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Thallium(III)-Mediated Allylation of Alcohols and Carboxylic Acids: Umpolung of Reactivity of Allylmetal (Group IVb) Compounds

MASAHITO OCHIAI,[a] EIICHI FUJITA,*,[a] MASAO ARIMOTO,[b]
and HIDEO YAMAGUCHI[b]

Institute for Chemical Research, Kyoto University,[a] Uji, Kyoto 611, Japan and
Osaka College of Pharmacy,[b] Matsubara, Osaka 580, Japan

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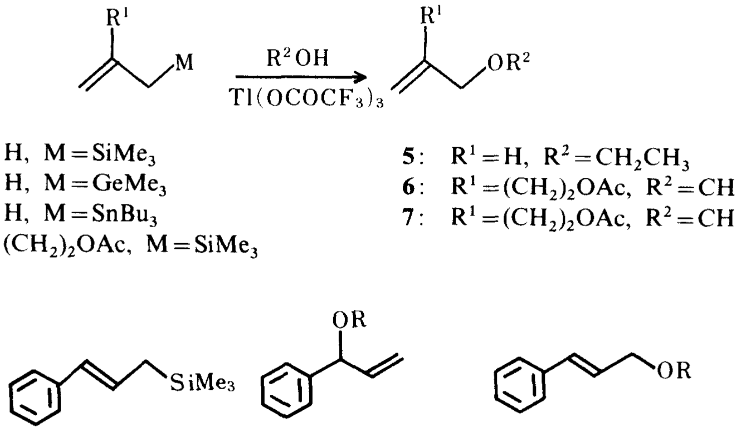
A new general method for the synthesis of allyl ethers and allyl acetates is described. Allylmetal (group IVb) compounds, on treatment with thallium(III) salts in alcohols or acetic acid, gave the corresponding allyl ethers or allyl acetates in good yields. The reaction was successfully applied to the synthesis of the 6-membered cyclic ether **20** *via* the intramolecular, thallium(III)-mediated allylation reaction of the allylsilane **18**.

Keywords——allyl ether; allyl acetate, thallium(III) salt; allylsilane; allylstannane; intramolecular cyclization; umpolung

Allylmetal (group IVb) compounds occupy an important role in synthetic organic chemistry.[1)] They usually act as allyl anion-equivalent species and transfer the allyl group to various kinds of electrophiles. In a series of studies on the reaction of allylmetal (group IVb) compounds, we have reported that they can also act as equivalent species of allyl cation *via* their transmetalation with thallium(III) salts to produce highly reactive allylorganothallium(III) derivatives.[2)] Thus, allyl-substituted aromatic compounds,[3)] *N*-allylamides,[4)] and allyl nitrates[5)] were prepared from allylmetal (group IVb) compounds in good yields. We now wish to report a general method for the synthesis of allyl ethers and allyl acetates as a further application of this umpolung of reactivity of allylmetal (group IVb) compounds.



1: $R^1=H$, $M=SiMe_3$
2: $R^1=H$, $M=GeMe_3$
3: $R^1=H$, $M=SnBu_3$
4: $R^1=(CH_2)_2OAc$, $M=SiMe_3$

