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Application of Free Radical Substitution Reaction into Interconversion of 1-Alkenylsulfides, 1-Alkenylgermanes, and 1-Alkenylstannanes

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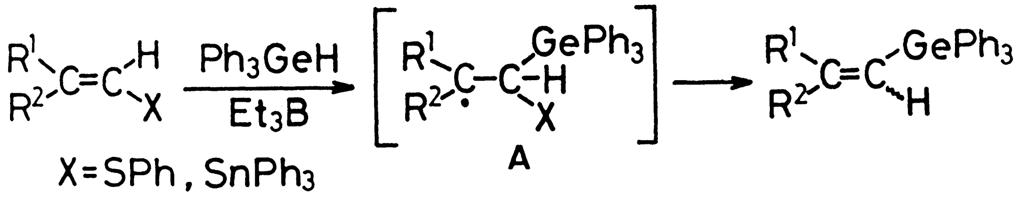
Treatment of 1-alkenylsulfides or 1-alkenylstannanes with Ph_3GeH in the presence of Et_3B provides 1-alkenyltriphenylgermanes in good yields. 1-Alkenylstannanes are converted into 1-alkenylsulfides easily with $PhSH-Et_3B$, whereas 1-alkenyltriphenylgermanes are recovered unchanged upon treatment with $Ph_3SnH-Et_3B$ or $PhSH-Et_3B$.

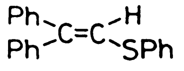
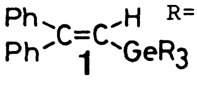
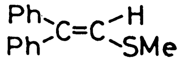
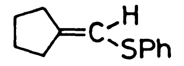
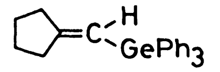
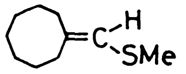
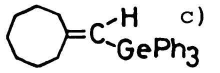
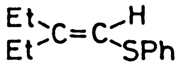
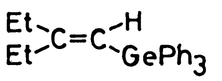
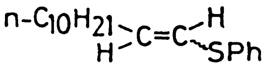
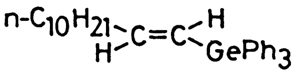
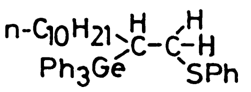
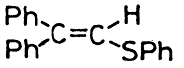
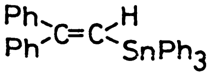
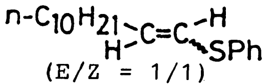
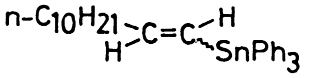
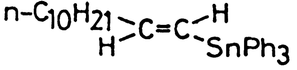
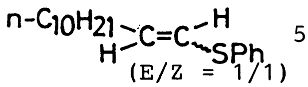
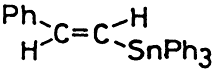
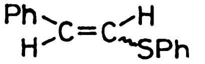
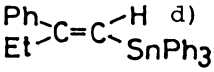
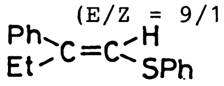
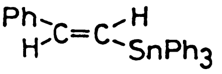
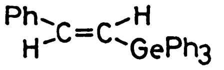
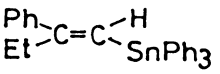
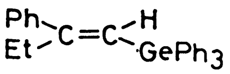
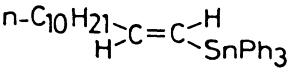
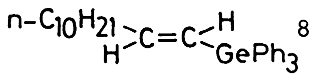
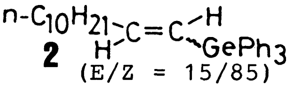
Recently, much attention has been paid to free radical reactions for the synthesis of organic molecules.1) We have shown that Et_3B is an efficient catalyst for the radical addition of triphenyltin hydride,2) triphenylgermyl hydride,3) or benzenethiol4) to acetylenes and that the isomerization of (Z)-olefins into (E)-isomers proceeds easily via addition-elimination sequences of triphenylgermyl radical.3) Here we wish to report further exploitation of this approach and the development of the method for the transformation of 1-alkenylsulfides or 1-alkenylstannanes into 1-alkenylgermanes and for the conversion of 1-alkenylstannanes into 1-alkenylsulfides.



A hexane solution of Et_3B5) (1.0 M, 1 M = 1 mol dm^{-3}, 1.2 ml, 1.2 mmol) was added to a solution of 2,2-diphenylethenyl phenyl sulfide6) (0.29 g, 1.0 mmol) and triphenylgermane (0.37 g, 1.2 mmol) in benzene at 25 °C under an argon atmosphere. The resulting mixture was heated at 60 °C for 2 h. Workup (1 M NH_4Cl, AcOEt) followed by purification by silica gel column chromatography gave (2,2-diphenyl)ethenyltriphenylgermane (0.41 g, 85% yield).7) The results are summarized in Table 1.

