Radical Germylzincation of Aryl- and Alkyl-Substituted Internal Alkynes

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Cu(I)-mediated electrophilic substitution of the $C(sp^2)$ -Zn bond to obtain synthetically challenging tetrasubstituted vinylgermanes.

he increasing demand in germanium-containing com-L pounds has raised considerable interest in the regio- and stereocontrolled preparation of vinylgermanes.¹ For this, carbon-germanium bond-forming addition reactions to alkynes using hydrogermanes as a germanium source are most popular. The regio- and stereoselective hydrogermylation of alkynes was disclosed under several conditions, including thermal, sonochemical, or microwave activation,² transitionmetal catalysis,³ and main-group Lewis-acid catalysis⁴ as well as in the presence of radical initiators.^{2,3c,5} However, these methods share the common intrinsic limitation that they cannot give access to tetrasubstituted or 1,2,2-substituted vinylgermanes, which have two substituents distal to the germyl group.⁶ Alkyne germylmetalation is attractive in this context, as the newly formed $C(sp^2)$ -metal bond can serve as a linchpin for further functionalization, but it remains virtually unexplored: Reports on alkyne germylcupration are scarce^{7,8} and are limited to terminal alkynes.⁹ Moreover, subsequent $C(sp^2)$ -Cu bond functionalization is poorly effective or impeded by the reversible character of the addition step. Alkyne germylstannylation was also considered for the same purpose¹⁰ but, again, only on terminal alkynes, and $C(sp^2)$ -Sn bond functionalization required an additional synthetic step.

To overcome these shortcomings, we recently disclosed the germylzincation reaction of α -heteroatom-substituted alkynes, relying on their reaction with a hydrogermane and Et₂Zn in a radical chain process¹¹ (Scheme 1). The decisive feature of this new germylmetalation reaction is the possibility to combine it readily in one-pot with a subsequent stereoretentive electrophilic substitution reaction of the created $C(sp^2)$ –Zn bond. In a continuation of this work and given that organogermyl radicals add across various types of C–C triple bonds, we became interested in applying the method to other alkynes.¹² In this Letter, we report the radical germylzincation of internal alkynes, including symmetrical diaryl- and dialkylacetylenes,

Scheme 1. Radical Germylzincation of Internal Alkynes



nonsymmetrical (aryl, alkyl)-substituted alkynes, and aryl-, alkyl-, or trimethylsilyl-substituted propargylic alcohols. High levels of regio- (where appropriate) and stereocontrol can be achieved through the modulation of the operating conditions for germylzincation reactions that can be either *trans-* or *cis*-selective depending on the substrate type.

We commenced our study by investigating the reaction of diphenylacetylene 1a with a combination of Ph₃GeH and Et₂Zn (Table 1).

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Table 1. Germylzincation of Diphenylacetylene (1a)



<i>Z</i> -3a (E=H)	<i>E-</i> 3a (E=H)
[² H] Z 3a (E=D)	[² H] <i>E</i> 3a (E=D

entry	solvent	conditions	AIBN (mol %)	Е	d.r. 3a (Z/E) ^a	yield 3a (%) ^b
1	THF	40 °C, 16 h		Н	88:12	49 ^{c,d}
2	THF	80 °C, 1 h	25	Н	92:8	67 ^d
3	THF	80 °C, 1 h	25	D	92:8	71 ^d
4	THF	80 °C, 1 h		Н	>98:2	<10 ^e
5	THF	80 °C, <i>f</i> 1 h	25	Н	84:16	74
6	THF	80 °C, 1 h	50	Н	80:20	85 ^e
7	benzene	100 °C, 16 h	10	Н	23:77	88 ^e
8	benzene	100 °C, <i>f</i> 1 h	10	Н	26:74	78 ^e
9	heptane	120 °C, 16 h	100	Н	30:70	83 ^e

^{*a*}Determined by ¹H NMR prior to purification. ^{*b*}Isolated yield of both diastereomers. ^{*c*}Ph₃GeH (1.3 equiv). ^{*d*}Ref 11. ^{*c*}Yield estimated by ¹H NMR analysis of the crude reaction mixture using butadiene sulfone as internal standard. ^{*f*}Microwave heating.