5: $R^1=H$, $R^2=CH_2CH_3$
6: $R^1=(CH_2)_2OAc$, $R^2=CH_3$
7: $R^1=(CH_2)_2OAc$, $R^2=CH_2CH_3$

8

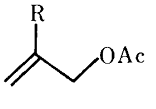
9: $R=CH_3$
10: $R=CH_2CH_3$

11: $R=CH_3$
12: $R=CH_2CH_3$
13: $R=NO_2$

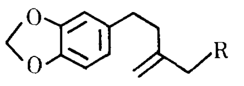
Chart 1

Allylation of alcohols using allylsilanes proceeded smoothly under mild conditions. Allyltrimethylsilane (**1**), on treatment with 1.2 eqs of thallium(III) trifluoroacetate (TTFA) in a large excess of ethanol at 0°C for 30 min, afforded allyl ethyl ether (**5**) in 86% yield. Allyltrimethylgermane (**2**) and allyltributylstannane (**3**) were also shown to be effective as transfer reagents of the ally group to the alcohol; the allyl ether **5** was obtained in 60 and 78% yields, respectively. A regioisomeric mixture of products was produced from the reaction of cinnamyltrimethylsilane (**8**) with TTFA in alcohols: in methanol, the rearranged allyl methyl ether (**9**) and the thermodynamically more stable cinnamyl methyl ether (**11**) were obtained in a ratio of 75 : 25. The ratio was determined from the nuclear magnetic resonance (NMR) spectrum of the crude reaction mixture. The reaction with ethanol similarly gave rise to the rearranged allyl ether (**10**) as the major product, in a ratio of 70 : 30 of **10** to the minor product **12**.[6] The usage of thallium(III) nitrate (TTN) instead of TTFA gave the same ratio of products. A minor by-product **13** was also produced in 13% yield.

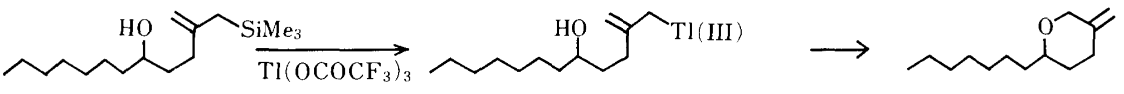
Acetic acid was also shown to be a good nucleophile toward the allylorganothallium(III) species. Thallium(III) acetate (TTA) seems to be better than the other thallium(III) salts such



14 : R=H
15 : R= $(CH_2)_2OAc$



16 : R=$SiMe_3$
17 : R=OAc



18 19 20

Chart 2

Table I. Synthesis of Allyl Ethers and Allyl Acetates[a]

Allylmetal compound	Nucleophile	Tl(III)	Reaction conditions (h)	Product	Yield[b] (%)
1	EtOH	TTFA	0°C (0.5)	**5**	(86)
2	EtOH	TTFA	0°C (0.5)	**5**	(60)
3	EtOH	TTFA	0°C (0.5)	**5**	(78)
4	MeOH	TTFA	−20°C (0.5)	**6**	49
4	EtOH	TTFA	−20°C (0.5)	**7**	47
8	MeOH	TTFA	0°C (0.5)	**9**+**11**[c]	88[d]
8	MeOH	TTN	0°C (0.5)	**9**+**11**[e]	70[d]
8	EtOH	TTFA	RT (1.5)	**10**+**12**[f]	43[d]
1	AcOH	TTA	RT (1)	**14**	(81)
3	AcOH	TTA	RT (2)	**14**	(73)
4	AcOH	TTA	RT (1)	**15**	70
16	AcOH	TTA	RT (0.5)	**17**	72

a) The molar ratio of allylmetal compound to thallium(III) salt to nucleophile was 1 : 1–1.2 : 50–100.
b) Isolated yield and GLC yield (shown in parentheses).
c) The ratio of **9** to **11** was 75 : 25.
d) NMR yield.
e) The ratio of **9** to **11** was 73 : 27.
f) The ratio of **10** to **12** was 70 : 30. RT = room temperature.

as TTFA or TTN for the transmetalation of allylmetal (group IVb) compounds, because some ligands of thallium(III) salts may act as potential nucleophiles toward the reactive allylorganothallium(III) species.[4,5] The reaction of allylsilane **1** with TTA in a large excess of acetic acid at room temperature gave an allyl acetate **14** in 81% yield. The results of allylation of alcohols and acetic acid are summarized in Table I.

In a previous communication we have reported that the allylsilane **18**, containing a suitably substituted hydroxy group, on treatment with iodosylbenzene in the presence of BF_3–Et_2O in an ether solvent, gave the 6-membered β-methylene cyclic ether **20** in good yield, presumably *via* the reactive allyliodine(III) compound.[7] We therefore examined the thallium(III)-mediated intramolecular cyclization reaction of the allylsilane **18**. The reaction of **18** with TTFA in tetrahydrofuran (THF) afforded the desired cyclic ether **20** in 71% yield. The cyclization reaction seems to occur *via* the intramolecular nucleophilic attack of the hydroxyl group on the allylthallium(III) group of the reactive intermediate **19**.

Thus, we have developed a new general method for the synthesis of allyl ethers and allyl acetates.

