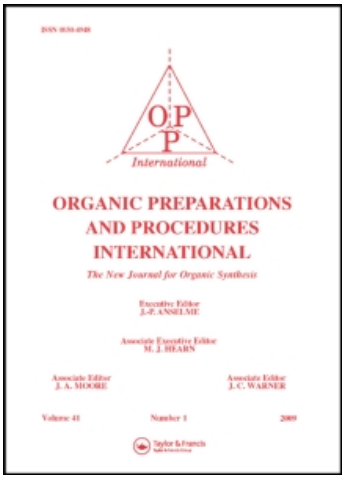

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SYNTHESIS OF ALLYL ETHENYL ETHERS USING S-ETHENYLSULFILIMINES†

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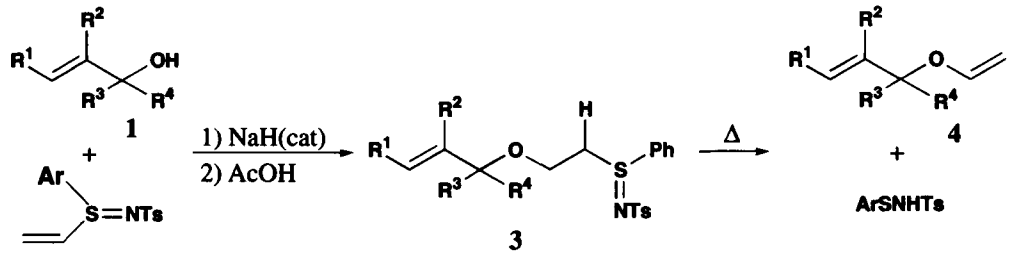
Allyl ethenyl ethers are useful as intermediates for the preparation of 1,4-enals,[1,2] ethenyl monomers,[3] and crosslinking agents in place of diethenyl ethers.[4] They have been prepared by the reaction *i*) of allyl bromide with ethylene glycol monosodium salt followed by bromination of allyl 2-hydroxyethyl ether and dehydrobromination,[2] *ii*) of allyl alcohols with ethenyl ethers (ether exchange),[5] *iii*) of allyl alcohols with ethenyl acetates,[6] *iv*) of ethenyllithium and magnesium compounds with β-haloethoxymethyl halides followed by dehydrohalogenation,[7] *v*) of allyl alcohols with α-haloaldehyde followed by dehydrohalogenation,[7] *vi*) of acetylenes with allyl alcohols.[2] In the course of studies on the synthetic uses of S-ethenylsulfilimines,[8] we developed a convenient and effective route to allyl ethenyl ethers by the nucleophilic addition and intramolecular β-elimination as shown in the equation.



a) Ar = C_6H_5
b) Ar = *p*-ClC_6H_4

a) $R^1 = R^2 = R^3 = R^4 = H$ b) R^1 = Me, $R^2 = R^3 = R^4 = H$
c) R^2 = Me, $R^1 = R^3 = R^4 = H$ d) R^3 = Me, $R^1 = R^2 = R^4 = H$
e) $R^1 = R^2 = H$, $R^3 = R^4$ = Me

The ethenylation of allyl alcohol (**1a**) was accomplished by a complete two-pot procedure. Michael addition of **1a** to the S-ethenyl-S-phenyl-N-tosylsulfilimine (**2a**) under the conditions described in Table 1 gave the corresponding adduct (**3a**) in a 94% yield. The structure of **3a** was confirmed by IR and NMR spectra and elemental analysis. The decomposition (intramolecular β-elimination) of **3a** at 110-120° was carried out using a microdistillation apparatus to give the corresponding allyl ethenyl ether (**4a**) in a 94% yield. The structure of **4a** was confirmed by the comparison of its IR and NMR spectra with those described in the literature.

As the other allyl alcohols, crotyl (**1b**), 2-methallyl (**1c**),1-methallyl (**1d**) and 1,1-dimethallyl alcohols (**1e**) were selected. The corresponding Michael addition products **3** were obtained in yields exceeding 80%, the structures of which were checked by IR and NMR spectra. The decomposition of the adducts **3**, without further purification, was carried out in a similar manner to **3a**, to give the corre-

sponding allyl ethenyl ethers **4** in 88-93% yields. Except for **4e** which contained rearranged compound, the products (**4**) are spectrophotometrically pure by NMR. The results are listed in Table 1.