Under the operating conditions previously applied for the germylzincation of internal ynamides, that is, Ph₃GeH (1.3 equiv) and Et₂Zn (3.0 equiv) in THF at 40 °C (entry 1), after 16 h, and following workup, vinylgermane 3a was obtained with high *Z* stereoselectivity (Z/E = 88:12), albeit in moderate 49% yield because conversion was not complete (\sim 35–40% unreacted 1a was recovered). Using higher amounts of Ph₃GeH (2.0 equiv), adding AIBN (25 mol %) as a radical initiator, and operating at 80 °C to ensure decomposition of the latter made it possible to reduce the amount of unreacted 1a to \sim 20% and allowed for improved results: A 67% yield was observed within a much shorter reaction time (1 h) along with a significant enhancement in the stereoselectivity (Z/E = 92.8)(entry 2). Under these conditions, D-labeling confirmed the formation of a vinylzinc intermediate, as $[^{2}H]$ -3a was obtained (98% D incorporation) upon quenching with ND_4Cl (entry 3). Importantly, the critical role played by AIBN here was established through a control experiment: Under the same conditions but in the absence of the radical initiator, 3a was detected in amounts <10% (entry 4). Conversely, heating through microwave irradiation instead of an oil bath (entry 5) or increasing to 50 mol % the amount of AIBN (entry 6) led to full or close-to-full conversion. However, this was not beneficial overall because the stereoselectivity dropped. In benzene at 100 °C (entries 7 and 8), 88 and 78% yields were achieved with only 10 mol % AIBN, but a reversal of stereoselectivity was observed, and vinylgermane 3a was delivered in a $E/Z \approx 75.25$ ratio both upon heating in an oil bath (for 16 h) and through microwave irradiation (1 h). A similar outcome was observed when operating in heptane at 120 °C in the presence of 100 mol % AIBN (entry 9).

These results point toward the coexistence of two regimes: a nonequilibrating regime that is *trans*-stereoselective¹³ and an equilibrating regime that is (moderately) *cis*-stereoselective. In

line with analogous observations for radical hydrogermylation reactions of terminal alkynes, we surmise that the triphenylgermyl radical is responsible for the isomerization of the β triphenylgermyl vinylzinc intermediates **2a**.^{5a} Accordingly, kinetic selectivity is prevalent for short reaction times and in THF, wherein radical chains are short, whereas thermodynamic selectivity is observed for long reaction times and in benzene or heptane, wherein the triphenylgermyl radicalpromoted isomerization is facilitated by the existence of longer radical chains.

Having identified these two possibilities, we focused on assessing their scope. In THF at 80 $^{\circ}$ C (Scheme 2), other diaryl-substituted acetylenes also readily underwent *trans*-selective germylzincation.





^{*a*}Configuration of each isomer could not be determined unequivocally. The two major isomers had a *Z* configuration. ^{*b*}AIBN (25 mol %). ^{*c*}Microwave heating. ^{*d*}Yield calculated by ¹H NMR analysis of the crude reaction mixture using butadiene sulfone as an internal standard. ^{*e*}Only β -regioisomers were detected.

Symmetrical diphenylacetylenes **1b**,**c** afforded the corresponding vinylgermanes **3b**,**c** in good yields (66–68%) with high Z selectivity ($Z/E \ge 87:13$). In the case of nonsymmetrical diarylacetylenes, however, the regioselectivity of the process could not be controlled. Illustratively, the germylzincation of diphenylacetylene **1d** having both an electron-rich *para*-OMe-phenyl substituent and an electron-deficient *para*-CF₃-phenyl substituent delivered **3d** (in 76% yield) as an α/β = 50:50 mixture of regioisomers, thus evidencing that an

electronic bias of the carbon–carbon triple bond has no influence on the regioselectivity of the addition. The poor regioselectivity observed in the germylzincation of 1e, substituted by a 3-pyridyl group and a phenyl group, further confirmed this fact. Here, however, the major (β) regioisomer of 3e, formed as a single Z diastereomer, was isolated in a decent 57% yield.