Some conclusions follow from the results. (1) Transformation of 1-alkenylsulfides into 1-alkenylgermanes proceeded easily upon treatment with $Ph_3GeH-Et_3B$ system. Triphenylgermyl radical has to attack the sulfur-substituted olefinic C-atom in order to give substitution products via β-elimination of thiyl radical

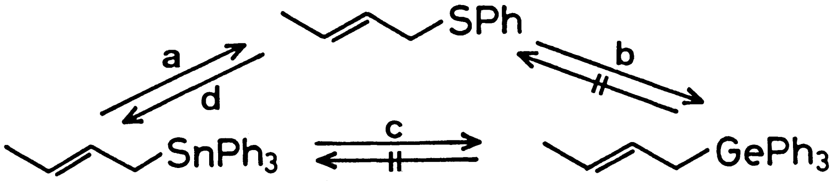
Table 1. Interconversion of 1-alkenylsulfides, 1-alkenylgermanes, and 1-alkenylstannanes[a)]

Entry	Starting material	Reagent	Reaction time/h	Product yield/%
1		$Ph_3GeH-Et_3B$	4	 R=Ph 85
2		$i-Pr_3GeH-AIBN$	8	R=i-Pr 28[b)]
3		$Ph_3GeH-Et_3B$	4	1 R=Ph 90
4		$Ph_3GeH-Et_3B$	4	 75
5		$Ph_3GeH-Et_3B$	5	 c) 83
6		$Ph_3GeH-Et_3B$	16	 93
7	 (E/Z = 1/1)	$Ph_3GeH-Et_3B$	13	 44  50
8		$Ph_3SnH-Et_3B$	5	 15
9	 (E/Z = 1/1)	$Ph_3SnH-Et_3B$	13	 20
10		$PhSH-Et_3B$	11	 59 (E/Z = 1/1)
11		PhSH-AIBN	4.5	 94 (E/Z = 9/1)
12	 d)	$PhSH-Et_3B$	17	 65
13		$Ph_3GeH-Et_3B$[e)]	12	 93
14		$Ph_3GeH-Et_3B$[e)]	11	 81
15		$Ph_3GeH-Et_3B$[e)]	12	 82
16	 2 (E/Z = 15/85)	$Ph_3SnH-Et_3B$	5	2 92 (E/Z=100/0)
17	2	$PhSH-Et_3B$	5	2 85 (E/Z=100/0)

a) Substrate (1.0 mmol), Ph_3GeH (or Ph_3SnH, PhSH (1.2 mmol)), and Et_3B (1.2 mmol) were employed unless otherwise noted. b) Starting vinylsulfide (42%) was recovered. c) See Ref. 8. d) See Ref. 9. e) Excess (3.0 mmol) of Ph_3GeH was used per 1.0 mmol of substrate.

from the intermediary radical **A**. The distribution of the products heavily depends on the substitution pattern of the double bond. 2-Ethyl-1-butenyl phenyl sulfide gave 2-ethyl-1-triphenylgermyl-1-butene as a single product, while 1-dodecenyl phenyl sulfide afforded a mixture of the desired (E)-1-triphenylgermyl-1-dodecene and 2-triphenylgermyl-1-dodecyl phenyl sulfide generated by the attack of Ph_3Ge radical on distal olefinic carbon to phenylthio group. (2) Conversion of 1-alkenylsulfides into 1-alkenylstannanes could not be performed effectively. Thus, the reaction of 1-phenylthio-1-dodecene with Ph_3SnH-Et_3B resulted in a formation of 1-triphenylstannyl-1-dodecene in only 20% yield along with a recovered starting sulfide (70%).10) In contrast, the conversion of 1-alkenylstannanes into 1-alkenylsulfides took place smoothly.11) (3) 1-Alkenylstannanes were easily transformed into 1-alkenylgermanes. However, the use of large amount of Ph_3GeH (3.0 mmol per 1.0 mmol of 1-alkenylstannane) was essential for the successful substitution reaction. The reaction did not reach completion with a slight excess of Ph_3GeH. For instance, treatment of 1-triphenylstannyl-1-dodecene (1.0 mmol) with Ph_3GeH (1.2 mmol) in the presence of Et_3B gave a mixture of 1-triphenylgermyl-1-dodecene (70%) and starting alkenylstannane (20%) after heating at 60 °C for 10 h. (4) 1-Alkenyltriphenylgermanes were reluctant to react with PhS or Ph_3Sn radical. Treatment of a mixture of (Z)-1-triphenylgermyl-1-dodecene and (E)-isomer with PhSH-Et_3B or Ph_3SnH-Et_3B did not provide any trace of 1-alkenylsulfides or 1-alkenylstannanes and (E)-1-triphenylgermyl-1-dodecene was recovered. (5) Although the longer reaction period was required, the amount of Et_3B could be reduced from 1.2 mmol to 0.1 mmol per 1.0 mmol of substrate.

