A Convenient, High-Yielding Copper-Free Synthesis of Skipped 1,4-Diynes

Jilali Kessabi, Renaud Beaudegnies, Pierre M. J. Jung, Benjamin Martin, Florian Montel, Sebastian Wendeborn*

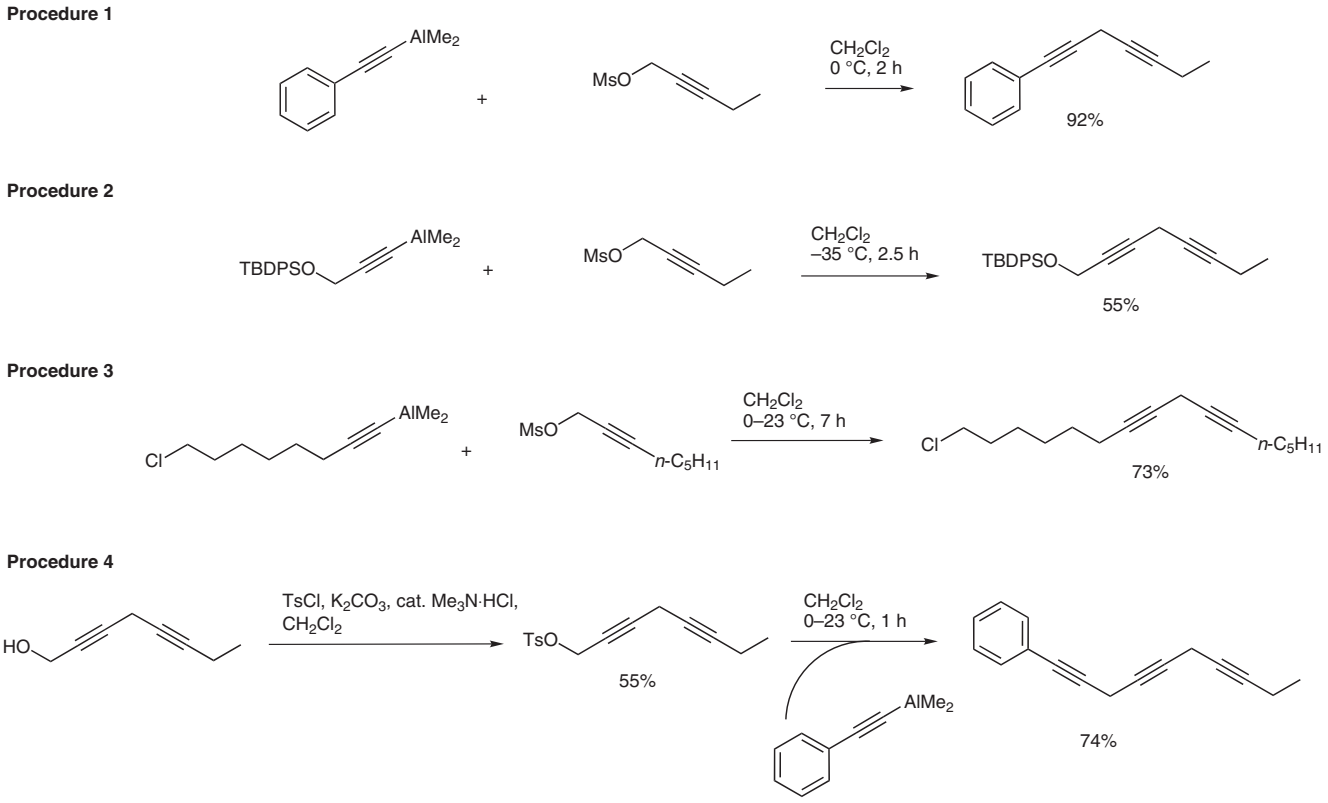
Research Chemistry, SYNGENTA Crop Protection AG, 4002 Basel, Switzerland
Fax +41(61)3238529; E-mail: sebastian.wendeborn@syngenta.com

Received 14 August 2007; revised 29 August 2007

PSP No 114

Abstract: Alkynylalanes were found to react efficiently with propargylic electrophiles, such as propargyl mesylates and propargyl diethylphosphates. The reaction proceeds with high regioselectivity and does not require copper or any other transition metal.

