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Umpolung of Reactivity of Allylsilane, Allylgermane, and Allylstannane:
Allylation of Aromatic Compounds with Allylmetal and
Arylthallium Bis(trifluoroacetate)

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A direct allylation of aromatic compounds using allylsilane, allylgermane, or allylstannane (**1**) and arylthallium bis(trifluoroacetate) has been developed. The actual transmetalation reagent for **1** in the reaction was proposed to be thallium (III) trifluoroacetate (**2**), which was produced together with diarylthallium trifluoroacetate by the disproportionation of arylthallium bis(trifluoroacetate).

Keywords—allylation of aromatic compound; allylsilane; allylgermane; allylstannane; arylthallium bis(trifluoroacetate)

Allylmetal (Si, Ge, Sn) compounds (**1**) play a very important role as synthetic intermediates in organic chemistry.¹⁾ They usually act as equivalent species of allyl anion and transfer the allyl group to various kinds of electrophiles as shown in equation 1.²⁾ Recently, we found that they can also act as equivalent species of allyl cation *via* their transmetalation with thallium (III) salts to produce allylorganothallium (III) derivatives (**3**) as shown in equation 2.³⁾ Thus, allylaromatic compounds were obtained in good yield by the reaction of allylmetal (Si, Ge, Sn) compounds (**1**) with a variety of aromatic compounds in the presence of thallium (III) trifluoroacetate (**2**).

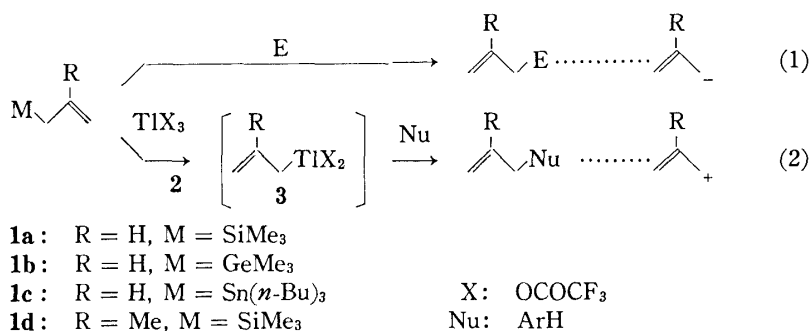


Chart 1

It is well-known that the direct allylation of aromatic compounds by means of the Friedel-Crafts reaction is usually very difficult, because of the intervention of redox reaction and instability of the products under the necessary reaction conditions.^{4,5)} Hence our direct allylation of aromatic compounds employing umpolung of reactivity of allylmetal compounds is a potentially valuable synthetic method.

We wish to report here another application of this new concept using arylthallium bis(trifluoroacetate) as the transmetalation reagent for allylmetal compounds (**1**). The direct allylation reaction of benzene with allylmetal compounds (**1a**—**1c**) and phenylthallium bis(trifluoroacetate) (**4**) prepared according to the method of McKillop and Taylor⁶⁾ was investigated in detail and the results are summarized in Table I. Allylbenzene was obtained in 44% yield on the reaction of equal amounts of allyltrimethylsilane (**1a**) and phenylthallium (III) salt (**4**) in benzene (run 2). The yield of the product reached 64% when **1a** and two molar

TABLE I. Synthesis of Allylbenzene^{a)}

Run	Allylmetal compd. 1	Molar ratio 1: 4 : benzene	Product ^{b)} yield (%)
1	1a	1:1:0 ^{c)}	0.5
2	1a	1:1:100	44
3	1a	2:1:100	46
4	1a	1:2:100	64
5	1b	1:1:0 ^{c)}	0.8
6	1b	1:1:100	29
7	1b	1:2:100	59
8	1c	1:1:0 ^{c)}	0
9	1c	1:1:100	32
10	1c	1:2:100	76

a) Reaction conditions: room temperature, 2.5 h except for run 1 (12 h).

b) Yields were determined by GLC.

c) Dichloromethane was used as the reaction solvent.

equivalents of phenylthallium (III) salt (**4**) were used (run 4). In contrast to the result of run 4, the use of excess amounts of allylsilane (**1a**) relative to **4** had little effect in the reaction (run 3). Without benzene, however, the reaction was shown to proceed only slightly and a trace amount of allylbenzene was detected (run 1). Similar results were obtained with allyltrimethylgermane (**1b**) or allyltri-*n*-butylstannane (**1c**). During these reactions the formation of a white precipitate was usually observed; it was proved to be diphenylthallium trifluoroacetate (**6**).⁷⁾ In fact, the diphenylthallium (III) salt (**6**) was isolated in 76% yield based on the allylsilane (**1a**) in run 4.

