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Et_3B Induced Stereoselective Radical Addition of Ph_3GeH to Acetylenes and its Application to Isomerization of Olefins

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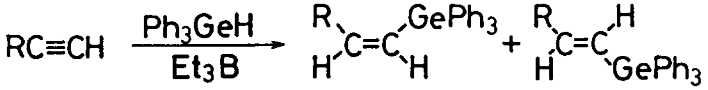
Abstract: Triphenylgermane adds easily to acetylenes in the presence of Et_3B to give (E)- or (Z)-alkenyltriphenylgermanes, respectively, under excellent control of regio- and stereoselectivities.

Free radical reactions have been used increasingly in recent years for the synthesis of organic molecules.[1] The hydrogermylation[2] or hydrostannation[3] of acetylenes takes place readily either in the absence of a catalyst or in the presence of catalytic amount of free radical initiator such as azobisisobutyronitrile (AIBN).[4] These reactions producing the corresponding alkenyltrialkylgermane or alkenyltrialkylstannane are of particular synthetic interest, however, they have a serious limitation. Thus, the reactions are generally not highly regio- and stereoselective. Moreover, the mechanism of the reactions does not appear to have been well established mainly because the products can undergo isomerization under the hydrogermylation or hydrostannation reaction conditions. Here we wish to report that trialkylborane facilitates the addition of Ph_3GeH[5] to acetylenes to give (E)- or (Z)-alkenyltriphenylgermanes, respectively under excellent control of regio- and stereoselectivities.

A hexane solution of Et_3B[6] (1.0 M, 1.0 ml, 1.0 mmol) was added to a solution of 1-dodecyne (0.18 g, 1.1 mmol) and Ph_3GeH (0.30 g, 1.0 mmol) in toluene (8 ml) at -78°C under an argon atmosphere. After stirring for 3 h at -78°C, the reaction mixture was poured into ice-cooled water and extracted with ethyl acetate three times. Combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residual oil was submitted to preparative tlc on silica gel to give (Z)-1-triphenylgermyl-1-dodecene exclusively (0.36 g, 76% yield, Z/E = >20/1). The representative results are summarized in Table 1.[7]

The isomeric ratios of the products heavily depend on the reaction temperature and the ratio [acetylene]/[Ph_3GeH]. The reaction at -78°C[9] in toluene in the presence of slight excess of the acetylene provides (Z)-alkenyltriphenylgermane exclusively, whereas the reaction at 60°C in benzene with slight excess of Ph_3GeH gives (E)-alkenyltriphenylgermane as a single product. Solvent also affects the isomeric ratio of the products. In polar solvents, the (Z)-isomer was obtained as major product. For instance, treatment of 1-dodecyne with Ph_3GeH-Et_3B in THF at 0°C for 2 h gave a

Table 1. Stereoselective hydrogermylation of acetylenes



Entry	Acetylene R	Reaction Conditions Temp(°C)	Time(h)	Y(%)[a]	Product Ratio of Z/E[b]
1	$^{n}C_{10}H_{21}$	-78^{c}	3	76	>20/1
2		-20^{d}	2	78	2/1
3		25^{d}	2	77	1/9
4		60^{d}	2	99	<1/20
5		0^{d}	(THF) 2	84	8/1
6		0^{d}	($PhCH_3$-MeOH) 2	80	10/1
7	CH_3	-78^{e}	2	65	>20/1[f]
8	$HOCH_2CH_2$	-78^{c}	5	80	>20/1
9		60^{d}	15	75	<1/20
10	$HOCH_2CH_2CH_2CH_2$	-78^{c}	5	80	>20/1
11	$EtOOC(CH_2)_9$	-78^{c}	12	64	>10/1
12		60^{d}	15	93	<1/20
13	6-dodecyne	-78^{c}	8	65	>20/1

a) Isolated yields. b) Determined by GC and/or NMR. c) Acetylene (1.1 mmol), Ph_3GeH (1.0 mmol), and Et_3B (1.0 mmol) were employed. Toluene was used as solvent. d) Acetylene (1.0 mmol), Ph_3GeH (1.1 mmol), and Et_3B (1.0 mmol) were employed. Benzene was used as solvent unless otherwise stated. e) Propyne (3.0 mmol), Ph_3GeH (1.0 mmol), and Et_3B (1.0 mmol) were employed. f) See ref. 8.

mixture of (Z)-1-triphenylgermyl-1-dodecene and (E)-isomer (Z/E = 8/1) in 84% yield. Addition of methanol (10 mmol per 1.0 mmol of substrate) to toluene is also effective for the selective formation of (Z)-isomer (entry 6 in Table 1).