Key words: alkynes, alanes, aluminum, cross-coupling, regioselectivity



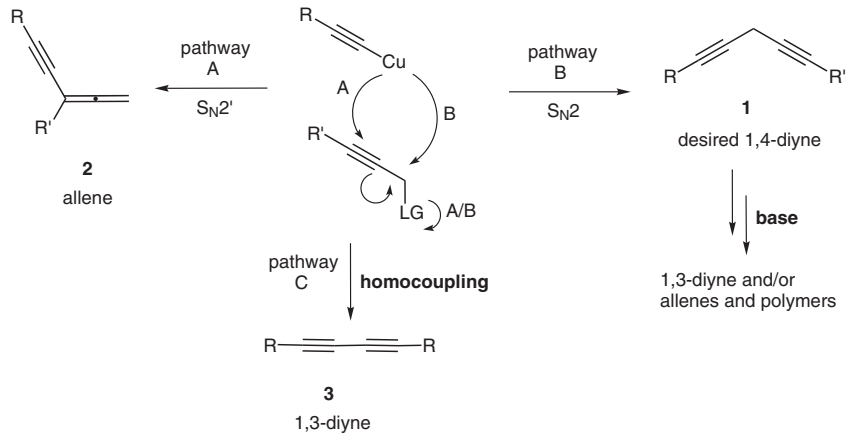
Scheme 1 Copper-free synthesis of skipped 1,4-diynes

Introduction

C_{sp}–C_{sp3} cross-coupling reactions typically still rely on the generation of a copper acetylide which reacts with an electrophilic halide or sulfonate.[1] In particular, the preparation of methylene-bridged 1,4-diynes (commonly referred to as skipped diynes) involves cross-coupling of copper acetylides with propargylic electrophiles.[2] The requisite acetylenic copper species is usually generated in situ using stoichiometric amounts of copper(I) in the presence of a weak base such as potassium carbonate. Alternatively, catalytic quantities of copper(I) are sufficient when preformed magnesium acetylides are employed as coupling partners.[3]

Although widely employed, this copper-mediated cross-coupling approach to 1,4-diynes can suffer from a number of limitations (Scheme 2). Firstly, the yield of the desired coupled product **1** can be reduced due to competitive formation of regioisomeric alkynylallenes **2** which result from an undesired nucleophilic attack by the acetylenic

SYNTHESIS 2008, No. 4, pp 0655–0659
Advanced online publication: 13.11.2007
DOI: 10.1055/s-2007-990885; Art ID: Z19407SS

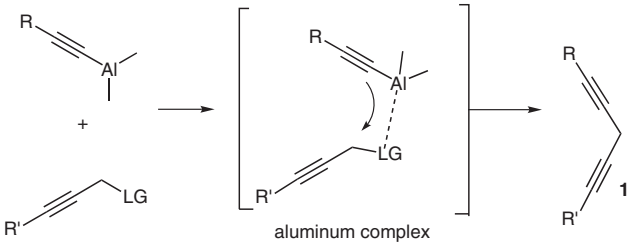


Scheme 2 Competitive reactions involved in the formation of 1,4-skipped diynes **1**

copper species at the triple bond (S_N2') rather than at the sp^3 carbon of the electrophile (pathways A and B, respectively). In turn, these allenic products are prone to polymerization.

Secondly, undesired isomerization of the 1,4-diyne **1** to the corresponding allenes and eventually the 1,3-isomer is possible even under the weakly basic conditions, thus lowering the yield and complicating the isolation of the skipped diyne.[4] Finally, the acetylenic copper species can be prone to oxidative homocoupling (pathway C, Scheme 2).[5] In addition, copper waste can pose a significant issue for the commercialization of such chemical processes.

