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New Allylation Reaction using Allylmetal (Group IVb) Compounds: Synthesis of *N*-Allylamides

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Reaction of allylsilanes **1a** and **1d** or allylstannane **1b** with thallium(III) salts in nitriles such as acetonitrile, acrylonitrile, propionitrile, and benzonitrile afforded the corresponding *N*-allylamides. Thus, umpolung of reactivity of allylsilane and allylstannane has been established.

Keywords——umpolung of reactivity; allylsilane; allylstannane; *N*-allylamide; thallium(III) salt; nitrile

Allylmetal (group IVb) compounds occupy an important role in synthetic organic chemistry,[1] because they have a highly nucleophilic double bond.[2] They transfer the allyl group to various kinds of electrophiles[3] such as carbonyl compound, acetal, α-nitro olefin, epoxide, *etc.*, as shown in equation 1. Recently, it was found by us that allylmetal (group IVb) compounds also play a role as allyl cation-equivalent species; umpolung of their reactivity was realized. Thus the direct allylation of aromatic compounds using allylmetal (group IVb) compounds together with thallium (III) salts has been achieved to give good yields of the products[4] (see equation 2). In this paper, we wish to report the synthesis of *N*-allylamide as a further application of this umpolung of reactivity of allylmetal (group IVb) compounds.

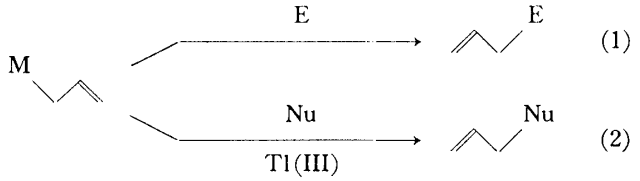
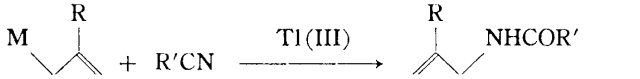


Chart 1

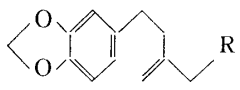
When allyltrimethylsilane (**1a**) was treated with an equivalent amount of thallium (III) trifluoroacetate (TTFA) in a large excess of acetonitrile, *N*-allylacetamide (**2a**) was obtained in 29% yield. Although the yield of the desired compound is not high, it should be emphasized that this is the first example of the displacement reaction of the trimethylsilyl group in allyltrimethylsilane (**1a**) by a nucleophilic nitrogen group.[5]



1a: R=H, M=SiMe3
1b: R=H, M=Sn(*n*-Bu)3
1c: R=H, M=GeMe3
1d: R=Me, M=SiMe3

2a: R=H, R'=Me
2b: R=H, R'=CH=CH2
2c: R=H, R'=CH2CH3
2d: R=H, R'=C6H5
2e: R=Me, R'=Me
2f: R=Me, R'=CH=CH2

Chart 2



3: R=SiMe3
4: R=NHCOCH3
5: R=OH

Chart 3

We investigated the reaction conditions in order to improve the yield of **2a**. The results are summarized in Table I. We anticipated that the use of an excess of **1a** might be desirable

for improving the yield of **2a**, since allylmetal (group IVb) compounds are relatively unstable and protodesilylation may occur in the presence of protic acids, which are expected to be produced during the reaction.[4] In fact, *N*-allylacetamide (**2a**) was obtained in 61% yield (on the basis of TTFA) by the use of 1.5 eq of allylsilane **1a**. The use of a greater excess of **1a**, however, gave a lower yield (Table I, runs 2—7). The reaction in the presence of potassium hydrogen carbonate for protection from protic acids resulted in a greatly reduced yield (Table I, run 8). Then the effect of the solvent polarity was investigated, but without success (Table I, runs 9—11).

Thallium (III) nitrate (TTN) was shown to be as effective as TTFA, but thallium (III) acetate (TTA) was less effective. In this allylation reaction, allyltrimethylsilane (**1a**) was shown to be a better reactant than allyltri-*n*-butylstannane (**1b**). Allyltrimethylgermane (**1c**) was not useful for this reaction.