It was anticipated that the trans addition products (i.e., (Z)-isomers) were kinetic-controlled products and isomerized into (E)-isomers under thermodynamic conditions. This was indeed the case as demonstrated by the isomerization of (Z)-1-triphenylgermyl-1-dodecene into the (E)-isomer. Heating a benzene solution of (Z)-1-triphenylgermyl-1-dodecene at 60°C in the presence of catalytic amount of Ph_3GeH and Et_3B gave (E)-isomer exclusively. The isomerization is explained by addition-elimination

Scheme 1

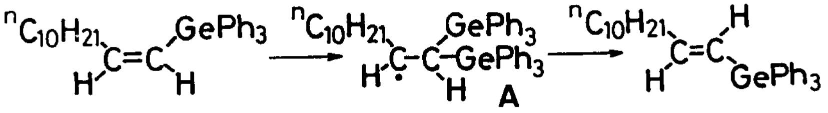
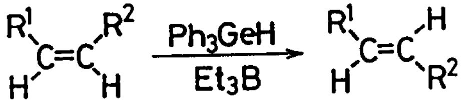
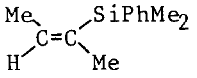
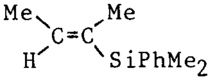


Table 2. Isomerization of olefins by means of $Ph_3GeH-Et_3B$ system[a]



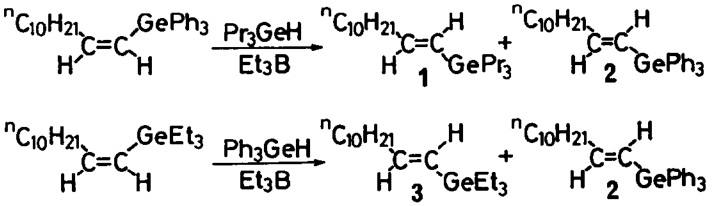
Entry	Substrate			Reaction	Product	
	R^1	R^2	Z/E	Time(h)	Y(%)	Z/E
1	$^nC_5H_{11}$	$^nC_5H_{11}$	>20/1	10	90	15/85
2	^tBu	$^nC_8H_{17}$	>20/1	10	91	0/100
3	$^nC_6H_{13}$	Ph	100/0	5	96	0/100
4	Ph	Ph	>20/1	2	81	<1/20
5	$^nC_6H_{13}$	$SiPhMe_2$	>20/1	10	84	<1/20
6	$^nC_{10}H_{21}$	$GePh_3$	10/1	4	88	<1/20
7	CH_3	$GePh_3$	>20/1	10	75	<1/20
8	$HOCH_2CH_2$	$GePh_3$	>20/1	10	70	<1/20
9	$EtOOC(CH_2)_9$	$GePh_3$	7/1	10	95	0/100
10			100/0	10	 71	<1/20
11	Me_3Si	$GeEt_3$	100/0	10[b]	89	0/100

a) See ref. 12. b) Et_3GeH was used instead of Ph_3GeH.

sequences of triphenylgermyl radical (Scheme 1). The germyl radical, $Ph_3Ge\bullet$, attacks the olefin to give a radical intermediate **A**. Free rotation scrambles the stereochemistry, so that the composition of the mixture reaches the thermodynamic equilibrium.[10] This mechanism is supported by the following facts that treatment of (Z)-1-triphenylgermyl-1-dodecene (1.0 mmol) with $^nPr_3GeH-Et_3B$ (1.0 mmol each) at 60°C gave a mixture of (E)-1-tripropylgermyl-1-dodecene (**1**) and (E)-1-triphenylgermyl-1-dodecene (**2**) (**1**/**2** = 2/5) and that treatment of (Z)-1-triethylgermyl-1-dodecene with $Ph_3GeH-Et_3B$ gave (E)-1-triethylgermyl-1-dodecene (**3**) and (E)-1-triphenylgermyl-1-dodecene (**2**) (**3**/**2** = 2/5, Scheme 2).