In the course of our search for an efficient and scalable process for the preparation of skipped diynes in the absence of copper, we discovered that alkynylalanes react smoothly and selectively with propargyl sulfonates and phosphates to give the corresponding skipped dienes in high yields.[6] The origin of this work rests on the expectation that if an alkynylalane is generated in the presence of a propargylic electrophile capable of complexing with the Lewis acid aluminum species, a coupling reaction could ensue and lead to the formation of a skipped diyne. The successful transfer of the alkynyl residue would rely in part on weakening the C_{sp}–aluminum σ bond, as well as the propargylic C_{sp3}–leaving group bond, as a consequence of the proposed complexation shown in Scheme 3.



LG: leaving group containing residues capable of complexing to the alane

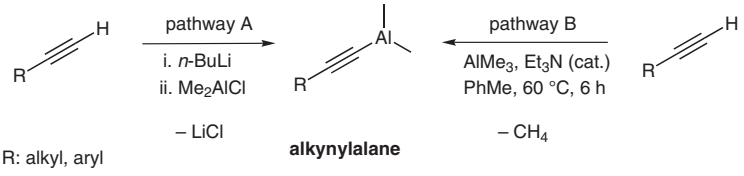
Scheme 3 1,4-Diynes via mutual activation of alkynylalanes and propargylic electrophiles

Scope and Limitations

For the preparation of our base-sensitive diynes (vide supra), it was preferable to avoid the use of strongly basic transmetalation methods (alkynyl–alkali metal–Al exchange) commonly applied for the generation of the requisite alkynylalane species[7] (pathway A in Scheme 4). We therefore opted for a salt-free method recently reported by Micouin[8] which involves treating terminal alkynes with trimethylaluminum in the presence of only catalytic amounts of triethylamine (pathway B in Scheme 4).

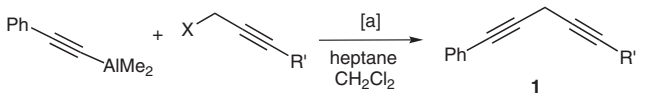
For our purposes, the alkynylalane of phenylacetylene was prepared according to Micouin's conditions[8] and was employed as a model substrate for coupling with numerous propargyl electrophiles. The coupling procedure is straightforward and simply involves dropwise addition of the phenylethynylalane to the electrophile in dichloromethane at 0 °C or at room temperature. The outcome of these reactions is reported in Table 1.

Initially, coupling of the easily prepared propargyl diethylphosphate with two equivalents of phenylethynylalane led to a clean reaction according to GC and ^{1}H NMR analysis of the crude material. Our desired skipped diyne **1**



Scheme 4 Approaches to alkynylalanes

Table 1 Cross-Coupling Reaction of Phenylethynylalane with Propargylic Electrophiles[a]



Entry	Equiv of alane	X	R′	Temp (°C)	Time (h)	Yield of **1** (%)[b]
1	2	$OPO(OEt)_2$	Et	0 to r.t.	8	79
2	2	$OPO(OPh)_2$	Et	r.t.	10	85
3	2	$OPOPh_2$	Et	r.t.	8	80
4	2	OMs	Et	0	2	92
5	1	OMs	H	0	0.5	88
6	2	OTs	Et	0	1	96
7	2	OTs	H	0	2	85

[a] Reaction conditions: $PhC{\equiv}CAlMe_2$ in CH_2Cl_2–heptane (1 M) was added to the electrophile in CH_2Cl_2 and the conversion was followed by GC.
[b] Isolated yields.

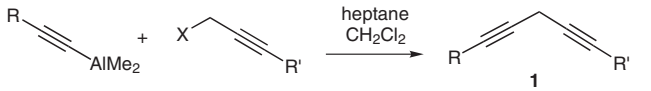
had been generated for the first time not only in high isolated yield (79%, entry 1) but also free from the regioisomeric alkynylallene. Attempts to carry out the reaction of propargyl phosphates with just one equivalent of the alkynylalane resulted in absolutely no consumption of the electrophile even in the presence of different Lewis acids [$ZnCl_2$, ZnI_2, $Al(O\textit{i}\text{-}Pr)_3$, $Al(O\textit{i}\text{-}Bu)_3$]. In addition, the cross-coupling reactions of the corresponding readily available, diphenylphosphate and diphenylphosphinate with phenylethynylalane were similarly regioselective and equally effective (entries 2,3, respectively).

