1-Halo-Substituted Allenes, 11[≠]

Yne-Allenes from 1-Bromoallenes and Trimethylstannylacetylenes via Palladium-Mediated C–C Coupling Reactions

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The Stille cross-coupling of the bromoallenes **3** with the stannylalkynes **6** or distannylalkyne **8** provided a convenient route for the synthesis of the conjugated yne-allenes **7** or the diastereomeric yne-diallenes, *meso*-**9** and (*R*,*R*)/(*S*,*S*)-**9**. Analogously to **7**, the phosphorylyne-allenes **14** were also prepared under Stille conditions, starting from the phosphorylallenes **12** and propargylstannane **6a**. Alternatively, yne-allenes **17** and **18** were obtained from hexadiynol **16** with orthoester **2b** or diethoxychlorophosphane **13a** by [3.3]- and [2.3]-sigmatropic rearrangements.

Introduction

The cumuhomologation reaction of propadienes to give butatrienes is impressive in its simplicity and in the high yields obtained.[1] Key intermediates in this transformation are the bromopropadienes **3**. Elimination of hydrogen bromide from **3** was accomplished by reaction with sodium bis(trimethylsilyl)amide. The bromopropadienes **3** were generated starting from the bromoalkynols **1**. Reaction of **1** with the orthoesters **2** formed bromoalkynyl ketene acetal intermediates which, in a [3.3]-sigmatropic rearrangement, spontaneously yielded **3**.[2,3] The bromoallenes **3** were also subject to a Suzuki coupling to give enyne-allenes. Spontaneous cation-mediated C^2-C^7-cycloaromatization of the enyne-allenes with a concomitant 1,2-shift of a trimethylsilyl group yielded naphthalene derivatives.[4]

In this paper we report on the palladium-catalyzed coupling reactions of the bromoallenes **3** with trimethylstannylacetylenes to give yne-allenes. This route is an alternative to the formation of 1,2-dien-4-ynes by the palladium-catalyzed coupling of terminal alkynes with propargylic compounds, which was applied to the synthesis of 2,3-octadiene-5,7-diyn-1-ol, a fungus metabolite, from 4-trimethylsilylbutadiynylzinc chloride with 2-ethynyloxirane.[5] In an attempt to generalize the methodology, yne-allenes were also prepared starting from a suitable hexa-3,5-diyn-2-ol by [2.3]- or [3.3]-sigmatropic rearrangements.

Results and Discussion

Palladium-Mediated Transformations of Bromoallenes

Stannylallenes

In particular, the bromoallenes **3** were subjected to an umpolung reaction. The stannylallenes **5** were prepared from **3** with hexamethyldistannane **4** and a palladium(0) catalyst in toluene at 110°C (Scheme 1).

Yne-Allenes and Yne-Diallenes by Stille Coupling

The Stille cross-coupling of the bromoallenes **3** with the stannylalkynes **6** provided a convenient route for the synthesis of the conjugated yne-allenes **7**. The key palladium(0)-catalyzed coupling step was carried out with 10 mol-% $Pd_2(dba)_3{\cdot}CHCl_3$ in dimethylformamide at 20°C. The propargylstannanes **6** were obtained from **1** by protection of the hydroxyl group with trimethylsilyl chloride in the presence of triethylamine. Bromine/lithium exchange of the trimethylsilyl ethers with *n*BuLi, followed by acetylide-stannylation with trimethyltin chloride provided **6**.

Furthermore, reaction of two equivalents of the racemic bromoallenes **3** with distannylalkyne **8**[6] in the presence of 10 mol-% $Pd(PPh_3)_4$ in 1-methyl-2-pyrrolidinone gave, through a double Stille cross-coupling reaction, the yne-diallenes **9**. In the ^{1}H- and ^{13}C-NMR spectra of **9b**−**e** only one set of signals is present. Since the synthesis involves the racemate of **3**, we expected the formation of two diastereomers. However, we could not separate *meso*-**9b**−**e** from (*R*,*R*)/(*S*,*S*)-**9b**−**e** by column chromatography. Initially this led us to the erroneous conclusion that only one diastereomer of **9b**−**e** was formed. However, more elaborate NMR spectroscopic techniques confirmed that both diastereomers had formed in the expected ca. 50:50 ratio.

In none of the ^{13}C-NMR spectra of **9b**−**e** did any signal show splitting, even upon application of strong resolution enhancement − all signals of the *meso*- and the (*R*,*R*)/(*S*,*S*)-diastereomers overlap. Likewise, in the ^{1}H-NMR spectra of **9b**−**e** all *meso*- and (*R*,*R*)/(*S*,*S*)-resonances completely overlap. Application of strong resolution enhancement to these spectra gives two sets of signals for the protons at the stereocenters in the case of **9c** and **9e**. The complete identity of all resonances of the two diastereomers both in the ^{1}H- and ^{13}C-NMR spectra is highly surprising. We attribute this phenomenon to the relative remoteness of the stereogenic centers. Upon addition of the chiral shift reagent