Table I. Synthesis of *N*-Allylacetamide (**2a**)

Run	1	Tl(III)	Molar ratio 1: Tl(III): CH_3CN	Reaction conditions	Additive	Yield[a] %
1	**1a**	TTFA	1: 1: 100	−20°C (1 h) then 0°C (1 h)		16 (29)
2	**1a**	TTFA	1.25: 1: 100	−20°C (1 h) then 0°C (1 h)		(37)
3	**1a**	TTFA	1.5: 1: 100	−20°C (1 h) then 0°C (1 h)		44 (61)
4	**1a**	TTFA	1.75: 1: 100	−20°C (1 h) then 0°C (1 h)		48 (55)
5	**1a**	TTFA	2: 1: 100	−20°C (1 h) then 0°C (1 h)		34 (48)
6	**1a**	TTFA	2.5: 1: 100	−20°C (1 h) then 0°C (1 h)		34 (48)
7	**1a**	TTFA	4: 1: 100	−20°C (1 h) then 0°C (1 h)		32 (46)
8	**1a**	TTFA	2: 1: 100	−20°C (1 h) then 0°C (1 h)	$KHCO_3$[b]	(6)
9	**1a**	TTFA	2: 1: 100	−20°C (1 h) then 0°C (1 h)	CH_3NO_2[c]	(30)
10	**1a**	TTFA	2: 1: 100	−78°C (2 h) then 0°C (1 h)	CH_2Cl_2[c]	(23)
11	**1a**	TTFA	2: 1: 100	r.t. (1 h)	CH_3CONH_2[d]	17
12	**1a**	TTN	2: 1: 100	−20°C (4 h) then 0°C (2.5 h)		(51)
13	**1a**	TTA	2: 1: 100	0°C(7.5 h)		(25)
14	**1a**	TTN	2: 1: 100	−20°C (1 h) then 0°C (1 h)	$KHCO_3$[e]	(48)
15	**1a**	TTN	2: 1: 100	−20°C (1 h) then 0°C (2 h)	$KHCO_3$[b]	(15)
16	**1b**	TTFA	1.5: 1: 100	−20°C (2 h) then 0°C (2 h)		(21)
17	**1c**	TTFA	1.5: 1: 100	−20°C (1 h) then 0°C (1 h)		(1)

a) Isolated yield (GLC yield) based on the thallium(III) salt.
b) 20 equivalents of $KHCO_3$ were used.
c) The same amount as acetonitrile was added.
d) 10 equivalents of acetamide were used.
e) 3 equivalents of $KHCO_3$ were used.

Other nitriles such as acrylonitrile, propionitrile, and benzonitrile were shown to be available for use as nucleophiles in the reaction. Allyltrimethylsilane (**1a**) on treatment with TTFA in an excess of acrylonitrile gave *N*-2-propenylpropenamide (**2b**). A substituted allylsilane, (2-methyl-2-propenyl)trimethylsilane (**1d**), was also shown to be effective; the

Table II. Reaction of **1** with TTFA in Various Kinds of Nitriles[a]

1	R'CN	Reaction conditions	Product	Yield[b] %
1a	CH_2=CHCN	−20°C (1 h) then 0°C (2 h)	**2b**	37 (55)
1a	CH_3CH_2CN	−20°C (1 h) then 0°C (1 h)	**2c**	29 (37)
1a	C_6H_5CN	−15°C (1 h) then 0°C (1 h)	**2d**	21 (25)
1d	CH_3CN	−20°C (1 h) then 0°C (1 h)	**2e**	37 (40)
1d	CH_2=CHCN	−20°C (1 h) then 0°C (1 h)	**2f**	26 (26)

a) Molar ratio of **1** to TTFA to R'CN is 1.5: 1: 100.
b) Isolated yield and GLC yield (shown in parentheses) based on the thallium(III) salt.

results of the reactions with **1d** are summarized in Table II. The reaction of allylsilane **3** with TTFA in acetonitrile gave *N*-allylamide **4** and allyl alcohol **5** (after hydrolysis with aqueous potassium hydroxide) in 9 and 11% yields, respectively.

The reaction process may be represented as in Chart 4. The first step of the reaction may be the formation of a π-complex between **1** and thallium (III) salts;[6] it then gives a reactive allyl organothallium species **6**[7] or an equivalent intermediate such as the allyl cation **7**. Subsequent nucleophilic attack of nitriles on **6** or **7** to produce the cation **8** followed by its conversion to *N*-allylamide **2** seems reasonable.