TABLE 1. Allyl Ethenyl Ethers **4** and Their Precursors **3** from S-Ethenylsulfilimines **2** and Allyl Alcohols **1**[a]

Entry No.	Cmpd	Ratio **1**:**2** (mmol/mmol)	Solv	Conditions (°C)	(hrs)		Yields (%) **3**		**4**[b]
1	**1a**	10	THF	35-40	5	aa	94	a	90
2[c]	**1a**	10	THF	rt	0.5	ba	95		
3	**1b**	10	THF	rt	3d	ab	88	b	93
4	**1b**	cosolv		35-40	5	ab	97		
5	**1c**	10	THF	rt	3d	ac	59		
6	**1c**	cosolv		35-40	5	ac	88	c	91
7	**1d**	10	THF	35-40	5	ad	64		
8	**1d**	cosolv		35-40	10	ad	84	d	90
9[c]	**1d**	10	THF	rt	35	bd	97		
10	**1e**	10	THF	rt	3d	ae	63		
11	**1e**	cosolv		35-40	10	ae	90	e	88[d]

a) The addition reactions were carried out under the conditions noted in the table in the presence of catalytic amounts of NaH and the thermal decomposition of **3** to **4** at 110-120° for 30 min. b) Based on decomposed **3**. c) Sulfilimine **2b** was used. d) Determined by NMR. The value contains rearranged compound (5-methyl-4-hexenal: 40%).

In the addition reaction of **1** to **2a**, increased bulkiness in **1** tends to retard the reaction. In cases where **1** is bulky, the use of **1** as cosolvent gave good results (Entry 8 and 10). On the other hand, S-(4-chlorophenyl)-S-ethenyl-N-tosylsulfilimine (**2b**), which is more susceptible to nucleophilic attack on β-carbon,[9] reacts with bulky **1** in tetrahydrofuran (THF) to give the corresponding adduct in high yield (Entry 2 and 9).

As described above, the present method is an effective and general method to obtain allyl ethenyl ethers even though the reagent **2** must be prepared *via* four reaction steps.[10a]

EXPERIMENTAL SECTION

All melting points are uncorrected. The IR spectra were recorded on a Shimadzu IR-435 spectrophotometer and ^{1}H NMR spectra on a JEOLJNM-PMX60 and JNM-270 spectrometers using TMS as the internal standard in $CDCl_3$. Mass spectra were recorded on a JEOL JMS D300. All allyl alcohols (Tokyo Kasei Kogyo Co., Ltd.) were used after purification. S-Aryl-S-ethenyl-N-tosylsulfilimines were prepared by reported methods.[10b, c] (**2a**: mp. 111-112°, lit.[10c] 111-113°; **2b**: mp. 112-114°, lit.[11] 111-114°). THF which was dried with metallic sodium followed by distillation was used.

General Procedure for Michael Addition. Method A.- To a solution of 2 mmol of **2** in 30 mL of THF was added 1 mL of the allyl alcohol and catalytic amounts (1-2 mg) of sodium hydride at room temperature. The mixture was stirred at 35-40° for 5 hrs and then neutralized by addition of two drops of acetic acid. After removing the precipitated, sodium acetate, the solution was evaporated to dryness. The residue was dissolved in 30 mL of dichloromethane, washed with water and dried over anhydrous sodium sulfate. The dried solution was evaporated and the oily residue was precipitated by treatment with ether. The resulting solid was collected and purified by crystalization if necessary.

Method B.- To a mixture of 2 mmol of **2** and 3 mL of an allyl alcohol was added catalytic amounts of sodium hydride. The resulting mixture was stirred at 35-40° for 5 hrs and neutralized by addition of two drops of acetic acid. From the mixture excess of the allyl alcohol was removed by distillation under reduced pressure. The residue obtained was treated in a similar manner to that in Method A.

S-(2-Allyloxyethyl)-S-phenyl-N-tosylsulfilimine (3aa): yield 94%, mp. 91-92° (from CH_2Cl_2-Et_2O). IR (KBr): 1281 and 1137 (SO_2), 968 cm^{-1} (S=N). NMR: δ 2.35 (s, 3H), 3.09-3.31 (m, 2H), 3.51-3.68 (m, 2H), 3.75-3.77 (m, 2H), 5.16-5.27 (m, 2H), 5.70-5.86 (m, 1H), 7.18 (d, 2H, J = 8.3 Hz), 7.46-7.55 (m, 3H), 7.73 (d, 2H, J = 8.3 Hz), 7.73-7.79 (m, 2H).

Anal. Calcd. for $C_{18}H_{21}NO_3S_2$: C, 59.48; H, 5.82; N, 3.85. Found: C, 59.64; H, 5.75; N, 3.76.