Dialkyl-substituted acetylenes were also amenable to *trans*germylzincation in THF at 80 °C (Scheme 2).¹⁴ In the presence of 25 mol % AIBN, the reaction of 4-octyne **4a** delivered vinylgermane **5a** in 31% yield with Z/E = 93:7. A more satisfactory 58% yield was obtained with 100 mol % AIBN using microwave heating. Here also, fully D-labeled [²H]-**5a** was recovered on quenching the reaction with ND₄Cl, thus confirming the formation of vinylzinc intermediates. Note that the formation of bisgermylated byproduct **6**, the structure of which was determined by X-ray crystallographic analysis, was also detected under these harsher conditions (4% yield).¹⁵ The same protocol was also applied to alkyne **4b** having two different alkyl substituents, but poor regiocontrol was observed despite the recognizable steric bias, and product **5b** was obtained as a mixture of regio- and stereoisomers.

Conversely, regiocontrol was not a problem in the case of 1phenyl-1-propyne 7**a**, which has substituents that are different in nature. As for the diaryl-substituted alkynes, 25 mol % AIBN sufficed to achieve a good 66% germylzincation yield. Only the β -regioisomers were detected, which can be ascribed to stabilization by the adjacent phenyl group of the vinyl radical intermediate (I (R¹ = Ph), Scheme 1) arising from the triphenylgermyl radical addition. Nevertheless, the isomerization of the *E*-vinylzinc adduct is more facile and observable to some extent, even if full conversion requires 1 h of reaction time. Hence vinylgermane 8**a** was obtained as a Z/E = 65:35mixture of stereoisomers. The structure of *E*-8**a** was confirmed by X-ray crystallography.

We next surveyed the possibilities offered by operating in heptane at 100 $^{\circ}$ C (Scheme 3). The reaction of 4-octyne 4a in the presence of 50 mol % AIBN and under microwave





^aAIBN (50 mol %), microwave heating (1 h). ^bMicrowave heating (1 h). ^c94% yield was obtained on a 1 mmol scale (25 mol % AIBN).

irradiation delivered vinylgermane **5a** in 52% yield as a Z/E = 75:25 mixture of isomers. Hence, whereas some isomerization was observed, the process did not seem suitable to steer the reaction toward *E* stereoselectivity for this substrate class. In addition, bisgermylated product **6** was formed in 32% yield. As previously observed in THF, nonsymmetrical dialkyl-substituted alkyne **4b** led to a mixture of regio- and stereoisomers.

By contrast, with 1-phenyl-1-propyne 7a, for which the isomerization occurs more readily,¹⁶ performing the reaction in the presence of 10 mol % AIBN delivered the desired product **8a** in an excellent 93% yield with perfect regioselectivity and remarkable *E* stereoselectivity (E/Z = 95:5). No difference was observed using conventional heating (2 h) or microwave irradiation (1 h). Again, D-labeling experiments ascertained that germylzincation was also under these conditions the exclusive reaction pathway accounting for vinylgermane formation. The protocol appears to be general for (alkyl, aryl)-substituted alkynes, as, similarly, 1-phenyl-1-butyne 7b afforded vinylgermane **8b** in 91% yield with E/Z = 95:5 ratio and complete control of the regioselectivity. Importantly, no appreciable difference in the outcome was noted on running the reaction on a 1 mmol scale.

