allene **9**. The major product **10**, which was isolated in 70% yield, resulted from C-to-O migration of the triethylsilyl group. A similar silicon migration, mediated by fluoride anion, has been described by Chan and Mychajlowskij.[3e] A cyclic, fluoride-bridged transition state was postulated for their process, involving the development of a strong hydrogen bond to fluoride. However, a bimolecular mechanism can reasonably be postulated for both the KH and the fluoride mediated reactions.

The reaction sequence appears to be limited to aromatic Grignard reagents. For example, when the adduct of **2** ($R^1 = n$-hexyl) with *n*-butyllithium was exposed to thionyl chloride, a mixture of allylically rearranged chlorides was formed. Treatment of the chloride mixture with tetra-*n*-butylammonium fluoride

gave a chromatographically inseparable mixture of allene and 1,3-dienes (ca. 1/1).

In conclusion, conditions have been developed and optimized for the hydrosilylation of ynals.[9] In the case of 3-cyclohexylprop-2-ynal, the hydrosilylation is regio- and stereospecific. The products of the hydrosilylation have been used for the synthesis of a series of 1,3-aryl substituted allenes. The α-triethylsilyl enals **2** are potentially versatile synthetic intermediates, as are the products of sequential C–C and C–O hydrosilylation.

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9. *Hydrosilylation of 3-cyclohexylprop-2-ynal* (entry 1). Into a dry flask 513 mg (4.41 mmol) triethylsilane and ca. 1 mol%

$RhCl(PPh_3)_3$ was added. The mixture was heated to 50°C for 10 min and to the orange homogeneous mixture was added 200 mg (1.47 mmol) 3-cyclohexylprop-2-ynal. The reaction was stirred at 45°C for 5 h, at which time TLC indicated that some unreacted starting material remained. The mixture was cooled, diluted with ether, filtered through Celite and concentrated to give 370 mg (99% yield) of crude (2*E*)-3-cyclohexyl-2-(triethylsilyl)prop-2-enal: $R_f = 0.70$ (2.5% EtOAc in hexane); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta$ 10.30 (s, 1H), 6.59 (d, $J = 9.8$ Hz, 1H), 3.08 (m, 1H), 0.88 (t, $J = 8.0$ Hz, 9H), 0.65 (q, $J = 8.0$ Hz, 6H).