Interconversion of crotyl phenyl sulfide, crotyltriphenylstannane, and crotyltriphenylgermane was also examined. Treatment of crotyl phenyl sulfide or crotyltriphenylstannane12,13) with Ph_3GeH-Et_3B afforded crotyltriphenylgermane in good yield, whereas crotyltriphenylgermane was recovered unchanged upon treatment with PhSH-Et_3B or Ph_3SnH-Et_3B.14)



a: PhSH-Et_3B, 60 °C, 10 h, 75% b: Ph_3GeH-Et_3B, 60 °C, 8 h, 80%
c: Ph_3GeH-Et_3B, 60 °C, 9 h, 98% d: Ph_3SnH-Et_3B, 60 °C, 10 h, 19%

References

1) M. Ramaiah, Tetrahedron, 43, 3541 (1987); B. Giese, "Radicals in Organic Synthesis," ed by J. E. Baldwin, Pergamon Press, Oxford (1986); G. Stork, "Selectivity — A Goal for Synthetic Efficiency," ed by W. Bartmann and B. M. Trost, Verlag Chemie, Weinheim (1984), pp. 281-298; B. Giese, Angew. Chem., Int. Ed. Engl., 24, 553 (1985).

2) K. Nozaki, K. Oshima, and K. Utimoto, J. Am. Chem. Soc., 109, 2547 (1987); idem, Bull. Chem. Soc. Jpn., 60, 3465 (1987).

3) Y. Ichinose, K. Nozaki, K. Wakamatsu, K. Oshima, and K. Utimoto, Tetrahedron Lett., 28, 3709 (1987).

4) Y. Ichinose, K. Wakamatsu, J-L. Birbaum, K. Oshima, and K. Utimoto, Chem. Lett., 1987, 1647.

5) We thank Toyo Stauffer Chemical Co. for a gift of Et_3B.

6) E. J. Corey and J. I. Shulman, J. Org. Chem., 35, 777 (1970); I. Shahak and J. Almong, Synthesis, 1, 170 (1969).

7) IR (neat) 3132, 1586, 1560, 1485, 1430, 1090, 1069, 1027, 765, 696 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.85-7.10 (m, 6H), 7.23-7.49 (m, 20H); ^{13}C-NMR ($CDCl_3$) δ 124.9, 127.3, 127.6, 127.7, 127.8, 127.9, 128.1, 128.3, 128.5, 129.6, 134.8, 137.6, 143.5. Found: C, 79.41; H, 5.36%. Calcd for $C_{32}H_{26}Ge$: C, 79.55; H, 5.43%.

8) IR (neat) 3064, 3046, 2920, 2850, 1600, 1485, 1431, 1090, 733, 697 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.06-1.25 (m, 2H), 1.33-1.59 (m, 6H), 1.64-1.80 (m, 2H), 2.17 (t, J = 5.9 Hz, 2H), 2.39 (t, J = 6.1 Hz, 2H), 5.30 (s, 1H), 7.30-7.46 (m, 9H), 7.46-7.66 (m, 6H); ^{13}C-NMR ($CDCl_3$) δ 24.1, 25.7, 25.9, 27.7, 31.0, 36.7, 37.6, 118.2, 128.1, 128.6, 134.9, 138.2. Found: C, 75.86; H, 7.15%. Calcd for $C_{27}H_{30}OGe$: C, 75.93; H, 7.08%.

9) H. Westmijze, J. Meijer, and P. Vermeer, Recl. Trav. Chim. Pays-Bas, 96, 194 (1977).

10) Only (E)-isomer of 1-phenylthio-1-dodecene was recovered as a result of a facile isomerization of Z-isomer. The use of large excess of Ph_3SnH (3 equiv.) improved the yield of alkenylstannane up to 49%.

11) The conversion of 1-alkenylstannanes into 1-alkenylsulfides with PhSSPh has been reported. G. A. Russell, P. Ngoviwatchai, H. Tashtoush, and J. Hershberger, Organometallics, 6, 1414 (1987). Baldwin and Russell have used 1-alkenylstannanes for C-C bond forming reactions. J. E. Baldwin and D. R. Kelly, J. Chem. Soc., Chem. Commun., 1985, 682; G. A. Russell, H. Tashtoush, and P. Ngoviwatchai, J. Am. Chem. Soc., 106, 4622 (1984).

12) Allylstannanes and allylsulfides have been used for the synthesis of C-C bonds. J. Grignon and M. Pereyre, J. Organomet. Chem., 61, C33 (1973); M. Kosugi, M. Kurino, K. Takayama, and T. Migita, ibid., 56, C11 (1973); G. E. Keck, J. B. Yates, J. Am. Chem. Soc., 104, 5829 (1982); G. A. Keck, D. F. Kachensky, and E. J. Enholm, J. Org. Chem., 50, 4317 (1985); Y. Ueno, S. Aoki, and M. Okawara, J. Am. Chem. Soc., 101, 5415 (1979); Y. Ueno, K. Chino, and M. Okawara, Tetrahedron Lett., 23, 2575 (1982).

13) Photostimulated substitution of crotyltributylstannane with PhSSPh has been reported to give a mixture of 3-phenylthio-1-butene and crotyl phenyl sulfide (1:1). G. A. Russell and L. L. Herold, J. Org. Chem., 50, 1037 (1985).

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