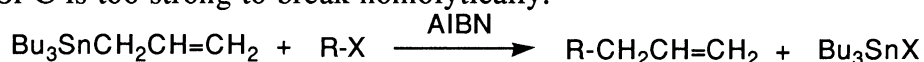


Allyltris(trimethylsilyl)silane as Radical Allylating Agent for Organic Halides

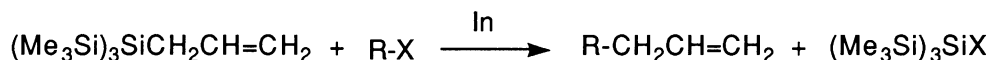
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Reaction of allyltris(trimethylsilyl)silane with organic halides under the free radical conditions resulted in allylation of the halides in moderate to good yields. The presence of three trimethylsilyl groups on the silicon could enhance the homolytic dissociation of a Si-C bond in the β -silylalkyl radical.

We previously reported that allyltributyltin reacted with organic halides under free radical conditions to give allylated product through S_H' process.¹⁾ The reaction was so far applied to the variety of organic syntheses.²⁾ However, allyltributyltin is a toxic substance and has a problem to apply to food or medicinal chemistry. On the other hand, the corresponding less toxic silane does not react through such process, because the bond dissociation energy of Si-C is too strong to break homolytically.



Recently Chatgililogulu *et al.* reported that tris(trimethylsilyl)silane was an effective radical reducing agent of organic halides because of the low bond-dissociation energy (79 kcal/mol) of its Si-H.³⁾ This value is very close to that of the Sn-H (74 kcal/mol) in tributylstannane rather than that of the Si-H (90 kcal/mol) in triethylsilane. This means that the presence of three trimethylsilyl groups on the silicon makes the silyl radical more stable. If this is true, the Si-C bond energy of allyltris(trimethylsilyl)silane should also be lower. This paper describes the radical reaction of allyltris(trimethylsilyl)silane with organic halides.



As Table 1 shows, the reaction took place for the negatively substituted halides in the presence of a radical initiator to give the allylated product in moderate to good yields. We used AIBN (α,α' -azobisisobutyronitrile) or dichlorotris(triphenylphosphine)ruthenium which was reported by Matsumoto *et al.* as a radical initiator for the radical addition of carbon tetrachloride to the olefins.⁴⁾ Although the radical reaction of bromotrichloromethane with allyltrimethylsilane has been reported to give 4,4,4-trichlorobutene by way of an addition-elimination mechanism,⁵⁾ the reaction of allyltrimethylsilane or allyltriethoxysilane with carbon tetrachloride in the presence of AIBN did not give the 4,4,4-trichlorobutene at all, and only a trace amount of the chlorinated olefin was detected in the reaction of allyltriphenylsilane. These facts imply that the allylation by allyltris(trimethylsilyl)silane should not proceed through an addition-elimination mechanism, but through the S_H' process.

Table 1. The Reaction of Allyltris(trimethylsilyl)silane with Organic Halides

R-X	Catalyst(mol%)	Temp/°C	Time/h	GLC yield of RCH ₂ CH=CH ₂ /%
Cl ₃ C-Cl	AIBN(5)	80	3	24
Cl ₃ C-Cl	AIBN(10)	80	3	46
Cl ₃ C-Cl	AIBN(10)	100	1	66
Cl ₃ C-Cl	RuCl ₂ (PPh ₃) ₃ (1)	80	3	66
Cl ₃ C-Cl	RuCl ₂ (PPh ₃) ₃ (1)	100	12	75
Cl ₂ HC-Cl	AIBN(10)	100	1	36
Cl ₂ HC-Cl	RuCl ₂ (PPh ₃) ₃ (1)	100	5	16
CH ₃ Cl ₂ C-Cl	AIBN(10)	100	1	49
CH ₃ Cl ₂ C-Cl	RuCl ₂ (PPh ₃) ₃ (1)	100	24	63
EtO ₂ CCH ₂ -Br	AIBN(10)	100	1	54
EtO ₂ CCH ₂ -Br	RuCl ₂ (PPh ₃) ₃ (1)	100	24	31
NCCH ₂ -Br	AIBN(10)	100	1	68
NCCH ₂ -Br	RuCl ₂ (PPh ₃) ₃ (1)	100	5	trace

The reactions were carried out as follows; A tube containing the mixture of allyltris(trimethylsilyl)silane(0.5 mmol), the halide(0.55 mmol), AIBN(10 mol%), and benzene(1 cm³) as a solvent was sealed *in vacuo* and immersed in a thermobath. The product was analyzed by GLC. And the structure of the products was identified by ¹H NMR and GC-MS spectrum.

To our knowledge, this is the first example which shows that a Si-C bond in the allylsilane could dissociate homolytically. Allyltris(trimethylsilyl)silane seems to be an alternative radical allylating agent instead of allyltributylstannane.

References

- 1) M. Kosugi, K. Kurino, K. Takayama, and T. Migita, *J. Organomet. Chem.*, **56**, C11 (1977); T. Migita, K. Nagai, and M. Kosugi, *Bull. Chem. Soc. Jpn.*, **56**, 2480 (1983); J. Grignon and M. Pereyre, *J. Organomet. Chem.*, **61**, C33 (1973); J. Grignon, C. Servens, and M. Pereyre, *ibid.*, **96**, 225 (1975).
- 2) G. E. Keck and J. B. Yates, *J. Am. Chem. Soc.*, **104**, 5829 (1982).
- 3) B. Giese, B. Kopping, and C. Chatgililoglu, *Tetrahedron Lett.*, **30**, 681 (1989).
- 4) H. Matsumoto, T. Nakano, and Y. Nagai, *Tetrahedron Lett.*, **1973**, 5147.
- 5) H. Sakurai, A. Hosomi, and M. Kumada, *J. Org. Chem.*, **34**, 1764 (1969).

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