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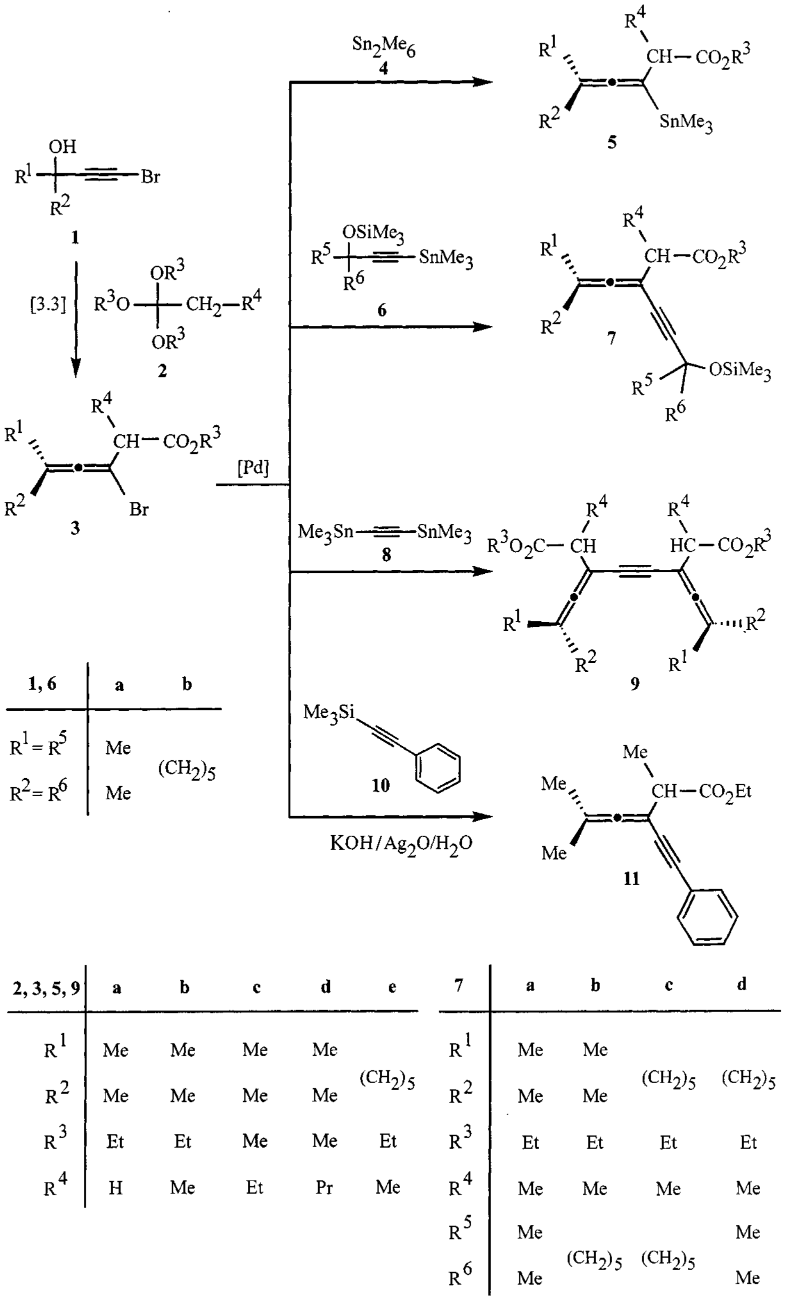
$Eu(tfc)_3$ to a $CDCl_3$ solution of **9e**, clear splitting was observed in the ^1H-NMR spectrum for the resonance line of the proton at the stereogenic center and the signal of the adjacent methyl group. The ^{13}C-NMR spectrum of the **9e**/$Eu(tfc)_3$ mixture shows splitting of all resonances into two signals. Such splitting is expected for both the *meso*- and the (*R*,*R*)/(*S*,*S*)-diastereomer. However, further splitting is observed for the stereogenic center carbon resonance line and the signal of the adjacent CH_3 group. As for the ^1H-NMR spectrum this indicates the presence of both diastereomers.

The yne-allene **11** was also obtained from this reaction. A key intermediate in the formation of **11** is phenylacetylene, which is generated by spontaneous alkaline desilylation from phenylethynyltrimethylsilane **10**. The further metal-catalyzed [Pd^0/Ag^I] reaction of phenylacetylene with the bromoallene **3b** yields the yne-allene **11**. The proposed mechanism is supported by a control experiment, as the [Pd^0/Ag^I] catalyzed cross-coupling of phenylacetylene with **3b** also yields the yne-allene **11** (Scheme 1).

In an analogous synthesis to that of the yne-allenes **7**, the phosphorylyne-allenes **14** were prepared starting from the 1-bromo-1-phosphorylallenes **12** and propargylstannane **6a** under Stille conditions. For the synthesis of **12** the bromoalkynol **1** was treated with the chlorophosphanes **13** and triethylamine (Scheme 2).[2]

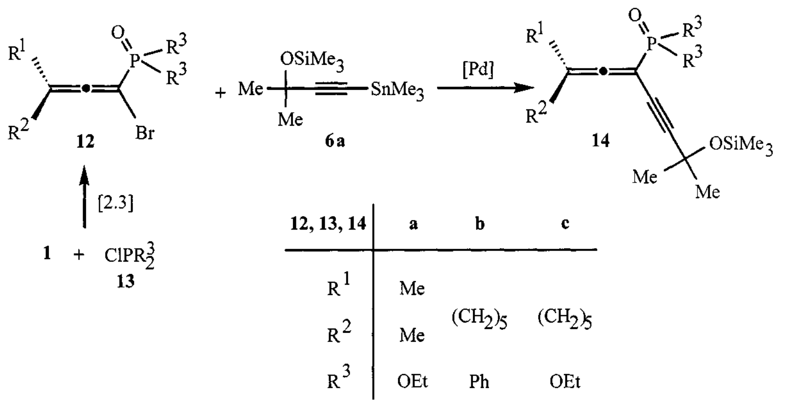


1, 6	a	b
$R^1 = R^5$	Me	$(CH_2)_5$
$R^2 = R^6$	Me	

2, 3, 5, 9	a	b	c	d	e
R^1	Me	Me	Me	Me	$(CH_2)_5$
R^2	Me	Me	Me	Me	
R^3	Et	Et	Me	Me	Et
R^4	H	Me	Et	Pr	Me

7	a	b	c	d
R^1	Me	Me	$(CH_2)_5$	$(CH_2)_5$
R^2	Me	Me		
R^3	Et	Et	Et	Et
R^4	Me	Me	Me	Me
R^5	Me	$(CH_2)_5$	$(CH_2)_5$	Me
R^6	Me			Me

Scheme 1. Umpolung and palladium-mediated cross-coupling reactions of bromoallenes **3**