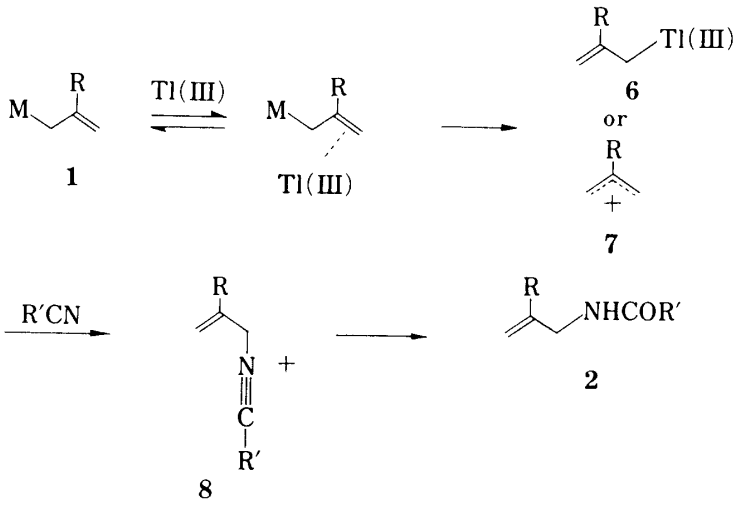


Chart 4

Experimental

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-FX 100 or JEOL JNM-PMX 60 spectrometer. Chemical shifts are reported relative to internal tetramethylsilane. Mass (MS) spectra were determined on a JEOL JMS-01SG double-focusing mass spectrometer. Analytical gas–liquid chromatography (GLC) was performed on a Shimadzu GC-4CM gas chromatograph with 2.5% Versamid 900 on Chromosorb W.

Materials——Allyltrimethylsilane (**1a**) is commercially available (Shin-etsu Silicon Chem.) and was used without purification. Allyltri-*n*-butylstannane (**1b**) was prepared by the reaction of allylmagnesium chloride with tri-*n*-butyltin chloride.[8] Allyltrimethylgermane (**1c**) was prepared from allylmagnesium chloride and trimethylgermanium chloride.[9] (2-Methyl-2-propenyl)trimethylsilane (**1d**) was similarly prepared from 2-methyl-2-propenylmagnesium chloride and trimethylchlorosilane in tetrahydrofuran (THF).[10] All of the thallium(III) salts are commercially available (Aldrich Chem. Co.).

General Procedure for Synthesis of *N*-Allylamides——To a stirred mixture of allylmetal compound **1** with or without additive in an appropriate nitrile was added thallium(III) salt in nitrogen. The mixture was stirred under the conditions described in Tables I and II. A solution of an internal standard in the same amount of dichloromethane as the nitrile was added; the yield was determined by gas chromatography. The reaction mixture was concentrated *in vacuo* to leave a crude residue, which was chromatographed on neutral alumina (Woelm, activity grade II) and eluted with chloroform to give *N*-allylamide **2**. The yields are given in Tables I and II. This procedure was used throughout except for runs 10 and 15 in Table I.

***N*-2-Propenylacetamide (2a)**[11]——Run 10 in Table I: To a mixture of thallium(III) trifluoroacetate (315 mg, 0.58 mmol) and *n*-tetradecane (11 mg) (as an internal standard) in dichloromethane (3 ml) was added dropwise a solution of **1a** (1.15 mmol) in acetonitrile (3 ml, 58 mmol) at −78°C. After being stirred at −78°C for 2 h and then at 0°C for 1 h, the reaction mixture was analyzed by gas chromatography, which indicated the formation of **2a** in 23% yield.

***N*-2-Propenylacetamide (2a)**——Run 15 in Table I: To a mixture of thallium(III) nitrate (118 mg, 0.26 mmol) and potassium hydrogen carbonate (517 mg, 5.2 mmol) in acetonitrile (0.67 ml, 12.9 mmol) was added dropwise a solution of **1a** in acetonitrile (0.67 ml, 12.9 mmol) at −20°C. The mixture was stirred at −20°C for 1 h and then at 0°C for 2 h. After the addition of *n*-tetradecane (5.1 mg), the reaction mixture was analyzed by gas chromatography, which indicated the formation of **2a** in 15% yield. **2a**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}:

3460, 3330, 1665, 1520, 925. MS *m/e*: 99 (M^+), 43 (base peak). PMR ($CDCl_3$) δ: 2.01 (3H, s, $COCH_3$), 3.88 (2H, tt, J=5.5, 1.0 Hz, NCH_2), 5.0—5.3 (2H, m, $C=CH_2$), 5.6—6.1 (1H, m, CH=C), 5.7 (1H, br s, NH).

***N*-2-Propenylpropenamide (2b)**[12]——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3440, 3310, 1670, 1630, 1520, 925. MS *m/e*: 111 (M^+), 96, 83, 68, 55 (base peak). PMR ($CDCl_3$) δ: 3.95 (2H, tt, J=5.5, 1.5 Hz, NCH_2), 5.0—5.3 (2H, m), 5.55—5.7 (1H), 5.7—6.1 (1H, m), 5.8 (1H, br s, NH), 5.9—6.4 (2H, m).

