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REGIOSELECTIVE GERMYLCUPRATION OF ACETYLENES

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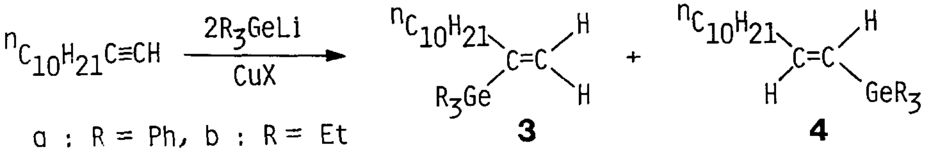
Abstract: The reaction of terminal acetylenes with $(Ph_3Ge)_2Cu(CN)Li_2$ (**1**) or $(Et_3Ge)_2Cu(SMe_2)Li$ (**2**) provides vinylgermanes in good yields. Whereas germylcupration of 1-dodecyne gives 2-germyl-1-dodecene as a main product, germylmetalation of phenylacetylene or 3-methyl-3-buten-1-yne affords 1-germyl compounds preferentially.

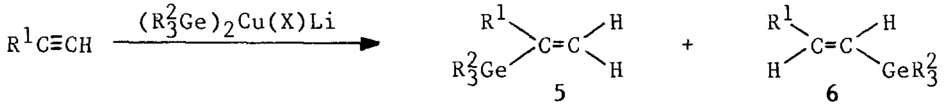
The reaction of compounds such as $PhMe_2SiMtl$[1] or Bu_3SnMtl[2] (Mtl = MgMe, $AlEt_2$) with an acetylenic linkage affords simple and general access to the cis-addition products of the component elements. The regiochemistry depends on the nature of the transition-metal catalysts and the reaction is useful in synthetic work. Here we wish to report that germylcopper reagent **1** or **2** reacts with terminal acetylenes to give vinylgermanes under good control of the regio- and stereoselectivity.



A THF solution of Ph_3GeLi (0.73 M, 2.1 ml, 1.5 mmol) derived from Ph_4Ge and Li[3] was added to a suspension of CuCN (67 mg, 0.75 mmol) in THF (2.0 ml) at 0°C. After stirring for 15 min, a solution of 1-dodecyne (83 mg, 0.5 mmol) and ^nBuOH (0.17 g, 2.3 mmol) in THF (3.0 ml) was added and the resulting mixture was stirred for an additional 20 min. Workup (Et_2O, aq NH_4Cl) followed by silica gel thin layer chromatography gave a mixture of 2-triphenylgermyl-1-dodecene (**3a**) and 1-triphenylgermyl-1-dodecene (**4a**) (0.17 g, **3a**/**4a** = 80/20)[4] in 71% combined yield. The representative results are summarized in Table 1.

Treatment of 1-dodecyne with 1.5 equiv of the triphenylgermylcopper reagent generated from $2Ph_3GeLi$ and CuCN (or CuI, $CuBr{\cdot}SMe_2$) at 25°C for 5 h gave no trace of triphenylgermylalkenes **3a** and **4a**. Starting acetylenic compound was recovered unchanged (>90%). Coexistence of proton donor such as ^nBuOH or water[5] is essential for the formation of **3a** and **4a**. These weakly acidic proton donors react easily only with the intermediary