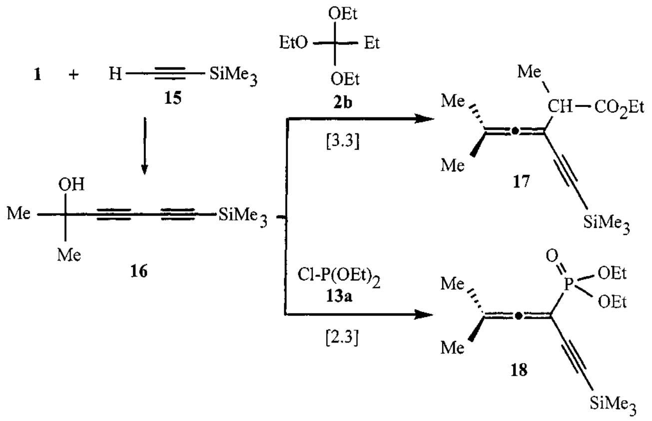


12, 13, 14	a	b	c
R^1	Me	$(CH_2)_5$	$(CH_2)_5$
R^2	Me		
R^3	OEt	Ph	OEt

Scheme 2. Phosphorylyne-allenes **14** by Stille coupling

Yne-Allenes by Sigmatropic Rearrangements

The unsymmetrically substituted starting hexadiynol **16** was prepared in a Cadiot-Chodkiewicz cross-coupling reaction from 1-bromoalkynol **1** with ethynyltrimethylsilane **15**.[7,8] The acid-catalyzed reaction of the bisalkynol **16** with the orthoester **2b** in toluene at 110°C yielded the yne-allene **17** by a [3.3]-sigmatropic rearrangement. Alternatively, reaction of the bisalkynol **16** with diethoxychlorophosphane **13a** and triethylamine in dichloromethane followed by a [2.3]-sigmatropic rearrangement furnished the phosphorylyne-allene **18** (Scheme 3).



Scheme 3. Yne-allenes **17** and **18** from hexadiynol **16** by [3.3]- and [2.3]-sigmatropic rearrangements

Experimental Section

General Methods: Unless otherwise noted, all reactions were carried out under argon in flame-dried glassware with standard syringe, cannula and septum techniques. Tetrahydrofuran was freshly distilled from sodium/benzophenone and stored under nitrogen. Bromoallenes **3** were prepared by literature methods.[1,2] Column chromatography was performed with 230−400 mesh silica gel.

Tetramethylsilane and $CDCl_3$ were used as internal standards in the ^1H- and ^{13}C-NMR spectra, respectively. ^{119}Sn-NMR spectra were referenced to $SnMe_4$ (ext.), ^{31}P-NMR spectra were referenced to 85% H_3PO_4 (ext.). IR spectra were obtained on a FT-IR spectrophotometer.

Stannylallenes 5. − General Procedure: To a solution of the appropriate bromoallene **3** (35.83 mmol) in toluene (20 mL) was added $Pd_2(dba)_3{\cdot}CHCl_3$ (10 mol-%) followed by hexamethyldistannane **4** (14.1 g, 43 mmol). The mixture was heated at reflux for 18 h and, after cooling to 25°C, the reaction was quenched with saturated aqueous KF solution (20 mL). The mixture was extracted with diethyl ether and the organic extracts were washed with brine (25 mL), saturated aqueous $NaHCO_3$ solution (25 mL) and water (25 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residues were chromatographed on silica gel to afford **5**.

5a: Yield 6.82 g (60%), colorless liquid, (pentane/ethyl acetate, 5:1) − IR (film): $\tilde{\nu}$ = 1945 (C=C=C), 1732 (C=O) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 0.09 [s, $^2J_{Sn,H}$ = −54.43 Hz, 9 H, $Sn(CH_3)_3$], 1.19 (t, J = 7.1 Hz, 3 H, CH_3), 1.58 (s, 6 H, 2 CH_3), 3.03 (s, 2 H, CH_2), 4.06 (q, J = 7.1 Hz, 2 H, OCH_2). − ^{13}C NMR ($CDCl_3$): δ = −8.43 [$Sn(CH_3)_3$], 14.12, 20.19 (3 CH_3), 38.34 (CH_2), 60.34 (OCH_2), 86.59, 87.44 (2 C=), 172.40 (C=O), 203.19 (=C=). − ^{119}Sn NMR ($CDCl_3$): δ = −20.51. − MS (70 eV); m/z (%): 318 (4) [M^+], 303 (100) [$M^+ - CH_3$].

5b: Yield 6.76 g (57%), colorless liquid, (pentane/diethyl ether, 10:1) − IR (film): $\tilde{\nu}$ = 1966 (C=C=C), 1739 (C=O) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 0.13 [s, $^2J_{Sn,H}$ = −52.49 Hz, 9 H, $Sn(CH_3)_3$], 1.21 (d, J = 6.8 Hz, 3 H, CH_3), 1.24 (t, J = 7.1 Hz, 3 H, CH_3), 1.63 (s, 6 H, 2 CH_3), 3.12 (q, J = 6.8 Hz, 1 H, CH), 4.08−4.13 (m, 2 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = −7.96 [$Sn(CH_3)_3$], 14.23, 18.01, 20.36 (4 CH_3), 43.06 (CH), 60.45 (CH_2), 89.17, 94.30 (2 C=), 175.31 (C=O), 202.33 (=C=). − ^{119}Sn NMR ($CDCl_3$): δ = −14.6. − MS (70 eV); m/z (%): 332 (2) [M^+], 317 (100) [$M^+ - CH_3$].

5c: Yield 7.7 g (65%), yellow liquid, (pentane/diethyl ether, 20:1) − IR (film): $\tilde{\nu}$ = 1942 (C=C=C), 1732 (C=O) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 0.10 [s, $^2J_{Sn,H}$ = −53.98 Hz, 9 H, $Sn(CH_3)_3$], 0.86 (t, J = 7.4 Hz, 3 H, CH_3), 1.49−1.61 (m, 2 H, CH_2), 1.61 (s, 6 H, 2 CH_3), 2.94 (t, J = 7.2 Hz, 1 H, CH), 3.62 (s, 3 H, OCH_3). − ^{13}C NMR ($CDCl_3$): δ = −8.0 [$Sn(CH_3)_3$], 11.96, 20.17, 20.33 (3 CH_3), 26.00 (CH_2), 50.98 (CH), 51.50 (OCH_3), 88.28, 92.48 (2 C=), 175.24 (C=O), 202.33 (=C=). − ^{119}Sn NMR ($CDCl_3$): δ = −15.02. − MS (70 eV); m/z (%): 332 (2) [M^+], 317 (63) [M^+ − Et].