An added improvement for the preparation of methylene-bridged diynes such as **1** came from the observation that inexpensive propargylic methyl- and tolylsulfonates were even better partners in this novel alkynylalane-mediated cross-coupling than phosphate and phosphinate – they led to the highest yields of the skipped diyne (cf. entries 4–7 vs entries 1–3). Advantageously, in selected instances just stoichiometric amounts of alkynylalane were required when the sulfonate was used as the coupling partner (entry 5).[9] Furthermore, the propargylic sulfonates – whether derived from terminal or internal acetylenes – were found to be as reactive at lower temperatures (–30 °C for the mesylate and 0 °C for the tosylate) as they were at room temperature.

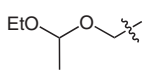
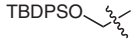
Particularly noteworthy is the high yield of the regioselective reaction between the terminal propargylic sulfonates and the alkynylalane (entries 5,7) since literature precedent,[10] as well as our own experiences,[11] have shown that S_N2' attack predominates on terminal propargylic electrophiles when the nucleophilic coupling partner is an alkynylcopper (presumably resulting in allene formation and subsequent polymerization). Electrophiles which possess a chloride, methoxy, or methoxymethyl substituent at the propargylic position did not cross-couple with the alkynylalane under these conditions.

The preparation of dialkyl substituted methylene-bridged diynes was also shown to be possible using this alkynylalane-mediated cross-coupling as shown in Scheme 1 and Table 2. Firstly, the use of a propargyl diethylphosphate as the electrophilic coupling partner provided dodeca-3,6-diyne regioselectively, albeit in low yield (entry 1, 23%). In contrast, the coupling of the corresponding mesylate was significantly higher yielding (entry 2, 77%) and advantageously could be carried out at temperatures much lower than that required for the phosphate (0 °C vs 90 °C).

Table 2 Cross-Coupling Reaction of Alkyl-Substituted and Functionalized Alkynylalanes with Propargylic Electrophiles



R' = Et, *n*-C_5H_{11}, $EtC{\equiv}CCH_2$

Entry	R	Alane (equiv)	X	Temp (°C)	Time (h)	Yield of **1** (%)[a]
1[b]	*n*-C_5H_{11}	2	$OPO(OEt)_2$	0–90	73	23
2[b]	*n*-C_5H_{11}	1	OMs	0–23	1	77
3[b]		2	OMs	–35 to r.t.	4	49
4[b,c]		2	OMs	–35 to r.t.	4	55
5[d]	$Cl(CH_2)_6$	1	OMs	0–23	7	73
6[e]	Ph	1	OTs	0 to r.t.	1	74

[a] Isolated yields.
[b] R′ = Et.
[c] The alane was added to the mesylate in toluene.
[d] R′ = *n*-C_5H_{11}.
[e] R′ = $EtC{\equiv}CCH_2$.

Moreover, the mesylate necessitated a significantly shorter reaction time compared to the phosphate (1 h vs 73 h), and only required the use of stoichiometric amounts of the alane which is consistent with what was previously observed (cf. Table 1, entry 5).

A useful extension of this methodology would be its application for the preparation of functionalized diynes which are amenable to further transformations. To this end, the propargyl alcohol-derived ethoxyethyl ether and *tert*-butyldiphenylsilyl ether were selected as precursors to representative functionalized alkynylalanes (entries 3 and 4, respectively). While Micouin's conditions for alkynylalane preparation failed to provide the requisite nucleophilic coupling partners in these instances, they were attainable on treatment with *n*-BuLi and transmetalation with $AlMe_2Cl$ at –35 °C. Their subsequent cross-couplings with the mesylate derived from pent-2-yn-1-ol were regioselective and afforded the desired acetal and silyloxy functionalized diynes in moderate yields [49% and 55%, respectively, Table 2 (R′ = Et)].