We then considered propargylic alcohols (Scheme 4), a synthetically important family of substrates for which we have



awaited the achievement of high levels of regio- and stereocontrol. An O-directing effect allowing for exquisite vicinal regiocontrol in the addition of triorganostannyl radicals is well documented for radical hydrostannation reactions of propargyloxy dialkylacetylenes with tin hydrides,¹⁷ and we observed similar levels of regioselectivity in a preliminary survey of AIBN-initiated radical hydrogermylation reactions with Ph₃GeH.¹⁸ Stereocontrol could be secured through chelate formation (**11**).

Aryl- or alkyl-substituted primary (9a, 9c) and secondary (9b, 9d) propargylic alcohols performed well, and germylated alcohols 13a-d were obtained in good-to-high yields with excellent β regioselectivity and Z stereoselectivity. The methodology was also amenable to the utilization of trimethylsilyl-substituted propargylic alcohol 9e, which afforded β -trimethylsilyl vinylgermane 13e in 65% yield. Lastly, homopropargylic alcohol 10 was investigated. Here, given that pubs.acs.org/OrgLett

the hydroxy unit is too far away from the alkyne and no regiocontrol is induced in the germyl radical addition,^{18,19} a mixture of regioisomers was obtained in a β -14/ α -14 57:43 ratio in a 57% combined yield. Nevertheless, chelate formation remains possible for both regioisomers of the germylzinc adducts β -12 and α -12 (not shown in the scheme) and allows for almost complete stereocontrol in favor of the Z isomers of β -14 and α -14.

In the final part of our study, we established the potential of our new germylzincation procedures to prepare tetrasubstituted vinylgermanes through functionalization in one pot of the $C(sp^2)$ -Zn bond of the vinylzinc adducts formed. Cu(I)mediated allylation was performed for each substrate class: Tetrasubstituted vinylgermanes 15–18 were obtained from 1a, 4a, 7a, and 9b in good-to-excellent yields (58–93%) and with exquisite retention of the geometry of the vinylzinc intermediates (Scheme 5). The configuration of products Z-15 and E-17 was established by X-ray crystallography.

Scheme 5. Preparation of Tetrasubstituted Vinylgermanes through Alkyne Germylzincation/Cu(I)-Mediated Electrophilic Substitution



^{*a*}AIBN (25 mol %). ^{*b*}AIBN (100 mol %), microwave heating. ^{*c*}5% of **6** was detected. ^{*d*}AIBN (10 mol %). ^{*e*}Only β -regioisomers were detected.

Benzoyl chloride and tributyltin chloride were also competent electrophiles, leading to benzoylated vinylgermane **19** and β -stannyl vinylgermane **20** as single regio- and stereoisomers. The domino alkyne germylzincation/Cu(I)mediated stannylation reaction giving **20** is remarkable because it allows for the direct synthesis of these tetrasubstituted 1,2dimetalated alkenes that are not accessible through the oxidative addition chemistry of Ge–Sn compounds.²⁰

In summary, we describe here the germylzincation of internal alkynes by reaction with Ph_3GeH and Et_2Zn in the presence of AIBN as a radical initiator. Upon tuning of the reaction conditions, an array of substrate-types is amenable to germylzincation with high levels of stereoselectivity, including symmetrical diaryl- or dialkylsubstituted acetylenes, nonsymmetrical (alkyl, aryl)-substituted acetylenes, and propargylic

alcohols. Superb regiocontrol is obtained for alkyl-substituted arylacetylenes and propargylic alcohols. As part of this work, we demonstrate the possibility of engaging the $C(sp^2)$ –Zn bond formed in subsequent stereoretentive Cu(I)-mediated electrophilic substitution reactions. This two-step, one-pot protocol offers a versatile and modular route to access valuable tetrasubstituted vinylgermanes with substitution patterns that have so far remained synthetically challenging.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01367.

Additional data and discussion, experimental details, NMR spectra for new compounds, and X-ray crystal structures for compounds 6, *E*-8a, *Z*-15, and *E*-17 (PDF)

Accession Codes

CCDC 2077610–2077612 and 2077757 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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