5d: Yield 8.87 g (72%), yellow liquid, (pentane/diethyl ether, 20:1) − IR (film): $\tilde{\nu}$ = 1943 (C=C=C), 1730 (C=O) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 0.11 [s, $^2J_{Sn,H}$ = −54.93 Hz, 9 H, $Sn(CH_3)_3$], 0.87 (t, J = 7.3 Hz, 3 H, CH_3), 1.24−1.46 (m, 4 H, 2 CH_2), 1.62 (s, 6 H, 2 CH_3), 3.06 (t, J = 7.3 Hz, 1 H, CH), 3.64 (s, 3 H, OCH_3). − ^{13}C NMR ($CDCl_3$): δ = −7.94 [$Sn(CH_3)_3$], 13.77, 20.24, 20.36 (3 CH_3), 20.53, 34.91 (2 CH_2), 49.05 (CH), 51.60 (OCH_3), 88.35, 92.60 (2

C=), 175.46 (C=O), 203.01 (=C=). − ^{119}Sn NMR (CDCl$_3$): δ = −15.06. − MS (70 eV); *m/z* (%): 346 (3) [M$^+$]; 331 (100) [M$^+$ − CH$_3$].

5e: Yield 8.91 g (67%), yellow liquid, (hexane/ethyl acetate, 5:1) − IR (film): $\tilde{\nu}$ = 1940 (C=C=C), 1728 (C=O) cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 0.14 [s, $^2J_{\mathrm{Sn,H}}$ = −53.47 Hz, 9 H, Sn(CH$_3$)$_3$], 1.21 (d, *J* = 6.8 Hz, 3 H, CH$_3$), 1.22, 1.24 (d, *J* = 6.6, 7.3 Hz, 3 H, CH$_3$), 1.45−1.55 (m, 6 H, 3 CH$_2$), 2.03−2.06 (m, 4 H, 2 CH$_2$), 3.13 (q, *J* = 6.8 Hz, 1 H, CH), 4.04−4.11 (m, 2 H, OCH$_2$). − ^{13}C NMR (CDCl$_3$): δ = −7.92 [Sn(CH$_3$)$_3$], 14.23, 17.97 (2 CH$_3$), 26.28, 27.74, 31.44 (5 CH$_2$), 43.07 (CH), 60.43 (OCH$_2$), 94.19, 96.81 (2 C=), 175.29 (C=O), 199.0 (=C=). − ^{119}Sn NMR (CDCl$_3$): δ = −20.65 [Sn(CH$_3$)$_3$]. − MS (70 eV); *m/z* (%): 357 (100) [M$^+$ − CH$_3$].

Yne-Allenes 7. − General procedure: To a solution of the appropriate bromoallene **3** (5 mmol) in DMF (20 mL) was added Pd$_2$(dba)$_3$·CHCl$_3$ (10 mol-%) followed by the trimethyl[(trimethylstannylalkynyl)oxy]silane **6** (6 mmol). After stirring the mixture at 25°C for 18 h the reaction was quenched with saturated aqueous KF solution (20 mL), and extracted with diethyl ether. The organic extracts were washed with saturated aqueous KF solution (25 mL), brine (25 mL) and water (25 mL), dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The residues were chromatographed on silica gel to afford **7**.

7a: Yield 0.97 g (60%), yellow liquid, (hexane/ethyl acetate, 6:1) − IR (film): $\tilde{\nu}$ = 2200 (C$\equiv$C), 1960 (C=C=C), 1740 (C=O) cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 0.17 [s, 9 H, Si(CH$_3$)$_3$], 1.26 (t, *J* = 7.1 Hz, 3 H, CH$_3$), 1.28 (d, *J* = 7.1 Hz, 3 H, CH$_3$), 1.48 (s, 6 H, 2 CH$_3$), 1.74 (s, 6 H, 2 CH$_3$), 3.10 (q, *J* = 7.1 Hz, 1 H, CH), 4.14 (q, *J* = 7.1 Hz, 2 H, CH$_2$). − ^{13}C NMR (CDCl$_3$): δ = 1.68 [Si(CH$_3$)$_3$], 14.20, 15.86, 20.08, 32.99 (6 CH$_3$), 43.85 (CH), 60.62 (CH$_2$), 66.90 (q-C), 78.09, 88.15, 95.22, 99.66 (2 C=, 2 C$\equiv$), 173.58 (C=O), 206.65 (=C=). − MS (70 eV); *m/z* (%): 322 (73) [M$^+$], 307 (83) [M$^+$ − CH$_3$].

7b: Yield 1.12 g (62%), yellow liquid, (ethyl acetate/pentane, 5:1) − IR (film): $\tilde{\nu}$ = 2256 (C$\equiv$C), 1960 (C=C=C), 1719 (C=O) cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 0.13 [s, 9 H, Si(CH$_3$)$_3$], 1.24 (t, *J* = 7.1 Hz, 3 H, CH$_3$), 1.25 (d, *J* = 7.1 Hz, 3 H, CH$_3$), 1.40−1.80 (m, 10 H, 5 CH$_2$), 1.71 (s, 6 H, 2 CH$_3$), 3.10 (q, *J* = 7.1 Hz, 1 H, CH), 4.11 (q, *J* = 7.1 Hz, 2 H, OCH$_2$). − ^{13}C NMR (CDCl$_3$): δ = 1.81 [Si(CH$_3$)$_3$], 14.16, 15.86, 20.09 (4 CH$_3$), 23.29, 25.34, 41.31 (5 CH$_2$), 43.96 (CH), 60.62 (OCH$_2$), 70.49 (q-C), 80.33, 88.28, 94.20, 99.53 (2 C=, 2 C$\equiv$), 173.6 (C=O), 206.52 (=C=). − MS (70 eV); *m/z* (%): 362 (35) [M$^+$], 347 (38) [M$^+$−CH$_3$].