In addition, the chloroalkyl-substituted diyne was successfully prepared as shown in entry 5 via the intermediacy of 1-chlorooct-7-ynylalane, highlighting the chemoselective nature of the substitution at the mesylate centre rather than at the chloride during the cross-coupling. Further steps towards extending the utility of this method was the successful preparation of a skipped triyne, deca-1,4,7-triynylbenzene from 1,3-diyne tosylate and phenylethynylalane (entry 6).

In summary, a novel copper-free and regioselective synthesis of methylene-bridged skipped diynes has been developed, which relies on cross-coupling alkynylalanes with phosphinate-, phosphate- or sulfonate-based propargylic electrophiles capable of complexation with the nucleophile. The method is efficient, mild and advantageously does not lead to detrimental isomerization of the base-sensitive skipped diyne since only catalytic amounts of triethylamine are required for initial preparation of the alkynylalane.

All experiments sensitive to air and/or to moisture were carried out under argon in dried glassware assembled under a stream of argon. NMR spectra were recorded on Bruker Ultrashield Avance (^{1}H, 300 or 400 MHz; ^{13}C, 75 or 100 MHz) spectrometers. Mass spectra were obtained with GCMS conducted on a Thermo, MS: DSQ and GC: TRACE GC ULTRA with Zebron phenomenex column: Phase ZB-5ms 15 m, diam: 0.25 mm, 0.25 μm, H_2 flow 1.7 mL/min, temp injector: 280 °C, temp detector: 280 °C, method: 4 min at 40 °C, then 30 °C/min until 320 °C, then 5 min at 320 °C. All reagents and solvents, unless otherwise noted, were purchased from commercial vendors and used without further purification. GC analysis was conducted on a Varian CP-3800 + AutoSampler CP-8410 + H_2 generator Schmidlin SL-9100 with detector: FID, column: Chrompak CP-Sil24CB 15 m, diam: 0.32 mm, 0.25 μm, H_2 flow 1.7 mL/min, temp injector: 250 °C, temp detector: 300 °C, method: 4 min 40 °C, then 30 °C/min until 250 °C, then 5 min at 250 °C.

The electrophilic partners employed in this study were prepared according to literature procedures from commercially available alcohols: phosphoric acid diethyl ester pent-2-ynyl ester, phosphoric acid pent-2-ynyl ester diphenyl ester, diphenylphosphinic acid pent-2-ynyl ester,[12] methanesulfonic acid pent-2-ynyl ester,[13] methanesulfonic acid prop-2-ynyl ester,[14] toluene-4-sulfonic acid pent-2-ynyl ester,[15] and toluene-4-sulfonic acid prop-2-ynyl ester.[14]

The phenylethynyltrimethylaluminum was prepared according to the procedure described by Micouin et al.[8] This alane solution was diluted in CH_2Cl_2 to a final concentration of 1 M in order to avoid crystallization. This solution could be stored under argon in the dark for several days.

Procedure 1
Hepta-1,4-diynylbenzene

Phenylethynyltrimethylaluminum (1 M in CH_2Cl_2–heptane, 2 mL, 2.0 mmol, 1 equiv) was added dropwise to a stirred solution of pent-2-ynyl methanesulfonate (325 mg, 2.0 mmol, 1 equiv) in CH_2Cl_2 (3 mL) at 0 °C. The reaction progress was followed by GC. After stirring for 2 h at this temperature, the reaction was quenched carefully at 0 °C by dropwise addition of an aq Rochelle's salt solution (2 M, ~15 mL) and the resulting mixture was diluted with Et_2O (20 mL). The aqueous layer was extracted with Et_2O (2 × 20 mL). The combined Et_2O extracts were dried (Na_2SO_4) and concentrated in vacuo to give a clear oil, which was purified by flash chromatography (hexane, R_f = 0.8) to give the product as a clear oil (308 mg, 92%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 (t, ^3J = 6.0 Hz, 3 H, CH_3), 2.08–2.16 (m, 2 H, CH_2), 3.30 (t, ^3J = 3.0 Hz, 2 H, CH_2), 7.17–7.23 (m, 3 H, C_6H_5), 7.34–7.37 (m, 2 H, C_6H_5).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.4, 12.4, 13.8, 72.9, 80.3, 82.3, 80.3, 123.4, 128.0, 128.2, 131.7.