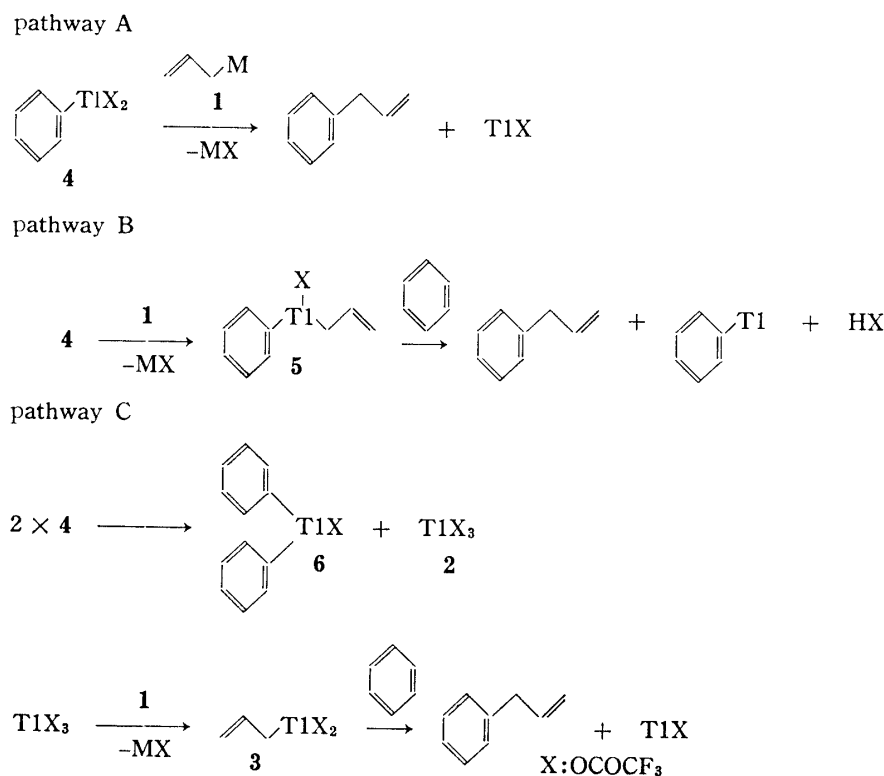


Chart 2

The following three reaction pathways can be considered. Pathway A involves the coupling reaction between the allylmetal compound (1) and phenylthallium (III) salt (4). Similar reactions have been reported. For instance, the regiospecific formation of aryl iodide by the reaction of 4 with aqueous potassium iodide⁶⁾ and the synthesis of aryl cyanide from the reaction of arylthallium (III) salt with copper (I) or (II) cyanide⁸⁾ are known. Pathway B involves the transient formation of allylphenylthallium (III) salt (5) followed by the attack of benzene to give allylbenzene. Pathway C involves disproportionation of the phenylthallium (III) salt (4) to give unreactive diphenylthallium trifluoroacetate (6) and thallium (III) trifluoroacetate (2) and successive reactions of 2 with allylmetal compound (1) and benzene as reported

