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UMPOLUNG OF REACTIVITY OF ALLYLSILANE, ALLYLGERMANE, AND ALLYLSTANNANE *VIA* THEIR REACTION WITH THALLIUM (III) SALT: A NEW ALLYLATION REACTION FOR AROMATIC COMPOUND

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Summary: A new direct allylation of the aromatic compound has been developed. A combination of allylsilane, allylgermane, or allylstannane and thallium (III) trifluoroacetate gave rise to an allyl cationic species which was allowed to react with an aromatic compound, a nucleophile, to give allylation product(s) in good yields.

Direct allylation of the aromatic compound by the electrophilic aromatic substitution reaction is usually very difficult. Friedel-Crafts reaction using allyl chloride or allyl alcohol and acid catalyst for allylation of the aromatic compound has been shown to be fruitless producing many by-products,[1] because of an intervention of redox reaction[2] and instability of the product in the reaction conditions.[1a,3] Allylsilane, allylgermane, and allylstannane **1** bearing a highly nucleophilic double bond[4] transfer the allyl group to various kinds of electrophiles (carbonyl compound,[5a] αβ-enone,[5b] acetal,[5c] acid chloride,[5d] α-nitro olefin,[5e] epoxide,[5f] *etc.*) as shown in eq. 1. In order to use these reagents for allylation of the aromatic compound, therefore, their reactivity must be reversed. We wish to report our device for this purpose as shown in eq. 2.

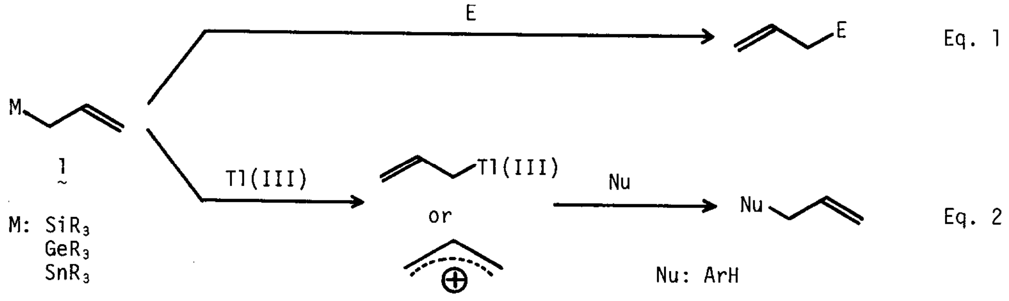
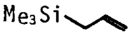
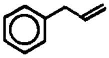
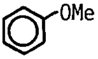
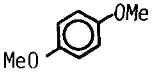
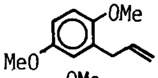
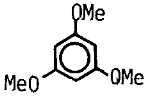
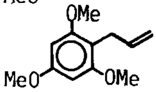
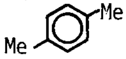
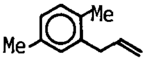
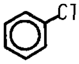
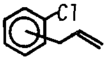
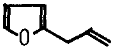
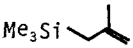
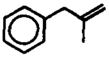
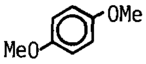
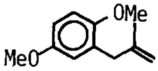
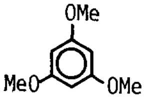
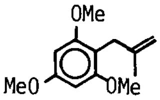
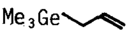
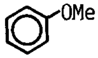
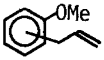
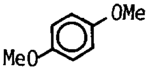
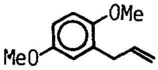
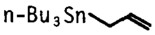
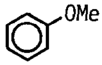
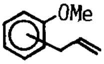
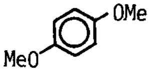
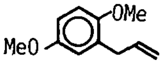


Table Allylation of Aromatic Compound Using Allylsilane, Allylgermane, and Allylstannane **1** and Thallium (III) Trifluoroacetate[a]

Allylsilane, allylgermane, or allylstannane		Aromatic compound	Reaction condition	Product	Yield[b] %
	**1a**		0°/5h RT/30min		56 (70)
	1a[c]		RT/30min		53 (74)[d]
	1a		RT/45min		46 (56)
	1a		RT/1.5h		53
	1a		RT/30min		67 (84)
	1a[c]		RT/1h		(19)[e]
	1a[c,f]		0°/1h		(89)
	**1b**[c]		RT/30min		28 (34)[g]
	1b		RT/1h		59 (83)
	1b[h]		RT/45min		54
	**1c**		0°/30min RT/30min		68 (84)[i]
	1c		0°/30min RT/1h		40 (41)
	**1d**		0°/1h RT/1h		40 (70)[j]
	1d		0°/1h RT/1h		40 (52)

a) Reactions were performed as described in the text unless otherwise noted. Molar ratio of thallium (III) trifluoroacetate to allylsilane, allylgermane, or allylstannane to aromatic compound is 1:1~1.2:10~100. b) Isolated yield (GLC yield). c) Reactions were carried out without solvent. d) The ratio of *o*- to *p*-isomer is 1: 1.7. e) The ratio of *o*- to *p*-isomer is 1:0.7. f) To a solution of **1a** in furan was added thallium (III) trifluoroacetate at 0°C. g) Usage of thallium (III) nitrate instead of thallium (III) trifluoroacetate did not increase the yield. h) 1.5 Equiv. of thallium (III) trifluoroacetate were used. i) The ratio of *o*- to *p*-isomer is 1:1.9. j) The ratio of *o*- to *p*-isomer is 1:1.8.