Procedure 2
***tert*-Butylocta-2,5-diynyloxydiphenylsilane**

A solution of *tert*-butylprop-2-ynyloxysilane (1.178 g, 4 mmol) in anhyd toluene (10 mL) under argon was metalated with *n*-BuLi (1.6 M in hexane, 2.8 mL, 4.4 mmol, 1.1 equiv) at –35 °C for 30 min. The resulting solution was treated with Me_2AlCl (1 M, 4.4 mL, 4.4 mmol, 1.1 equiv) at the same temperature and stirred at –35 °C for an additional 30 min. This solution was transferred via a cannula at this temperature to a solution of the pentyne mesylate (324 mg, 2 mmol). The stirring was continued at –35 °C for 2.5 h. The cooling bath was removed and on reaching r.t., the mixture was quenched with MeOH (1 mL), poured into H_2O (20 mL), and extracted with Et_2O (3 × 15 mL). The organic layers were dried (Na_2SO_4) and concentrated in vacuo to give a clear oil which was purified by flash chromatography (Et_2O–hexane: 0.5:10, R_f = 0.45) to give the protected diyne as an oil (397 mg, 55%); GC: t_R = 8.51 min.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (s, 9 H, CH_3), 1.04 (t, ^3J = 6 Hz, 3 H, CH_3), 2.06–2.13 (m, 2 H, CH_2), 3.03–3.05 (m, 2 H, CH_2), 4.23 (t, ^3J = 3 Hz, 2 H, CH_2), 7.28–7.37 (m, 3 H, C_6H_5), 7.63–7.65 (m, 2 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.9, 12.4, 13.8, 19.2, 26.8, 52.9, 72.9, 78.5, 80.0, 82.2, 127.8, 129.9, 133.2, 135.7.

CIMS: *m*/*z* = 237, 207.

Procedure 3
16-Chlorohexadeca-6,9-diyne

Me_3Al (3.75 mL, 7.48 mmol, 2 M in heptane) was transferred by a syringe to a flask, upon which Et_3N (94.5 μL, 0.68 mmol) was added, followed after 5 min by 8-chlorooct-1-yne (986 mg, 6.8 mmol). The stirred solution was heated to 60 °C for 6 h until methane evolution had ceased at which point an aliquot was taken, quenched with CD_3OD, and filtered before an ^{1}H NMR spectrum confirmed the total disappearance of the terminal alkyne proton. The prepared (8-chlorooct-1-ynyl)dimethylaluminum (1.28 mL, 2.0 mmol, 1.56 M in heptane) was then added dropwise to a stirred solution of oct-2-ynyl methanesulfonate (324 mg, 2.0 mmol) in CH_2Cl_2 (3 mL) at

0 °C. The solution was allowed to warm up to r.t. and the reaction progress followed by GCMS. After 7 h, the mixture was transferred to a separating funnel, diluted with Et_2O (20 mL), and quenched carefully by dropwise addition of an aq Rochelle's salt solution (2 M, 4 mL). The layers were separated and the aqueous layer extracted with Et_2O (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo to give the desired product as a yellow oil, which was purified by flash chromatography (hexane, R_f = 0.28) to give the product as a yellow liquid (368 mg, 73%); GC: t_R = 6.68 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.7 (t, J = 7 Hz, 3 H, CH_3), 1.4–1.1 (m, 12 H, CH_2), 1.6 (m, 2 H, CH_2), 2.0 (m, 4 H, CH_2), 3.0 (m, 2 H, CH_2), 3.4 (t, J = 7 Hz, 2 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.7, 14.0, 18.6, 18.7, 22.2, 26.4, 28.1, 28.5, 31.1, 32.5, 45.0, 74.4, 74.8, 80.2, 80.6.