7c: Yield 1.01 g (50%), yellow liquid, (hexane/diethyl ether, 15:1) − IR (film): $\tilde{\nu}$ = 2220 (C$\equiv$C), 1950 (C=C=C), 1730 (C=O) cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 0.17 [s, 9 H, Si(CH$_3$)$_3$], 1.22 (d, *J* = 7.1 Hz, 3 H, CH$_3$), 1.27 (t, *J* = 7.1 Hz, 3 H, CH$_3$), 1.50−1.87 (m, 16 H, 8 CH$_2$), 2.14 (m, 4 H, 2 CH$_2$), 3.13 (q, *J* = 7.1 Hz, 1 H, CH), 4.13 (q, *J* = 7.1 Hz, 2 H, OCH$_2$). − ^{13}C NMR (CDCl$_3$): δ = 1.92 [Si(CH$_3$)$_3$], 14.18, 15.97 (2 CH$_3$), 23.33, 25.36, 25.96, 27.19, 31.00, 31.08, 41.36 (10 CH$_2$), 43.98 (CH), 60.64 (OCH$_2$), 70.50 (q-C), 80.79, 87.95, 93.82, 106.59 (2 C=, 2 C$\equiv$), 173.71 (C=O), 203.08 (=C=). − MS (70 eV); *m/z* (%): 402 (25) [M$^+$], 387 (21) [M$^+$ − CH$_3$].

7d: Yield 1.00 g (55%), yellow liquid, (ethyl acetate/hexane, 5:1) − IR (film): $\tilde{\nu}$ = 2195 (C$\equiv$C), 1950 (C=C=C), 1730 (C=O) cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 0.14 [s, 9 H, Si(CH$_3$)$_3$], 1.22 (d, *J* = 7.1 Hz, 3 H, CH$_3$), 1.23 (t, *J* = 7.3 Hz, 3 H, CH$_3$), 1.44 (s, 6 H, 2 CH$_3$), 1.45−1.60 (m, 6 H, 3 CH$_2$), 2.10−2.13 (m, 4 H, 2 CH$_2$), 3.07 (q, *J* = 7.1 Hz, 1 H, CH), 4.10 (q, *J* = 7.3 Hz, 2 H, OCH$_2$). − ^{13}C NMR (CDCl$_3$): δ = 1.74 [Si(CH$_3$)$_3$], 14.20, 15.97 (2 CH$_3$), 25.94, 27.20, 30.95, 31.04 (5 CH$_2$), 33.01 (2 CH$_3$), 43.83 (CH), 60.62 (OCH$_2$), 66.90 (q-C), 78.51, 87.82, 94.86, 106.71 (2 C=, 2 C$\equiv$), 173.67 (C=O), 203.25 (=C=). − MS (70 eV); *m/z* (%): 362 (51) [M$^+$], 347 (66) [M$^+$ − CH$_3$].

Yne-Diallenes 9. − General procedure: Bis(trimethyl)ethynyldistannane **8**[6] (1.91 g, 5.43 mmol) was added to a solution of the appropriate bromoallenes **3** (9.9 mmol) and (PPh$_3$)$_4$Pd (10 mol-%) in NMP (20 mL). After stirring the mixture at 25°C for 18 h, it was quenched with saturated aqueous KF solution (20 mL). The mixture was extracted with diethyl ether and the organic extracts were washed with saturated aqueous KF solution (25 mL), brine (25 mL), and water (25 mL), dried with MgSO$_4$, filtered, and concentrated under reduced pressure. The residues were chromatographed on silica gel to afford **9**.

9a: Yield 1.06 g (65%), yellow liquid, (diethyl ether/hexane, 4:1) − IR (film): $\tilde{\nu}$ = 2260 (C$\equiv$C), 1950 (C=C=C), 1738 (C=O) cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 1.24 (t, *J* = 7.2 Hz, 6 H, 2 CH$_3$), 1.69 (s, 12 H, 4 CH$_3$), 3.04 (s, 4 H, 2 CH$_2$), 4.12 (q, *J* = 7.2 Hz, 4 H, 2 OCH$_2$). − ^{13}C NMR (CDCl$_3$): δ = 14.16, 20.11 (6 CH$_3$), 40.33 (2 CH$_2$), 60.70 (2 OCH$_2$), 82.13, 85.30, 98.54 (4 C=, 2 C$\equiv$), 170.43 (2 C=O), 207.69 (2 =C=). − MS (70 eV); *m/z* (%): 330 (100) [M$^+$], 285 (8) [M$^+$ − 3 CH$_3$].

9b: Yield 1.17 g (66%), yellow liquid, (pentane/diethyl ether, 5:1) − IR (film): $\tilde{\nu}$ = 2200 (C$\equiv$C), 1960 (C=C=C), 1736 (C=O) cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 1.26 (t, *J* = 7.1 Hz, 6 H, 2 CH$_3$), 1.28 (d, *J* = 7.1 Hz, 6 H, 2 CH$_3$), 1.73 (s, 12 H, 4 CH$_3$), 3.15 (q, 2 H, *J* = 7.1 Hz, 2 CH), 4.14 (q, *J* = 7.1 Hz, 4 H, 2 CH$_2$). − ^{13}C NMR (CDCl$_3$): δ = 14.10, 15.83, 20.14 (8 CH$_3$), 44.26 (2 CH), 60.50 (2 CH$_2$), 85.33 (2 C$\equiv$), 88.84, 99.67 (4 C=), 173.49 (2 C=O), 206.08 (2 =C=). − MS (70 eV); *m/z* (%): 358 (59) [M$^+$], 343 (44) [M$^+$ − CH$_3$]. − HRMS: C$_{22}$H$_{30}$O$_4$ calcd. 358.214410; found 358.215116.