***N*-2-Propenylpropanamide (2c)**[13]——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3460, 3350, 1660, 1515, 927. MS *m/e*: 114, 113 (M^+), 83, 57, 27 (base peak). PMR ($CDCl_3$) δ: 1.16 (3H, t, J=7.5 Hz, CH_3), 2.23 (2H, q, J=7.5 Hz, $COCH_2$), 3.87 (2H, tt, J=6.0, 1.5 Hz, NCH_2), 5.0—5.3 (2H, m, $C=CH_2$), 5.6—6.05 (1H, m, CH=C), 5.75 (1H, br s, NH).

***N*-2-Tropenylbenzamide (2d)**[14]——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3460, 3360, 1655, 1580, 1520, 925. MS *m/e*: 161 (M^+), 105, 83, 77. PMR ($CDCl_3$) δ: 4.07 (2H, tt, J=5.5, 1.5 Hz, NCH_2), 5.1—5.4 (2H, m, $C=CH_2$), 5.7—6.2 (1H, m, CH=C), 6.33 (1H, br s, NH), 7.3—7.6 (3H, m, aromatic), 7.65—7.9 (2H, m, aromatic).

***N*-(2-Methyl-2-propenyl)acetamide (2e)**[15]——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 3340, 1660, 1520, 900. MS *m/e*: 113 (M^+), 98, 71, 56 (base peak). PMR ($CDCl_3$) δ: 1.73 (3H, s, $=CCH_3$), 2.01 (3H, s, $COCH_3$), 3.79 (2H, d, J=6.0 Hz, NCH_2), 4.82 (2H, $=CH_2$), 5.67 (1H, br s, NH).

***N*-(2-Methyl-2-propenyl)propenamide (2f)**[16]——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 3335, 1665, 1630, 1520, 900. MS *m/e*: 125 (M^+), 110, 81, 71, 55 (base peak). PMR ($CDCl_3$) δ: 1.74 (3H, s, CH_3), 3.88 (2H, d, J=6.0 Hz, NCH_2), 4.83 (2H), 5.6—5.7 (1H, m), 5.8 (1H, br s, NH), 5.9—6.5 (2H, m).

Acetamide 4——To a solution of allylsilane **3** (68 mg, 0.26 mmol) in acetonitrile (1.35 ml, 0.26 mmol) was added at −20°C thallium(III) trifluoroacetate (132 mg, 0.24 mmol) in nitrogen. The mixture was stirred at −20°C for 40 min and then at 0°C for 2 h. The reaction mixture was poured into brine and extracted with dichloromethane. The extract was washed successively with aqueous $NaHCO_3$ and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure to give an oil (58 mg). On preparative TLC (*n*-hexane–ethyl acetate (40: 9)), a mixture of allyl alcohol **5** and its trifluoroacetate was separated. The mixture was hydrolyzed using 2% aoueous KOH in THF to give the alcohol **5** (6 mg, 11%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3450, 1640, 1605, 1490, 1440, 930. MS *m/e*: 206 (M^+), 135 (base peak), 77. High resolution MS: Found 206.0959. Calcd for $C_{12}H_{14}O_3$ (M^+) 206.0942. PMR ($CDCl_3$) δ: 1.56 (1H, br s, OH), 2.16—2.44, 2.52—2.80 (each 2H, A_2B_2 type), 4.06 (2H, s, CH_2OH), 4.88, 5.03 (each 1H, $=CH_2$), 5.88 (2H, s, OCH_2O), 6.5—6.8 (3H, m, aromatic). The remaining more polar substance was developed with chloroform–acetone (4: 1) to give acetamide **4** (5.2 mg, 9%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3460, 3350, 1670, 1610, 1515, 1500, 930, 910. MS *m/e*: 247 (M^+), 188, 173, 135 (base peak), 85, 71. High resolution MS: Found 247.1229. Calcd for $C_{14}H_{17}NO_3$ (M^+) 247.1207. PMR ($CDCl_3$) δ: 2.00 (3H, s, $COCH_3$), 2.1—2.4, 2.6—2.8 (each 2H, A_2B_2 type), 3.83 (2H, d, J=6.0 Hz, CH_2N), 4.88 (2H, br s, $=CH_2$), 5.46 (1H, br s, NH), 5.89 (2H, s, OCH_2O), 6.5—6.8 (3H, m, aromatic).

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