EIMS: m/z = 252 (M^+).

Procedure 4

Octa-1,4-diynyl Tosylate

To a suspension of octa-1,4-diynyl alcohol (1.01 g, 8.25 mmol, 1.0 equiv), trimethylammonium hydrochloride (98%, 81 mg, 0.83 mmol, 0.1 equiv) and K_2CO_3 (1.37g, 1.2 equiv, 9.90 mmol) in CH_2Cl_2 (15 mL) was added TsCl (1.89 g, 9.90 mmol, 1.2 equiv) at 0 °C and the reaction progress was monitored by GC. After 1.5 h, the reaction was warmed to r.t., and after 4 h, TsCl (0.79 g, 4.13 mmol, 0.5 equiv) was added. After 21 h, an additional amount of TsCl (1.89 g, 9.90 mmol, 1.2 equiv) was added, and again at 45 h (1.89 g, 9.90 mmol, 1.2 equiv). At 68 h, GC confirmed 99% conversion and the reaction was cooled to 0 °C and quenched with H_2O (5 mL). CH_2Cl_2 (20 mL) was added and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL), the organic phases were combined, washed with H_2O (3 × 20 mL), dried (Na_2SO_4) and the solvent evaporated in vacuo to give an orange oil. The oil was purified by flash chromatography (10% EtOAc–hexane) to give the product as a light brown oil (1.26 g, 55%). GC: t_R = 9.44 min.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (t, J = 7 Hz, 3 H, CH_3), 2.10 (m, 2 H, CH_2), 2.98 (m, 2 H, CH_2), 4.62 (m, 2 H, CH_2), 7.28 (d, J = 9 Hz, 2 H, C_6H_5), 7.72 (d, J = 1 Hz, 2 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.82, 12.30, 13.75, 58.23, 71.96, 82.75, 84.64, 128.17, 129.76, 133.26, 144.96.

GCMS: m/z = 206 (M^+, 100%).

10-Phenyldeca-3,6,9-triyne

Phenylethynylaluminum (1 M in CH_2Cl_2–heptane, 2 mL, 2.0 mmol, 1.0 equiv) was added dropwise to a stirred solution of oct-3,6-diyne-8-*p*-toluenesulfonate (552 mg, 2.0 mmol, 1.0 equiv) in CH_2Cl_2 (3 mL) at 0 °C. The mixture was allowed to warm to r.t. and the progress was monitored by GC. After 1 h, the reaction was quenched carefully at 0 °C by dropwise addition of an aq Rochelle's salt solution (2 M, ~15 mL). The resulting mixture was then diluted with Et_2O (20 mL). The aqueous layer was extracted with Et_2O (3 × 20 mL). The combined Et_2O extracts were dried (Na_2SO_4) and concentrated in vacuo to provide a brown oil which was purified by flash chromatography (hexane, R_f = 0.2) to give the product as a brown oil (340 mg, 74%); GC: t_R = 11.23 min.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, J = 7 Hz, 3 H, CH_3), 2.11 (m, 2 H, CH_2), 3.10 (m, 2 H, CH_2), 3.31 (m, 2 H, CH_2), 7.18–7.42 (m, 5 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.8, 10.5, 12.4, 13.8, 73.0, 74.0, 75.4, 80.6, 82.3, 83.6, 123.1, 128.1, 128.2, 128.3, 128.8, 131.7, 132.1.

GCMS: m/z = 206 (M^+, 100%).