9c: Yield 0.98 g (55%), yellow liquid, (pentane/diethyl ether, 3:1) − IR (film): $\tilde{\nu}$ = 2192 (C$\equiv$C), 1960 (C=C=C), 1740 (C=O) cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 0.93 (t, 6 H, *J* = 7.3 Hz, 2 CH$_3$), 1.73 (s, 12 H, 4 CH$_3$), 1.76−1.82 (m, 4 H, 2 CH$_2$), 2.93 (t, *J* = 7.3 Hz, 2 H, 2 CH), 3.69 (s, 6 H, 2 OCH$_3$). − ^{13}C NMR (CDCl$_3$): δ = 11.93, 20.12, 20.23 (6 CH$_3$), 23.64 (2 CH$_2$), 51.80 (2 OCH$_3$), 51.89 (2 CH) 85.25, 87.22, 99.30 (4 C=, 2 C$\equiv$), 173.47 (2 C=O), 206.74 (2 =C=). − MS (70 eV); *m/z* (%): 358 (21) [M$^+$], 329 (100) [M$^+$ − Et]. − HRMS: C$_{22}$H$_{30}$O$_4$: calcd. 358.214410; found 358.214531.

9d: Yield 1.07 g (56%), yellow liquid, (pentane/diethyl ether, 3:2) − IR (film): $\tilde{\nu}$ = 2253 (C$\equiv$C), 1955 (C=C=C), 1740 (C=O) cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 0.92 (t, 6 H, *J* = 7.3 Hz, 2 CH$_3$), 1.28−1.69 (m, 8 H, 4 CH$_2$), 1.73 (s, 12 H, 4 CH$_3$), 3.02 (t, *J* = 7.33 Hz, 2 H, 2 CH), 3.69 (s, 6 H, 2 OCH$_3$). − ^{13}C NMR (CDCl$_3$): δ = 13.80, 20.09, 20.18 (6 CH$_3$), 20.47, 32.40 (4 CH$_2$), 49.85 (CH), 51.77 (2 OCH$_3$), 85.27, 87.32, 99.27 (4 C=, 2 C$\equiv$), 173.58 (2 C=O), 206.68 (2 =C=). − MS (70 eV); *m/z* (%): 386 (11) [M$^+$], 343 (49) [M$^+$ − Pr].

9e: Yield 1.30 g (60%), yellow liquid, (hexane/diethyl ether, 8:1) − IR (film): $\tilde{\nu}$ = 2200 (C$\equiv$C), 1965 (C=C=C), 1740 (C=O) cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 1.26 (t, *J* = 7.1 Hz, 6 H, 2 CH$_3$), 1.28 (d, *J* = 7.1 Hz, 6 H, 2 CH$_3$), 1.41−1.67 (m, 12 H, 6 CH$_2$), 2.12−2.28 (m, 8 H, 4 CH$_2$), 3.15 (q, *J* = 7.1 Hz, 2 H, 2 CH), 4.14 (q, *J* = 7.1 Hz, 4 H, 2 OCH$_2$). − ^{13}C NMR (CDCl$_3$): δ = 14.21, 16.06 (4 CH$_3$), 25.96, 27.24, 31.04, 31.15 (8 CH$_2$), 44.38 (2 CH), 60.62 (2 OCH$_2$), 85.52, 88.63, 106.79 (4 C=, 2 C$\equiv$), 173.69 (2 C=O), 202.78 (2 =C=). − MS (70 eV); *m/z* (%): 438 (21) [M$^+$], 423 (15) [M$^+$ − Et]. − HRMS: C$_{28}$H$_{38}$O$_4$: calcd. 438.277010; found 438.275932

Yne-Allene 11: To a stirred solution of phenylethynyltrimethylsilane **10** (0.70 g, 4 mmol) in THF (20 mL) at 0°C, silver(I) oxide (3.71 g in 16 mL water, 16 mmol), KOH (0.5 g, 9 mmol), $(PPh_3)_4Pd$ (5 mol-%), 40 mol-% triphenylarsane (0.49 g, 1.6 mmol) and ethyl 3-bromo-2,5-dimethyl-3,4-hexadienoate **3b** (0.99 g, 4 mmol) were successively added. The reaction was stirred at 25°C for 24 h. Silver(I) oxide was removed by filtration and the crude product was diluted in diethyl ether (40 mL). The organic layer was washed with distilled water (50 mL), saturated aqueous sodium hydrogencarbonate (50 mL), brine (50 mL), and dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure. The residue was purified by column chromatography (hexane/diethyl ether, 10:1) to afford **11** (0.44 g, 41%) as a pale yellow liquid. − IR (film): $\tilde{\nu}$ = 2208 (C≡C), 1965 (=C=), 1735 (C=O), 1598, 1559 (C=C) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 1.27 (t, J = 7.1 Hz, 3 H, CH_3), 1.34 (d, J = 7.1 Hz, 3 H, CH_3), 1.78 (s, 6 H, 2 CH_3), 3.23 (q, J = 7.1 Hz, 1 H, CH), 4.16 (q, J = 7.1 Hz, 2 H, CH_2), 7.26−7.28 (m, 3 H, Ar−H), 7.41−7.43 (m, 2 H, Ar−H). − ^{13}C NMR ($CDCl_3$): δ = 14.21, 15.88, 20.18 (4 CH_3), 44.26 (CH), 60.48 (CH_2), 84.38, 88.64, 90.45, 99.98 (2 C=, 2 C≡), 123.55 (Ar-q-C), 127.88, 128.14, 131.41 (5 Ar−CH), 173.56 (C=O), 206.53 (=C=). − MS (70 eV); *m/z* (%): 268 (100) [M^+], 253 (97) [$M^+ - CH_3$]. − HRMS: $C_{18}H_{20}O_2$: calcd. 268.146330; found 268.146095.