Experimental

Infrared (IR) spectra were recorded with a JASCO IR-A-1 spectrophotometer. NMR spectra were obtained with a JEOL JNM-FX 100 or Hitachi R40 spectrometer. Chemical shifts are reported relative to internal tetramethylsilane. Mass spectra (MS) were determined on a Hitachi RMU-7L spectrometer. Analytical gas-liquid chromatography (GLC) was performed on a Shimadzu GC-4CM gas chromatograph with 20% Silicone GE SE-30 or 20% Silicone DC-200 on Chromosorb W. Preparative thin layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, silica gel F-254). Kieselgel 60 (Merck) was used for column chromatography.

Materials——Allyltrimethylsilane (**1**) is commercially available (Shin-Etsu Silicon Chem.). Allylmetal compounds **2**, **3**, **4**, and **8** were prepared by the methods described previously.[3c,8] Synthesis of the allylsilanes **16** and **18** will be reported in detail elsewhere. All of the thallium(III) salts are commercially available (Aldrich Chem. Co.).

General Procedure for Synthesis of Allyl Ethers——An allylmetal compound (1 mol) was added dropwise to a stirred pale yellow solution of thallium(III) trifluoroacetate (1—1.2 mmol) in methanol or ethanol (100 mmol) under nitrogen. The reaction mixture was stirred under the conditions described in Table I. The mixture was poured into water or aqueous sodium bicarbonate solution and extracted with ether. The extract was washed with water and with brine. After being dried, the pure products were isolated by preparative TLC (hexane–ethyl acetate (10:1)). The yields are given in Table I. After the addition of appropriate internal standards, the yields were determined by analytical GLC or from the NMR spectrum in some experiments.

3-Ethoxy-1-propene (5)——bp 65—67 °C. NMR ($CDCl_3$) δ: 1.22 (3H, t, $J=7$ Hz), 3.51 (2H, q, $J=7$ Hz), 3.97 (2H, d, $J=6$ Hz), 5.1—5.4 (2H, m), 5.7—6.2 (1H, m). These analytical data were identical with those of an authentic sample prepared from allyl bromide by the reaction with sodium ethoxide.

4-Acetoxy-2-(methoxymethyl)-1-butene (6)——Colorless oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1740, 1660, 1455, 1370, 1230, 1100, 1040, 910. MS *m/e*: 157, 142, 130, 112, 83 (base peak), 55. NMR ($CDCl_3$) δ: 2.03 (3H, s), 2.40 (2H, t, $J=7$ Hz), 3.31 (3H, s), 3.88 (2H, s), 4.21 (2H, t, $J=7$ Hz), 4.98, 5.10 (each 1H, s). *Anal* Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.54; H, 9.01.

4-Acetoxy-2-(ethoxymethyl)-1-butene (7)——Colorless oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1740, 1660, 1370, 1230, 1100, 1040, 910. MS *m/e*: 131, 121 (base peak), 112, 103, 99, 81, 71, 43. NMR ($CDCl_3$) δ: 1.20 (3H, t, $J=7$ Hz), 2.03 (3H, s), 2.40 (2H, t, $J=7$ Hz), 3.46 (2H, q, $J=7$ Hz), 3.92 (2H, s), 4.20 (2H, t, $J=7$ Hz), 4.96, 5.10 (each 1H, s). *Anal.* Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.85; H, 9.25.

3-Methoxy-3-phenyl-1-propene (9)[9]——Colorless oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1640, 1455, 1090, 990, 930. NMR ($CDCl_3$) δ: 3.33 (3H, s), 4.63 (1H, d, $J=6$ Hz), 5.1—5.45 (2H, m), 5.75—6.2 (1H, m), 7.25—7.45 (5H, m).

3-Ethoxy-3-phenyl-1-propene (10)[10]——Colorless oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1640, 1600, 1450, 1400, 1305, 1070, 990, 930. NMR ($CDCl_3$) δ: 1.23 (3H, t, $J=6$ Hz), 3.3—3.7 (2H, m), 4.75 (1H, d, $J=7$ Hz), 5.1—5.4 (2H, m), 5.8—6.2 (1H, m), 7.2—7.5 (5H, m).

3-Methoxy-1-phenyl-1-propene (11)[9]——Colorless oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1600, 1455, 1380, 1120, 970. NMR ($CDCl_3$) δ: 3.40 (3H, s), 4.12 (2H, d, $J=6$ Hz), 6.28 (1H, dt, $J=15$, 6 Hz), 6.65 (1H, d, $J=15$ Hz), 7.2—7.5 (5H, m).