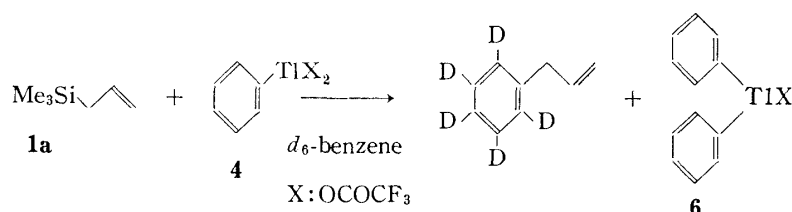


Chart 3

TABLE II. Allylation Reactions of Aromatic Compounds using 1 and 4^{a)}

Run	Aromatic compd.	Allylmetal compd. 1	Molar ratio 1:4:aromatic compd.	Product	Yield ^{b)} (%)
11		1a	1: 1 :100	1:1.5	49
12		1a	1: 2 :100	1:1.5	79
13		1a	1:2.5:100	1:1.4	88
14		1a	1: 3 :100	1:1.3	84
15		1b	1:2.5:100	1:1.5	69
16		1c	1:2.5:100	1:1.6	82
17		1a	1:2.5:100 ^{c)}		77
18		1a	1:2.5:100		80
19		1a	1:2.5:100		65
20		1d	1:2.5:100 ^{c)}		63

a) Reaction conditions: room temperature, 2.5 h.

b) Yields were determined by GLC.

c) Dichloromethane was used as the reaction solvent.

by us previously.³⁾ The regiospecific disproportionation of arylthallium bis(trifluoroacetate) on heating in acetone for 1 h to give diarylthallium trifluoroacetate and **2** has been reported.⁷⁾

In pathway A, the phenyl group of the product, allylbenzene, is derived from the phenylthallium (III) salt (**4**). In pathways B and C, however, it is derived from benzene. The experimental results of runs 1, 5, and 8 seem consistent with pathways B and C. The exclusion of pathway A was clearly confirmed by the following experiment. The deuterium content in the phenyl group of allylbenzene obtained by the reaction of allylsilane (**1a**) and **4** in *d*₆-benzene in a molar ratio 1:1:100, respectively, was shown to be greater than 99%, while the other product, diphenylthallium trifluoroacetate (**6**) showed no incorporation of deuterium in its aromatic rings.

The possibility of pathway B was eliminated by the isolation of the diphenylthallium (III) salt (**6**). Thus, the results mentioned above seem to be reasonably explained by pathway C, in which the actual transmetalation reagent for **1** is thallium (III) trifluoroacetate (**2**). In pathway C, 2 molar equivalents of **4** relative to **1** is required, because the diphenylthallium (III) salt (**6**) seems to be unreactive in the allylation reaction.

The results of allylation of other aromatic compounds using **1** and **4** are summarized in Table II. As can be seen in Table II, direct allylation of aromatic compounds including furan proceeded smoothly. A mixture of *o*- and *p*-isomers of the products was obtained from the reaction of **1a**—**c** with anisole, and their ratio is within the range of 1:1.3—1:1.6.

It is interesting that 2,5-dimethylphenylthallium bis(trifluoroacetate) (**7**) was shown to be a very useful transmetalation reagent for **1**. Allylsilane (**1a**) on treatment with 2.5 molar equivalents of **7** in excess benzene afforded allylbenzene and bis(2,5-dimethylphenyl)thallium trifluoroacetate (**8**) in 88 and 81% yields, respectively, based on allylsilane (**1a**) used. Allylation of anisole similarly afforded a mixture of *o*- and *p*-allylanisole and **8** in 91 and 79% yields (see Chart 4).