Phosphorylyne-Allenes 14. − General procedure: To a solution of the appropriate 1-bromophosphorylallene **12** (5 mmol) in THF (20 mL) was added $Pd_2(dba)_3 \cdot CHCl_3$ (5 mol-%), followed by **6a** (1.91 g, 6 mmol). After stirring the solution for 18 h at 25°C, the reaction mixture was quenched with saturated aqueous KF solution (20 mL). The mixture was extracted with diethyl ether and the organic extracts were washed with saturated aqueous KF solution (25 mL), brine (25 mL), and water (25 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residues were chromatographed on silica gel to afford **14**.

14a: Yield 1.21 g (68%), yellow liquid, (petroleum ether/ethyl acetate, 5:1) − IR (film): $\tilde{\nu}$ = 2198 (C≡C), 1949 (C=C=C), 1249 (P=O) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 0.18 [s, 9 H, $Si(CH_3)_3$], 1.35 (t, J = 7.1 Hz, 6 H, 2 CH_3), 1.50 (s, 6 H, 2 CH_3), 1.82 (d, $^5J_{P,H}$ = 6.4 Hz, 6 H, 2 CH_3), 4.12−4.17 (m, 4 H, 2 CH_2). − ^{13}C NMR ($CDCl_3$): δ = 1.68 [$Si(CH_3)_3$], 16.29 (d, $^3J_{P,C}$ = 7.3 Hz, 2 CH_3), 19.34 (d, $^4J_{P,C}$ = 5.5 Hz, 2 CH_3), 32.79 (2 CH_3), 62.84 (d, $^2J_{P,C}$ = 5.6 Hz, 2 CH_2), 66.92 (q-C), 74.06, 96.11, 99.50 (d, $J_{P,C}$ = 9.2 Hz; $J_{P,C}$ = 9.1 Hz; $J_{P,C}$ = 14.7 Hz, C= or 2 C≡), 77.99 (d, $^1J_{P,C}$ = 205.9 Hz, C=), 214.40 (d, $^2J_{P,C}$ = 3.7 Hz, =C=). − ^{31}P NMR ($CDCl_3$): δ = 19.53. − MS (70 eV); *m/z* (%): 358 (50) [M^+], 343 (100) [$M^+ - CH_3$].

14b: Yield 1.29 g (56%), yellow liquid, (ethyl acetate/pentane, 5:1) − IR (film): $\tilde{\nu}$ = 2184 (C≡C), 1943 (C=C=C), 1201 (P=O) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 0.08 [s, 9 H, $Si(CH_3)_3$], 1.15−2.11 (m, 10 H, 5 CH_2), 1.32 (s, 6 H, 2 CH_3), 7.42−7.53 (m, 6 H, Ar−H), 7.77−7.82 (m, 4 H, Ar−H). − ^{13}C NMR ($CDCl_3$): δ = 1.62 [$Si(CH_3)_3$], 25.24, 26.12, (3 CH_2), 29.67 (d, $^4J_{P,C}$ = 5.5 Hz, 2 CH_2), 32.51 (2 CH_3), 66.79 (q-C), 77.82, 97.84, 106.20 (d, $J_{P,C}$ = 9.2 Hz; $J_{P,C}$ = 5.5 Hz; $J_{P,C}$ = 11.1 Hz, C= or 2 C≡), 84.27 (d, $^1J_{P,C}$ = 110.3 Hz, C=), 128.11, 131.70, 131.86 (d, $J_{P,C}$ = 12.9 Hz; $J_{P,C}$ = 11.0 Hz; $J_{P,C}$ = 3.7 Hz, 10 Ar−CH), 131.80 (d, $^1J_{P,C}$ = 101.6 Hz, 2 Ar-q-C), 210.82 (d,$^2J_{P,C}$ = 5.5 Hz, =C=). − ^{31}P NMR ($CDCl_3$): δ = 28.31. − MS (70 eV); *m/z* (%): 462 (40) [M^+], 447 (14) [$M^+ - CH_3$].

14c: Yield 1.45 g (73%), yellow liquid, (pentane/ethyl acetate, 10:1) − IR (film): $\tilde{\nu}$ = 2140 (C≡C), 1942 (C=C=C), 1249 (P=O) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 0.15 [s, 9 H, $Si(CH_3)_3$], 1.31 (t, J = 7.1 Hz, 6 H, 2 CH_3), 1.46 (s, 6 H, 2 CH_3), 1.59−2.21 (m, 10 H, 5 CH_2), 4.08−4.12 (m, 4 H, 2 OCH_2). − ^{13}C NMR ($CDCl_3$): δ = 1.69 [$Si(CH_3)_3$], 16.28 (d, $^3J_{P,C}$ = 5.5 Hz, 2 CH_3), 25.57, 26.58 (3 CH_2), 30.02 (d, $^4J_{P,C}$ = 5.5 Hz, 2 CH_2), 32.75 (2 CH_3), 62.78 (d, $^2J_{P,C}$ = 5.5 Hz, 2 OCH_2), 66.86 (q-C), 74.43, 95.70, 105.72 (d, $J_{P,C}$ = 9.2 Hz; $J_{P,C}$ = 9.2 Hz; $J_{P,C}$ = 14.7 Hz, C= or 2 C≡), 79.16 (d, $^1J_{P,C}$ = 205.9 Hz, C=), 211.02 (d, $^2J_{P,C}$ = 5.5 Hz, =C=). − ^{31}P NMR ($CDCl_3$): δ = 13.53. − MS (70 eV); *m/z* (%): 399 (10) [M^+].