3-Ethoxy-1-phenyl-1-propene (12)[11]——Colorless oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1660, 1600, 1495, 1450, 1375, 1350, 1100, 965. NMR ($CDCl_3$) δ: 1.25 (3H, t, $J=7$ Hz), 3.56 (2H, q, $J=7$ Hz), 4.15 (2H, d, $J=6$ Hz), 6.28 (1H, dt, $J=16$, 6 Hz,), 6.65 (1H, d, $J=16$ Hz), 7.2—7.5 (5H, m).

3-Phenyl-2-propenyl Nitrate (13)[5,12]——Oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1645, 1280. NMR ($CDCl_3$) δ: 5.06 (2H, d, $J=$

7 Hz), 6.22 (1H, dt, $J=16$, 7 Hz), 6.79 (1H, d, $J=16$ Hz), 7.2—7.5 (5H, m).

General Procedure for Synthesis of Allyl Acetates——A solution of an allymetal compound (1 mmol) in acetic acid (0.57 g, 10 mmol) was added dropwise to a stirred solution of thallium(III) acetate (1—1.2 mmol) in acetic acid (50—100 mmol) under nitrogen. The mixture was stirred under the conditions described in Table I. The reaction mixture was poured into water and extracted with hexane–ether (1 : 1). The extract was washed with water several times and with brine, then dried. The pure products were isolated by preparative TLC (hexane–ethyl acetate (7 : 1)). The yields are given in Table I. After the addition of an appropriate internal standard, the yields were determined by analytical GLC in some experiments.

3-Acetoxy-1-propene (14)——The structure of the acetate **14** was determined by comparison of **14** with a commercially available authentic sample (Tokyo Kasei Kogyo Co.).

4-Acetoxy-2-(acetoxymethyl)-1-butene (15)——Colorless oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1750, 1665, 1370, 1230, 1035, 915. MS *m/e*: 126, 84 (base peak), 72, 43. NMR ($CDCl_3$) δ: 2.06, 2.12 (each 3H, s), 2.42 (2H, t, $J=7$ Hz), 4.22 (2H, t, $J=7$ Hz), 4.56 (2H, s), 5.04, 5.15 (each 1H, s). *Anal.* Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.98; H, 7.57.

2-(Acetoxymethyl)-4-(3,4-methylenedioxyphenyl)-1-butene (17)——Colorless oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1} 1730, 1650, 1495, 1240, 1140, 935, 925. MS *m/e*: 248 (M^+), 188, 135 (base peak), 105, 79, 77. High resolution MS: Found 248.1011. Calcd for $C_{14}H_{16}O_4$ (M^+) 248.1047. NMR ($CDCl_3$) δ: 2.11 (3H, s), 2.2—2.5 (2H, m), 2.5—2.9 (2H, m), 4.54 (2H, s), 4.96, 5.06 (each 1H, s), 5.92 (2H, s), 6.5—6.8 (3H, m).

Intramolecular Cyclization of Allylsilane 18——A solution of allylsilane **18** (11 mg, 0.04 mmol) in THF (1 ml) was added to an orange suspension of thallium(III) trifluoroacetate (28 mg, 0.05 mmol) in THF at 0°C under nitroen, and the mixture was stirred for 30 min at 0°C. The color of the mixture became pale yellow. After the addition of water, the mixture was extracted with ether. The extract was washed with brine, and dried. The solvent was removed under reduced pressure to give an oil, which was purified by silica gel column chromatography using hexane–ethyl acetate (98 : 2) as the eluting solvent to give the β-methylene cyclic ether **20** (5.6 mg, 71%) as a colorless oil. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1650, 1460, 1380, 1330, 1130, 1085, 1055, 900. MS *m/e*: 196 (M^+), 183, 125, 96 (base peak), 72, 55. NMR ($CDCl_3$) δ: 0.7—1.05 (3H), 1.1—2.0 (14H), 2.2—2.5 (2H), 3.2—3.5 (1H), 3.94, 4.20 (each 1H, AB type, $J=13$ Hz), 4.77 (2H, s). *Anal.* Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.70; H, 12.19.

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