Table 1. Germylcupration of acetylenes

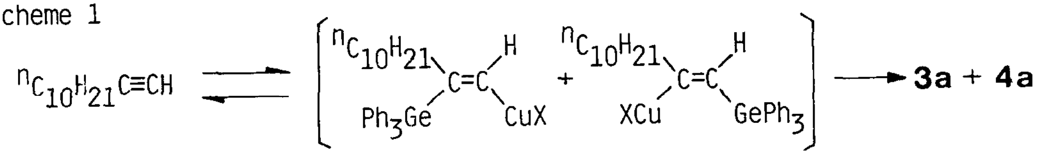


Acetylene	Reagent			Product	
R^1	R^2_3GeLi	Cu salt	Additive	Yield(%)^a	Ratio of **5**/**6**
$^nC_{10}H_{21}$	Ph_3GeLi^b	CuCN	^nBuOH	71	80 : 20
		CuCN	^nBuCHO	99	70 : 30
		CuI	^nBuOH	78	40 : 60
		$CuBr\cdot SMe_2$	^nBuCHO	81	75 : 25^c
	Et_3GeLi^d	$CuBr\cdot SMe_2$	-	(81)^e	70 : 30^f
$PhCH_2OCH_2CH_2$	Ph_3GeLi	CuCN	^nBuOH	46	5 : 95
		$CuBr\cdot SMe_2$	^nBuCHO	82	5 : 95
	Et_3GeLi	$CuBr\cdot SMe_2$	-	91	65 : 35^f
Ph	Ph_3GeLi	CuCN	^nBuOH	85	<5 :>95
	Et_3GeLi	$CuBr\cdot SMe_2$	-	91	15 : 85^f
$CH_2=C(CH_3)$	Ph_3GeLi	$CuBr\cdot SMe_2$	^nBuOH	98	1 : 99
	Et_3GeLi	$CuBr\cdot SMe_2$	-	95	13 : 87^f

a) Isolated yields unless otherwise noted. b) $(Ph_3Ge)_2CuX$ (0.75 mmol), ^nBuOH (or ^nBuCHO, 2.3 mmol), and acetylene substrate (0.5 mmol) were employed. c) Ether was used as solvent instead of THF. d) $(Et_3Ge)_2Cu(SMe_2)Li$ (0.5 mmol) and acetylene substrate (0.5 mmol) were employed. e) Glpc yield using octadecane as an internal standard (Silicone OV-17 3%, 2 m, 170°C). f) MeOH was used for quenching the reaction.

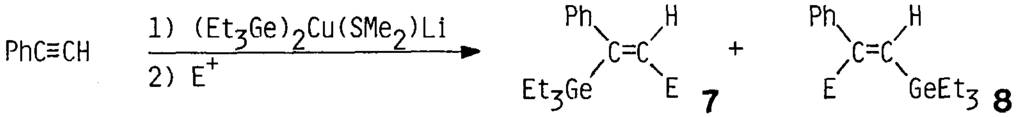
vinylcopper compound and are reluctant to react with triphenylgermylcopper reagents. Benzenethiol and aniline were ineffective because the former reacted with germylcopper reagents and the latter was inert to both copper species due to its lower acidity. These results indicated that the reaction is reversible and the equilibrium favours original system more than the intermediary vinylcopper species (Scheme 1).^{6} Valeraldehyde, 3-pentanone, and acetophenone were also effective to complete the reaction.^{7} The nature of the additives slightly affects the distribution of the isomeric

Scheme 1



vinylgermanes. The isomeric ratio of **3a**/**4a** = 80/20 was obtained with water and alcohols (MeOH, ^{n}BuOH, ^{s}BuOH, and ^{t}BuOH), and 70/30 was obtained with carbonyl compounds (nonanal, 3-pentanone, and acetophenone).[8]

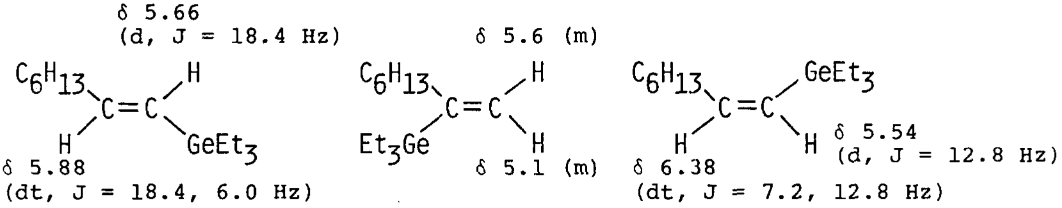
The reagent 2 prepared from Et_3GeLi and $CuBr \cdot SMe_2$ was also effective for the germylmetalation.[9] In contrast to the reagent **1**, the addition of the reagent 2 proceeded essentially to completion in the absence of proton donors. Thus, the intermediary alkenylcopper species could be trapped by various electrophiles. For instance, germylcupration of phenylacetylene followed by the addition of MeI gave the corresponding alkenylgermane in 82% combined yield.



a: E = D (D_2O, **7/8** = 7/93, 89%) b: E = Me (MeI, **7/8** = 17/83, 82%)
c: E = $CH_2{=}CHCH_2$ ($CH_2{=}CHCH_2Br$, **7/8** = 10/90, 96%)

The regiochemistry heavily depends not only on the nature of the copper reagent but also on the structure of the acetylenic compounds. Treatment of propyne or 1-dodecyne with the reagent **1** or **2** provided 2-germyl-1-alkenes as main products. Meanwhile, the germylcupration of the substrate bearing unsaturated groups α,β to the acetylenic linkage proved to give 1-germyl isomer preferentially.

cis-Addition of germylcopper reagents was confirmed by the examination of the products with the authentic samples prepared from the corresponding vinyl bromide and $^{t}BuLi/Et_3GeCl$.