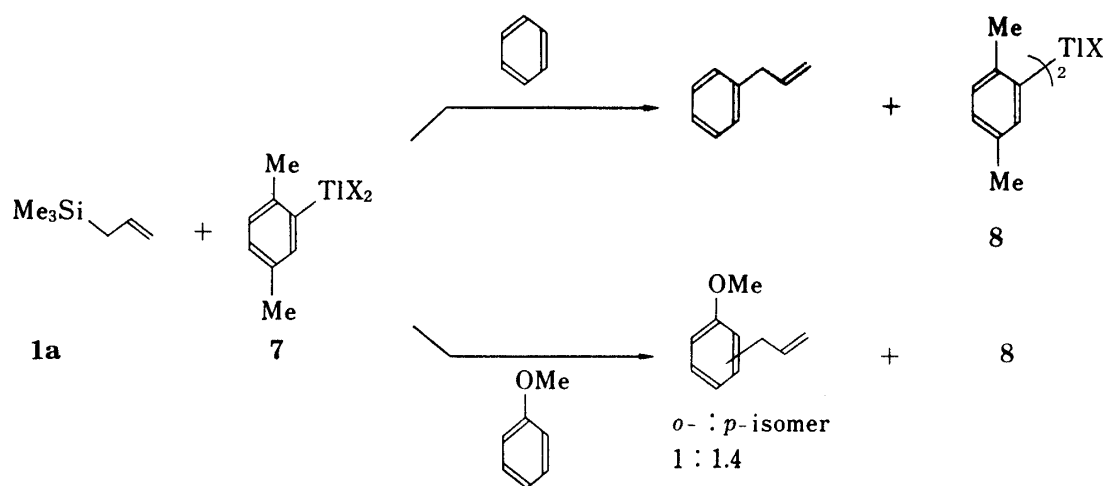


Chart 4

Thus phenyl-(**4**) and 2,5-dimethylphenylthallium bis(trifluoroacetate) (**7**) were also shown to be excellent reagents for allylation of several kinds of aromatic compounds with allylsilane, allylgermane, and allylstannane (**1**).

Experimental

Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded with a JASCO A-202 diffraction grating infrared spectrophotometer.

Proton magnetic resonance (PMR) spectra were obtained with a JEOL JNM-FX100 or JEOL JNM-PMX60 spectrometer. Chemical shifts are reported relative to internal tetramethylsilane. Mass spectra were determined on a JEOL JMS-OISG double-focusing mass spectrometer. Analytical gas chromatography was performed on a Shimadzu GC-4CM gas chromatograph with 20% Silicone DC-200 on a Celite 545 column (1 m). Preparative gas chromatography was performed on a Varian Aerograph Model 920 gas chromatograph with 10% Silicone DC-200 on a Chromosorb W column (1 m).

Materials—Allyltrimethylsilane (**1a**) is commercially available (Shin-etsu Silicon Chem.). Allyltri-*n*-butylstannane (**1c**),⁹ allyltrimethylgermane (**1b**),¹⁰ and (2-methyl-2-propenyl)trimethylsilane (**1d**)¹¹ were prepared by the Grignard reaction of the corresponding allylmagnesium chloride with tri-*n*-butyltin chloride, trimethylgermanium chloride, or trimethylchlorosilane. Benzene and thallium (III) trifluoroacetate (**2**) were treated according to the method of McKillop and Taylor⁶ to give phenylthallium bis(trifluoroacetate) (**4**), mp 185–189°C. IR ν_{\max}^{KBr} cm⁻¹: 1690, 1560, 1470, 1430, 1210, 1130, 1010, 990, 835, 800, 720, 675. PMR (DMSO-*d*₆) δ : 7.38 (1H, br d, $J=129$ Hz, C-4-H), 7.40 (2H, br d, $J=378$ Hz, C-3, C-5-H), 7.50 (2H, br d, $J=1002$ Hz, C-2, C-6-H). 2,5-Dimethylphenylthallium bis(trifluoroacetate) (**7**) was prepared by a similar method,⁶ mp 138–144°C. IR ν_{\max}^{KBr} cm⁻¹: 1690, 1490, 1440, 1035, 840, 820, 805, 725. PMR (DMSO-*d*₆) δ : 2.28 (3H, d, $J=55$ Hz, C-5-Me), 2.42 (3H, d, $J=112$ Hz, C-2-Me), 7.1 (1H, dd, $J=8, 114$ Hz, C-4-H), 7.29 (1H, br d, $J=1099$ Hz, C-6-H).

General Procedure for Allylation of Aromatic Compounds—An allylmetal (Si, Ge, Sn) compound (**1**) was added dropwise to a stirred suspension of phenylthallium bis(trifluoroacetate) (**4**) in various kinds of aromatic compounds at room temperature under nitrogen. The mixture was stirred under the conditions described in Tables I and II. A white precipitate of diphenylthallium trifluoroacetate (**6**) was usually observed. After the addition of water, the reaction mixture was extracted with ether. The yields of the products were determined by gas chromatography using an appropriate internal standard. The structures of the products were assigned on the basis of spectral data of pure samples isolated by preparative gas chromatography.