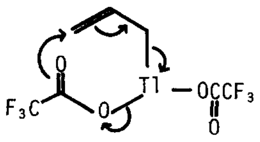
Thallium (III) salt has been shown to be a strong oxidizing reagent. The reaction of 1 with thallium (III) trifluoroacetate proceeded smoothly to give an allyl cationic species,[6] which was found to react with various kinds of aromatic compounds.

A typical example for allylation of the aromatic compound by this method is as follows. To a suspension of thallium (III) trifluoroacetate (10 mmol) in dichloromethane (30 ml) was added benzene (1 mol) at 0°C. Allyltrimethylsilane 1a (12 mmol) was then added dropwise into the mixture with stirring at the same temperature. After being stirred for 5h at 0°C then for 0.5h at room temperature, a usual work up and careful distillation of the resulting crude product gave allylbenzene in 56% yield. The results of allylation of aromatic compound through this procedure are summarized in Table.

As can be seen in Table, allylsilanes 1a and 1b on treatment with various kinds of aromatic compounds including furan gave allylation products smoothly. The yield in this reaction was found to be much higher than that in Friedel-Crafts allylation reaction, which may be attributed to the milder reaction conditions (lower temperature and shorter time) in our case. As expected, electron density on aromatic ring was shown to have a significant effect on the yield (compare the second run reaction to the reaction of 1a with chlorobenzene in the Table).

The reactions of allylgermane 1c or allylstannane 1d with thallium (III) salt followed by aromatic compounds proceeded also smoothly to afford allylation products. A mixture of *o*- and *p*-isomers of the products was obtained from the reaction of 1a, 1c, or 1d with anisole or chlorobenzene. The highest yield of the products was obtained in the reaction of anisole with 1c as compared with the reaction with 1a or 1d, while the ratio of *o*- to *p*-isomers in the product mixture was shown to be almost the same.

The amount of the aromatic compound used in this reaction has a large effect on the yield of the product; treatment of 1a with 1.2, 2, 10, and 100 equivalents of *p*-xylene afforded 2-allyl-1,4-dimethylbenzene in 15, 23, 76, and 84% yield (by GC), respectively. It can be assumed that the presence of an excess of the aromatic compound suppresses the possible side reactions: (i) the protonation of 1a by the trifluoroacetic acid generated during the reaction to give propene and (ii) the formation of allyl trifluoroacetate which could be produced by the intramolecular process 2 or by the nucleophilic attack of trifluoroacetic acid to allyl cationic species.



2

Thus we developed a new method of the direct allylation reaction for the aromatic compound using 1 and thallium (III) salt. The most important feature in this reaction consists in the establishment of usefulness of allylsilane, allylgermane, and allylstannane as the allyl cation equivalents.

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References and Notes

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4. (a) Theoretical calculation using Dewar's MINDO/3 method performed on 3-methyl-3-butenyl trimethylsilane shows that the silicon-allylic carbon bond is nearly parallel to the double bond π cloud: G. Deleris, J. P. Pillot, and J. C. Rayez, *Tetrahedron,* **36**, 2215 (1980). (b) The high reactivity of the double bond of **1** can be rationalized in terms of σ-π conjugation: H. Sakurai, T. Imai, and A. Hosomi, *Tetrahedron Lett.*, 4045 (1977); A. Schweig, U. Weinder, and G. Manuel, *J. Organometal. Chem.*, **54**, 145 (1967); H. Hanstein, H. J. Berwein, and T. G. Trayler, *J. Am. Chem. Soc.*, **92**, 7476 (1970).
5. (a) A. Hosomi and H. Sakurai, *Tetrahedron Lett.*, 1295 (1976); (b) A. Hosomi and H. Sakurai, *J. Am. Chem. Soc.*, **99**, 1673 (1977); (c) I. Fleming, A. Pearce, and R. L. Snowden, *J. Chem. Soc., Chem. Comm.*, 182 (1976); (d) I. Ojima, M. Kumagai, and Y. Miyazawa, *ibid.*, 1385 (1977); (e) M. Ochiai, M. Arimoto, and E. Fujita, *Tetrahedron Lett.*, **22**, 1115 (1981); (f) I. Fleming and I. Paterson, *Synthesis,* 446 (1979).
6. (a) The exact structure of the reactive intermediate in the reaction of **1** and Tl (III) salt is unknown. However, allyl organothallium (III) derivatives have been proposed in the reactions with olefins: A. McKillop, J. D. Hunt, F. Kienzle, E. Bigham, and E. C. Taylor, *J. Am. Chem. Soc.*, **95**, 3635 (1973); E. Fujita and M. Ochiai, *J. Chem. Soc., Perkin Trans. I,* 1948 (1977). (b) Mercury (II) and thallium (III) are isoelectronic; a stable allylmercuric chloride has been isolated from the transmetalation reaction of **1a** with mercuric chloride: R. M. G. Roberts, *J. Organomet. Chem.*, **12**, 89 (1968).

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