Copper reagent derived from R_3GeLi and CuX (1:1) was as effective as the digermylcuprates **1** and **2**. The use of catalytic amount of CuX (5 mol%) instead of stoichiometric amount decreased the yield of the corresponding germylalkenes (<5%). Many combinations of organometallic compounds and transition-metal catalysts were examined for the germylmetalation of 1-dodecyne. In contrast to silylmetalation[1] and stannylmetalation,[2] almost all combinations failed to give vinylgermanes. Only $Ph_3Ge{-}AlEt_2$ derived from Ph_3GeLi and Et_2AlCl provided the corresponding vinylgermanes in the presence of various kinds of transition-metal catalysts. For instance,

$PdCl_2(PPh_3)_2$ (2 mol%) catalyzed reaction of 1-dodecyne at 25°C for 14 h gave a mixture of **3** and **4** (**3**/**4** = 40/60) in 65% yield after hydrolysis.

Reference and Notes

1. H. Hayami, M. Sato, S. Kanemoto, Y. Morizawa, K. Oshima, and H. Nozaki, J. Am. Chem. Soc., **105**, 4491 (1983); Y. Morizawa, H. Oda, K. Oshima, and H. Nozaki, Tetrahedron Lett., **25**, 1163 (1984).
2. J. Hibino, S. Matsubara, Y. Morizawa, K. Oshima, and H. Nozaki, ibid., in press.
3. H. Gilman and C. W. Gerow, J. Am. Chem. Soc., **77**, 4675 (1955).
4. The isomeric ratio was determined by ^1H-NMR (200 MHz) spectrum. Physical and spectral data of the mixture are as follows: bp 120°C (bath temp)/0.1 Torr; ^1H-NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.1-1.5 (m, 16H), 2.2-2.4 (m, 2H), 5.3-5.4 (m, 0.8H, **3a**), 5.8-5.9 (m, 0.8H, **3a**), 6.1-6.2 (m, 0.4H, **4a**), 7.3-7.6 (m, 15H); IR (neat) 2880, 2820, 1420, 1080, 730, 690 cm^{-1}. Found: C, 76.23; H, 8.15%. Calcd for $C_{30}H_{38}Ge$: C, 76.47; H,8.13%.
5. The use of D_2O or MeOD provided the corresponding deuterated germylalkenes.
6. Similar results have been recently reported in the reaction of stannylcopper reagent with acetylenic substrates. E. Piers and J. M. Chong, J. Chem. Soc. Chem. Commun., **1983**, 934; S. D. Cox and F. Wudl, Organometallics, 2, 184 (1983).
7. The adducts between the intermediary vinylcopper species and carbonyl compounds could not be observed in the reaction mixture. The function of the carbonyl compounds has been unclear.
8. The nature of copper salts with or without ligands also affects the product distributions. Isomeric ratios (**3**/**4**) in the reaction between 1-dodecyne and the copper reagents derived from Ph_3GeLi and various kinds of copper salts in the presence of ^nBuCHO are given: (CuCN, 70/30), (CuI, 50/50), (CuSCN, 40/60), ($CuI/P(OPh)_3$,60/40), (CuI/PBu_3, 40/60).
9. A typical experimental procedure is as follows. Addition of MeLi (1.5 M ether solution, 1.0 mmol) to a solution of $Et_3GeGeEt_3$ (0.32 g, 1.0 mmol) in HMPA (1.0 ml) at 0°C to give an orange solution of Et_3GeLi.[10] After stirring for 15 min, the resulting solution was diluted with THF (5.0 ml) and $CuBr{\cdot}SMe_2$ (0.1 g, 0.5 mmol) was added. The mixture was stirred for another 15 min at 0°C and a solution of 1-dodecyne (83 mg, 0.5 mmol) in THF (3.0 ml) was added. The whole was stirred at 25°C for 30 min and recooled to 0°C and quenched with MeOH (0.2 ml) to give a mixture of 2-triethylgermyl-1-dodecene (**3b**) and 1-germyl isomer (**4b**) in 70:30 ratio in 81% combined yield.
10. E. J. Bulten and J. G. Noltes, J. Organometal. Chem., **29**, 397 (1971); K. Mochida and N. Matsushige, ibid., **229**, 11 (1982).

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