1-Phenyl-2-propene—IR $\nu_{\max}^{\text{CHCl}_3}$ cm⁻¹: 1645, 1605, 1500, 1455, 1000, 920. PMR (CDCl₃) δ : 3.35 (2H, d, $J=6$ Hz, CH₂), 4.8–5.3 (2H, m, C=CH₂), 5.6–6.3 (1H, m, CH=C), 7.0–7.5 (5H, aromatic H).¹²

1-(2-Methoxyphenyl)-2-propene⁵—IR $\nu_{\max}^{\text{CHCl}_3}$ cm⁻¹: 1645, 1605, 1500, 1470, 1035, 920. MS *m/e*: 148 (M⁺, base peak), 133, 119, 117, 115, 105, 91, 77. PMR (CDCl₃) δ : 3.38 (2H, d, $J=6$ Hz, CH₂), 3.82 (3H, s, OMe), 4.8–5.3 (2H, m, C=CH₂), 5.7–6.3 (1H, m, CH=C), 6.7–7.4 (4H, aromatic H). These analytical data were identical with those of an authentic sample prepared from 1-(2-hydroxyphenyl)-2-propene by methylation with NaH and methyl iodide.

1-(4-Methoxyphenyl)-2-propene⁵—IR $\nu_{\max}^{\text{CHCl}_3}$ cm⁻¹: 1645, 1615, 1590, 1515, 1470, 1040, 1000, 920. MS *m/e*: 148 (M⁺, base peak), 133, 121, 117, 105, 91, 77. PMR (CDCl₃) δ : 3.33 (2H, d, $J=6$ Hz, CH₂), 3.78 (3H, s, OMe), 4.8–5.3 (2H, m, C=CH₂), 5.6–6.3 (1H, m, CH=C), 6.6–7.3 (4H, aromatic H).¹²

1-(2,5-Dimethoxyphenyl)-2-propene¹³—IR $\nu_{\max}^{\text{CHCl}_3}$ cm⁻¹: 1640, 1605, 1595, 1505, 1470, 1050, 918. MS *m/e*: 178 (M⁺, base peak), 163, 135, 91, 77. PMR (CDCl₃) δ : 3.35 (2H, d, $J=6$ Hz, CH₂), 3.73, 3.76 (each 3H, s, 2 × OMe), 4.9–5.2 (2H, m, C=CH₂), 5.7–6.2 (1H, m, CH=C), 6.6–6.9 (3H, aromatic H).

1-(2,5-Dimethylphenyl)-2-propene⁵—IR $\nu_{\max}^{\text{CHCl}_3}$ cm⁻¹: 1635, 1605, 1505, 990, 915. MS *m/e*: 146 (M⁺), 131 (base peak), 91, 77. PMR (CDCl₃) δ : 2.24, 2.29 (each 3H, s, 2 × Me), 3.32 (2H, d, $J=6$ Hz, CH₂), 4.8–5.2 (2H, m, C=CH₂), 5.6–6.4 (1H, m, CH=C), 6.8–7.3 (3H, aromatic H).

2-(2-Propenyl)furan¹⁴—IR $\nu_{\max}^{\text{CHCl}_3}$ cm⁻¹: 1630, 1590, 910, 840. MS *m/e*: 216, 108 (M⁺), 73. PMR (CDCl₃) δ : 3.38 (2H, d, $J=6$ Hz, CH₂), 4.9–5.4 (2H, m, C=CH₂), 5.6–6.3 (1H, m, CH=C), 5.9–6.1 (1H, m), 6.2–6.4 (1H, m), 7.2–7.4 (1H, m).

1-(2,5-Dimethoxyphenyl)-2-methyl-2-propene¹⁵—IR $\nu_{\max}^{\text{CHCl}_3}$ cm⁻¹: 1655, 1610, 1595, 1500, 1470, 1280, 1050, 900. MS *m/e*: 192 (M⁺, base peak), 177, 161, 121, 91, 77. PMR (CDCl₃) δ : 1.72 (3H, s, Me), 3.30 (2H, s, CH₂), 3.73, 3.75 (each 3H, s, 2 × OMe), 4.64, 4.78 (each 1H, br s, C=CH₂), 6.5–6.9 (3H, m, aromatic H).