References

(1) (a) For a general review, see: Normant, J. F. *Synthesis* **1972**, 63. Exceptions include the use of tris(alkynyl)indiums with benzyl bromide catalyzed by Cl_2Pd(dppf) and the use of alkynylboron dichlorides with benzyl, benzylallyl and benzypropargyl secondary alcohols. (b) Perez, J.; Perez-Sestelo, L.; Sarandeses, A. *J. Am. Chem. Soc.* **2001**, *123*, 4155. (c) Kabalka, G. W.; Yao, M.-L.; Borella, S. *Org. Lett.* **2006**, *8*, 879.

(2) (a) Durand, S.; Parrain, J.-L.; Santelli, M. *J. Chem. Soc., Perkin Trans. 1* **2000**, 253. (b) Tedeschi, C.; Saccavini, C.; Maurette, L.; Soleilhavoup, M.; Chauvin, R. *J. Organomet. Chem.* **2003**, *670*, 151.

(3) (a) Brandsma, L. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, **2003**, and references cited therein. (b) Jeffery, T.; Guenot, S.; Linstrumelle, G. *Tetrahedron Lett.* **1992**, *33*, 5757. (c) Hansen, T. V.; Stenstrom, Y. *Tetrahedron: Asymmetry* **2001**, *12*, 1407. (d) Spinella, A.; Caruso, T.; Martino, M.; Sessa, C. *Synlett* **2001**, 1971. (e) For an exception: Padmanabhan, S.; Nicholas, K. M. *Tetrahedron Lett.* **1983**, *24*, 2239.

(4) (a) Mel'nikova, V. I.; Pivnitskii, K. K. *Zh. Org. Khim.* **1990**, *26*, 78; *Chem. Abstr.* **1990**, *113*, 23031. (b) Mathai, I. M.; Taniguchi, H.; Miller, S. I. *J. Am. Chem. Soc.* **1967**, *89*, 115. (c) Hungerford, N. L.; Kitching, W. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1839.

(5) (a) *Comprehensive Organic Synthesis*, Vol. 5; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, **1991**, 1543. (b) Bohlmann, F.; Schoenowsky, H.; Inhoffen, E.; Grau, G. *Chem. Ber.* **1964**, *97*, 794.

(6) Kessabi, J.; Beaudegnies, R.; Jung, P. M. J.; Martin, B.; Montel, F.; Wendeborn, S. *Org. Lett.* **2006**, *8*, 5629.

(7) (a) Shinoda, M.; Iseki, K.; Oguri, T.; Hayasi, Y.; Yamada, S.; Shibasaki, M. *Tetrahedron Lett.* **1986**, *27*, 87. (b) Fried, J.; Sih, J. C. *Tetrahedron Lett.* **1973**, *14*, 3899. (c) Fried, J.; Lin, C.; Ford, S. H. *Tetrahedron Lett.* **1969**, *10*, 1379. (d) Ben-Efraim, D. A.; Sondheimer, F. *Tetrahedron* **1969**, *25*, 2823.

(8) (a) Feuvrie, C.; Blanchet, J.; Bonin, M.; Micouin, L. *Org. Lett.* **2004**, *6*, 2333. (b) Wang, B.; Bonin, M.; Micouin, L. *Org. Lett.* **2004**, *6*, 3481.

(9) The need for two equivalents of alkynylalane when employing propargyl phosphates and phosphinates suggests that the reaction proceeds via an alternative mechanism, essentially involving Lewis acid activation prior to coordination and transfer brought on by the second equivalent of alkynylalane.

(10) Lapitskaya, M. A.; Vasiljeva, L. L.; Pivnitsky, K. K. *Synthesis* **1993**, 65.

(11) Unpublished results from this laboratory.

(12) Yanagisawa, A.; Nomura, N.; Yamamoto, H. *Tetrahedron* **1994**, *50*, 6017.

(13) White, W. L.; Anzeveno, P. B. *J. Org. Chem.* **1982**, *43*, 2379.

(14) Tanabe, Y.; Yamamoto, H.; Yoshida, Y.; Miyawaki, T.; Utsumi, N. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 297.

(15) Easton, C. J.; Ferrante, A.; Robertson, T. A.; Xia, L. *Aust. J. Chem.* **2002**, *55*, 647.