The new reaction was successfully applied to the isomerization of various kinds of olefins[11] and typical results are summarized in Table 2.

Scheme 2



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5. We have reported that Ph_3SnH adds easily to acetylenes in the presence of Et_3B (Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc*., in press). In contrast to the reaction with Ph_3GeH, the ratios of the products, (E)-alkenyltriphenylstannane and its (Z)-isomer, were always 8/2-7/3 and not affected by the reaction temperature and the ratio of [acetylene]/[Ph_3SnH].
6. The amount of Et_3B could be reduced to 0.1 mol per 1.0 mol of acetylene without decrease of the yield and the reaction rate at the temperature above 0°C. However, the reaction rate drops considerably at low temperature such as -78°C. Thus we recommend the use of stoichiometric amount of Et_3B in these cases. $^{i}Pr_3B$ and $(^{n}C_8H_{17})_3B$ were as effective as Et_3B. We thank Toyo Stauffer Chemical Company for a gift of a hexane solution of Et_3B (1.0 M).
7. Et_3B-induced addition of Pr_3GeH to acetylenes did not give high stereoselectivity as compared to the addition of Ph_3GeH. For instance, the reaction of 1-dodecyne with Pr_3GeH at 60°C in the presence of Et_3B gave a isomeric mixture of (E)-1-tripropylgermyl-1-dodecene and (Z)-isomer in 79% yield (E/Z = 2/1).
8. (Z)-1-Triphenylgermyl-1-propene: mp 35-37°C (toluene); IR (KBr) 3044, 2982, 1609, 1483, 1429, 1090, 1029, 1004, 734, 697 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.68 (d, J = 7 Hz, 3H), 6.1 (d, J = 13 Hz, 1H), 6.8 (dq, J = 13, 7 Hz, 1H), 7.33-7.48 (m, 6H), 7.48-7.65 (m, 9H); ^{13}C-NMR ($CDCl_3$) δ 21.2, 125.6, 129.1, 129.7, 135.7, 138.4, 146.1; Found: C, 73.25; H, 5.69%. Calcd for $C_{21}H_{20}Ge$: C, 73.11; H, 5.84%.
9. Et_3B initiates the radical reaction at low temperature such as -78°C. On the other hand, ordinary radical initiators such as AIBN and $^{t}BuOOBu^{t}$ requires the heating of the reaction mixture (80-130°C) to promote the reaction, so that the isomerization of the produced alkenylgermanes easily takes place under such conditions.
10. Same mechanism has been proposed for the partial isomerization of (Z)-1-tributylgermyl-2-phenylethene into (E)-isomer. See ref. 2(a).
11. Benzenethiyl radical initiated isomerization of double bonds has been reported. Moussebois, C.; Dale, J. *J. Chem. Soc. (C)* **1966**, 260; Corey, E. J.; Hamanaka, E. *J. Am. Chem. Soc*. **1967**, *89*, 2758.
12. The isomerization of (Z)-1-triphenylgermyl-1-dodecene into its (E)-isomer is representative. A hexane solution of Et_3B (1.0 M, 0.1 ml, 0.1 mmol) was added to a solution of (Z)-1-triphenylgermyl-1-dodecene (0.47 g, 1.0 mmol) and Ph_3GeH (31 mg, 0.1 mmol) in benzene (5 ml). The resulting mixture was heated at 60°C for 4 h under an argon atmosphere. Workup and purification by preparative tlc on silica gel gave (E)-1-triphenylgermyl-1-dodecene (0.41 g, 88% yield) as a colorless oil.

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