2-Methyl-6-trimethylsilyl-3,5-hexadiyn-2-ol (16): To a mixture of triethylamine (0.92 g, 9.1 mmol), CuCl (0.074 g, 0.75 mmol) and hydroxylamine hydrochloride (0.185 g, 2.7 mmol) in DMF (20 mL), ethynyltrimethylsilane (0.91 g, 9.26 mmol) and 1-bromo-3-methyl-1-butyn-3-ol **(1)** (1.51 g, 9.26 mmol) were successively added at 10°C. After 2 h of stirring at 25°C the mixture was cooled to 0°C and subsequently quenched by addition of 2N H_2SO_4 (50 mL). The solution was extracted with diethyl ether, dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography over silica gel (pentane/diethyl ether, 5:1) provided **16** (1.35 g, 81%) as colorless crystals; m.p. 62−64°C. − IR (film, $CHCl_3$): $\tilde{\nu}$ = 3252 (OH), 2232, 2101 (2 C≡C) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 0.13 [s, 9 H, $Si(CH_3)_3$], 1.46 (s, 6 H, 2 CH_3), 2.79 (s, 1 H, OH). − ^{13}C NMR ($CDCl_3$): δ = −0.57 [$Si(CH_3)_3$], 30.86 (2 CH_3), 65.37, 67.15, 81.96, 87.25, 87.44 (5 q-C). − MS (70 eV); *m/z* (%): 180 (6) [M^+], 165 (100) [$M^+ - CH_3$].

Yne-Allene 17: To a solution of **16** (0.11 g, 0.60 mmol) in toluene (20 mL) orthoester **2b** (0.32 g, 1.80 mmol) and propionic acid (1 mL) were added. The reaction mixture was heated for 3 h at 105−110°C, while the solvent and the generated alcohol were removed continuously by means of a gentle flow of nitrogen. The residue was cooled and concentrated under reduced pressure. Excess orthoester was distilled off at 65−70°C/0.5 Torr over a Vigreux column and the crude product was chromatographed on silica gel (diethyl ether/hexane, 4:1) to afford **17** (0.12 g, 75%) as a yellow liquid. − IR (film): $\tilde{\nu}$ = 2145 (C≡C), 1955 (=C=), 1739 (C=O) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 0.14 [s, 9 H, $Si(CH_3)_3$], 1.23 (t, J = 7.1 Hz, 3 H, CH_3), 1.24 (d, J = 7.1 Hz, 3 H, CH_3), 1.71 (s, 6 H, 2 CH_3), 3.10 (q, J = 7.1 Hz, 1 H, CH), 4.10 (q, J = 7.1 Hz, 2 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 0.11 [$Si(CH_3)_3$], 14.21, 15.77, 20.06, 20.09 (4 CH_3), 44.14 (CH), 60.64 (CH_2), 88.63, 95.39, 99.88, 100.08 (2 C=, 2 C≡), 173.49 (C=O), 206.65 (=C=). − MS (70 eV); *m/z* (%): 264 (13) [M^+], 249 (31) [$M^+ - CH_3$]. − HRMS: $C_{15}H_{24}O_2Si$: calcd. 264.154559; found 264.154594.

Phosphorylyne-Allene 18: To a solution of 2-methyl-6-trimethylsilyl-3,5-hexadiyn-2-ol **(16)** (0.1 g, 0.60 mmol) in CH_2Cl_2 (50 mL) was added triethylamine (0.06 g, 0.60 mmol). The solution was cooled to −90°C and diethoxychlorophosphane **(13a)** (0.09 g, 0.55 mmol) was added dropwise. After stirring for 10 min the solution was allowed to warm to 25°C and stirred for an additional hour. The reaction was stopped by addition of 50 mL of H_2O. The organic layer was separated, washed with brine (25 mL), water (25 mL), and dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (ethyl acetate/hexane, 3:1) to afford **18** (0.10 g, 55%) as a colorless liquid. − IR (film): $\tilde{\nu}$ = 2145 (C≡C), 1949 (=C=), 1260 (P=O) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 0.13 [s, 9 H, $Si(CH_3)_3$], 1.29 (t, J = 7.1 Hz, 6 H, 2 CH_3), 1.75 (d, $^5J_{P,H}$ = 6.3 Hz, 6 H, 2 CH_3), 4.07−4.11 (m, 4 H, 2 CH_2). − ^{13}C NMR ($CDCl_3$): δ = 0.19 [$Si(CH_3)_3$], 16.48 (d, $^3J_{P,C}$ = 7.3 Hz, 2 CH_3), 19.53 (d, $^4J_{P,C}$ = 7.3 Hz, 2 CH_3), 63.27 (d, $^2J_{P,C}$ = 7.4 Hz, 2 CH_2), 80.51 (d, $^1J_{P,C}$ = 202.2 Hz, C=), 95.68, 97.24, 99.75 (d, $J_{P,C}$ = 7.3 Hz; $J_{P,C}$ = 5.5 Hz; $J_{P,C}$ = 14.7 Hz; C= or C≡), 214.60 (d, $^2J_{P,C}$ = 3.7 Hz, =C=). − ^{31}P NMR ($CDCl_3$): δ = 12.95(s). − MS (70 eV); *m/z* (%): 300 (91) [M^+], 285 (20) [$M^+ - CH_3$]. − HRMS: $C_{14}H_{25}O_3PSi$: calcd. 300.131062; found 300.131027.

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[1] R. W. Saalfrank, A. Welch, M. Haubner, *Angew. Chem*. **1995**, *107*, 2937−2938; *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 2709−2710.

[2] R. W. Saalfrank, A. Welch, M. Haubner, U. Bauer, *Liebigs Ann*. **1996**, 171−181.

[3] S. Tsuboi, T. Masuda, A. Takeda, *J. Org. Chem*. **1982**, *47*, 4478−4482.

[4] R. W. Saalfrank, M. Haubner, C. Deutscher, W. Bauer, T. Clark, *J. Org. Chem*., in press.

[5] J. Tsuji and T. Mandai, *Angew. Chem*. **1995**, *107*, 2830−2854; *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 2589−2612.

[6] B. Wrackmeyer, H. Nöth, *J. Organomet. Chem*. **1976**, *108*, C21-C25.

[7] W. Chodkiewicz, *Ann. Chim. (Paris)* **1957**, *13/2*, 819−869; P. Cadiot, W. Chodkiewicz in H. G. Viehe, *Chemistry of Acetylenes*, Dekker, New York, **1969**, pp. 597−647.

[8] B. N. Ghose, D. R. M. Walton, *Synthesis* **1974**, 890−891.

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