Isolation of Diphenylthallium Trifluoroacetate (6). Run 4 in Table I—Allyltrimethylsilane (**1a**) (25 mg, 0.217 mmol) was added dropwise to a suspension of phenylthallium bis(trifluoroacetate) (**4**) (220 mg, 0.434 mmol) in benzene (1.7 g, 21.7 mmol) at room temperature under an atmosphere of nitrogen. The mixture was stirred for 2.5 h to give a white precipitate, which, after washing with *n*-pentane (3 times with each 2 ml), afforded the thallium salt (**6**) (78 mg, 76% yield based on **1a** used), mp 264–267°C (recrystallized from ethyl acetate) (lit.⁷ mp 258–264°C). IR ν_{\max}^{KBr} cm⁻¹: 1690, 1480, 1430, 1210, 1130, 1015, 995, 835, 800, 720, 680. PMR (DMSO-*d*₆) δ : 7.33 (2H, dt, $J=51, 6$ Hz, 2 × C-4-H), 7.49 (4H, dt, $J=139, 6$ Hz, 2 × C-3-H, 2 × C-5-H), 7.8 (4H, dd, $J=460, 6$ Hz, 2 × C-2-H, 2 × C-6-H). Anal. Calcd for C₁₄H₁₀F₃O₂Tl·H₂O: C, 34.34; H, 2.47. Found: C, 34.52; H, 2.40.

Reaction of Allylsilane (1a) with 4 in *d*₆-Benzene—Allylsilane (**1a**) (50 mg, 0.43 mmol) was treated with **4** (217 mg, 0.43 mmol) in *d*₆-benzene (3.6 g, 43 mmol) by a method similar to that described above (room temperature, 2.5 h). The precipitate was filtered off and washed with *n*-pentane to afford the thallium salt (**6**) (82 mg); its PMR spectrum (chloroform was used as an internal standard) showed no incorporation of deuterium. Allylbenzene was isolated from the filtrate by preparative gas chromatography and its deuterium content in the phenyl groups was determined from the PMR spectrum to be greater than 99%.

Allylation of Benzene using 2,5-Dimethylphenylthallium Bis(trifluoroacetate) (7)—Allylsilane (**1a**)

(26 mg, 0.224 mmol) was added dropwise to a suspension of thallium salt (7) (300 mg, 0.56 mmol) in benzene (1.75 g, 22.4 mmol) at room temperature under an atmosphere of nitrogen, and the mixture was stirred for 2.5 h. The precipitate was filtered off and washed with *n*-pentane to afford bis(2,5-dimethylphenyl)thallium trifluoroacetate (8) (96 mg, 81% yield based on 1a used), mp 255–257°C (recrystallized from ethyl acetate) (lit.⁷⁾ 260–264°C). IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 1690, 1650, 1490, 1450, 1210, 1190, 1150, 850, 810, 730. PMR (DMSO-*d*₆) δ : 2.30 (6H, d, *J* = 18 Hz, 2 × C-5-Me), 2.55 (6H, d, *J* = 47 Hz, 2 × C-2-Me), 7.07 (2H, dd, *J* = 42, 7 Hz, 2 × C-4-H), 7.23 (2H, dd, *J* = 222, 7 Hz, 2 × C-3-H), 7.50 (2H, d, *J* = 454 Hz, 2 × C-6-H). *Anal.* Calcd for C₁₈H₁₈F₃O₂Tl: C, 40.97; H, 3.44. Found: C, 40.63; H, 3.42. Analysis of the filtrate by gas chromatography showed an 88% yield of 1-phenyl-2-propene.

Allylation of Anisole using 2,5-Dimethylphenylthallium Bis(trifluoroacetate) (7)—Allylsilane (1a) (21 mg, 0.174 mmol) on treatment with the thallium salt (7) (236 mg, 0.44 mmol) in anisole (1.88 g, 17.4 mmol) by a method similar to that mentioned above afforded bis(2,5-dimethylphenyl)thallium trifluoroacetate (8) (73 mg, 79% yield based on 1a used), and analysis by gas chromatography showed the formation of 1-(2-methoxyphenyl)-2-propene and 1-(4-methoxyphenyl)-2-propene in 38 and 53% yields, respectively.

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