S-(2-Allyloxyethyl)-S-(4-chlorophenyl)-N-tosylsulfilimine (3ba): yield 95%, mp. 80-82° (from CH_2Cl_2-Et_2O). IR (KBr): 1280 and 1141 (SO_2), 988 cm^{-1} (S=N). NMR: δ 2.36 (s, 3H), 3.08-3.30 (m, 2H), 3.53-3.70 (m,2H), 3.76 (d, 2H, J = 5.9 Hz), 5.16-5.24 (m, 2H), 5.68-5.83 (m, 1H), 7.19 (d, 2H, J = 8.0 Hz), 7.48 (d, 2H, J = 8.6 Hz), 7.68 (d, 2H, J = 8.6 Hz), 7.75 (d, 2H, J = 8.0 Hz).

Anal. Calcd. for $C_{18}H_{20}ClNO_3S_2$: C, 54.33; H, 5.07; N, 3.52. Found: C, 54.24; H, 5.17; N, 3.44

S-(4-Chlorophenyl)-S-[2-(1-methylallyloxy)ethyl]-N-tosylsulfilimine (3bd): yield 97%, mp. 77-79° (from CH_2Cl_2-Et_2O). IR (KBr): 1280 and 1138 (SO_2), 960 cm^{-1} (S=N). NMR: δ 1.72 (d, 3H, J = 6.2 Hz), 2.36 (s, 3H), 3.04-3.33 (m, 2H), 3.40-3.78 (m, 5H), 5.05-5.18 (m, 2H), 5.51-5.67 (m, 1H), 7.19 (d, 2H, J = 8.0 Hz), 7.48 (d, 2H, J = 8.6 Hz), 7.69 (d, 2H, J = 8.6 Hz), 7.76 (d, 2H, J = 8.0 Hz).

Anal. Calcd. for $C_{19}H_{22}ClNO_3S_2$: C, 55.40; H, 5.38; N, 3.40. Found: C, 55.23; H, 5.40; N, 3.26

Thermal Decomposition of Adduct 3 to 4. General Procedure.- One or two mmol of adduct **3** was placed in a micro distillation apparatus. The contents was heated at 110-120° for 30 minutes under reduced pressure (ca. 50 mmHg) and the distillate of **4** was received into a mini-tube cooled at -30~-40°.

Allyl Ethenyl Ether (4a): bp. 63-64°/760 mm, lit.[7] 65°. NMR[12]: δ 4.03 (dd, 1H, J = 6.8 and 2.2 Hz), 4.14-4.27 (m, 3H), 5,13-5.39 (m, 2H), 5.87-6.10 (m, 1H), 6.47 (dd, 1H, J = 6.8 and 14.6 Hz).

Ethenyl 3-Methylallyl Ether (4b): bp. 96-97°/760 mm, lit.[7] 48-49°/120 mm. NMR: δ 1.72 (d, 3H, J = 4.7 Hz), 4.02 (dd, 1H, J = 2.2 and J = 6.7 Hz), 5.64-5.78 (m, 2H), 6.44 (dd, 1H, J = 6.5 and 14.5 Hz).

Ethenyl 2-Methylallyl Ether (4c): bp 87-88°/ 760 mm, lit.[13] 87-88°. NMR: δ 1.76 (s, 3H), 4.05 (dd, 1H, J = 2.1 and 6.5 Hz), 4.12 (s, 2H), 4.23 (dd, 1H, J = 2.1 and 14.5 Hz), 4.94 (d, 1H, J = 1.1 Hz), 5.00 (d, 1H, J = 1.1 Hz), 6.46 (dd, 1H, J = 6.5 and 14.5 Hz).

Ethenyl 1-Methylallyl Ether (4d): bp. 89-90°/760 mm. NMR: δ 1.33 (d, 3H, J = 6.3 Hz), 4.02 (dd,

1H, J = 1.2 and 6.7 Hz), 4.31 (dd, 1H, J = 1.2 and 14.7 Hz), 5.13-5.29 (m, 3H), 5.75-5.99 (m, 1H), 6.33 (dd, 1H, J = 6.7 and 14.7 Hz). HRMS (M^+) : Calcd for $C_6H_{10}O$ 98.0732. Found 98.0737.

Ethenyl 1,1-Dimethylallyl Ether (4e): bp. 94-95°/760 mm. NMR: δ 1.35 (s, 6H), 4.02 (dd, 1H, J = 6.7 and 0.3 Hz), 4.40 (dd, 1H, J = 14.4 and 0.3 Hz), 5.17 (dd, 1H, J = 11.1 and 0.2 Hz), 5.19 (dd, 1H, J =17.7 and 0.2 Hz), 5.88 (dd, 1H, J = 11.1 and 17.7 Hz), 6.33 (dd, 1H, J = 6.7 and 14.4 Hz). HRMS (M^+) : Calcd for $C_7H_{12}O$ 112.0890. Found 112.0895.

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