A Mild and Convenient Barbier-Type Allylation of Aldehydes to Homoallylic Alcohols via Iodide Ion Promoted Stannylation of Allylic Bromides and Chlorides with Tin(II) Chloride

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Barbier-type allylation of aldehydes with allylic bromides and tin(II) chloride dihydrate is largely accelerated by adding stoichiometric or substoichiometric amounts of sodium iodide. This method has some merits such as lower temperature, shorter reaction time and/or more choices of solvents for the reaction. Moreover, the activation by the iodide ion enables the use of relatively unreactive allylic chlorides of various structural types (e.g., 3-chloro-2-chloromethylpropene as an isobutene dianion equivalent) and, thus, expands synthetic applicability of this reaction. The major role of the iodide salt is attributed to the in situ generation of the corresponding allylic iodide.

Carbonyl allylation with allylic tin reagents generated in situ from allylic halides and tin(II) halides is a unique method among others for this synthetically important transformation.[1] The reaction proceeds smoothly at room temperature with allylic iodides, while heating is generally required when the bromides are used. Allylic chlorides, on the other hand, are practically unreactive under these conditions.[2,3] This limitation is obviously undesirable since the chlorides are less expensive, more stable, and available in greater structural variation than the corresponding bromides and iodides.

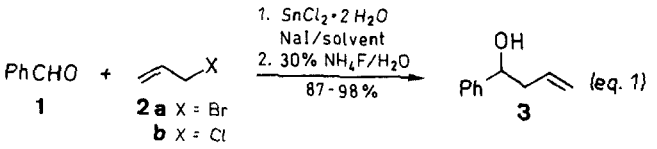
Recently, palladium-catalyzed stannylation of allylic alcohols and their derivatives has been developed.[4] In the study, allyl chloride has also been used but only for spectral comparison of the intermediates, and the scope and limitation of the reaction with this class of substrates are not clarified.

In one case, propargyl bromide has been stannylated at room temperature with tin(II) chloride in the presence of sodium iodide, and the results have been explained by in situ formation of propargyl iodide.[5] On the other hand, it is well known that tin(II) halides and alkali metal halides form stable alkali metal trihalostannates.[6] Therefore, the possible direct nucleophilic substitution of propargyl bromide by these anionic tin species should also be considered. There is also a precedent of utilizing lithium dibromochlorostannate to generate α-*tert*-butoxymethyltrihalotin from *tert*-butyl chloromethyl ether.[7]

We have recently obtained evidence, suggesting that such nucleophilic assistance indeed operates in the allylic stannylation with mixed reagents of tin(II) chloride and copper(I) halides or cyanide. For comparison, we also studied the effect of alkali metal halides and clarified that, in these cases, the nucleophilic assistance was relatively unimportant. During the investigation, however, the activation by sodium iodide was found generally applicable not only to allylic bromides but also to the chlorides, largely extending the scope of this reaction in organic synthesis. Here, we would like to describe the results for the iodide ion-promoted reactions. Those with copper(I) salts will be reported separately.

The reaction of benzaldehyde (**1**), allyl bromide (**2a**) and tin(II) chloride dihydrate in dimethylformamide proceeded only very slowly at room temperature. It was greatly enhanced by adding sodium iodide and was completed after 2 hours to give a high yield of the allylation product **3** (eq. 1, run 1 and 2 in Table 1). Although anhydrous tin(II) chloride or fluoride has been used in these reactions previously,[2,3] we chose the hydrate rather than handling the hygroscopic anhydrous salts since the related carbonyl allylation reactions with allylic halides and metallic tin are viable in the presence of water.[8] Dimethylformamide and other solvents (vide infra) were also used without drying. Additionally, it became apparent that the reaction can be conducted without exclusion of air.

Gratifyingly, allyl chloride (**2b**) also reacted with **1** smoothly at room temperature under similar conditions but with a longer reaction time (20 hours for completion) and gave a nearly quantitative yield of **3** (run 10).



With the aid of the iodide salt, the reaction of **2a** could also be run effectively in other solvents such as ethanol, acetonitrile and even tetrahydrofuran instead of the generally used highly polar aprotic solvents like dimethylformamide. It did not proceed smoothly, however, in dichloromethane, where the reaction mixture was heterogeneous throughout.

To assess the involvement of the nucleophilic substitution by the anionic tin species, the effect of some other alkali metal halides was examined. When **1** was treated with **2a**, tin(II) chloride dihydrate and NaX in dimethylformamide at room temperature, the results [X/reaction time (h)/yield of **3** (%)/recovery of **1** (%) were as follows: F/20/11/79; Cl/20/20/71; Br/20/32/63; and I/2/89/4. Addition of sodium bromide, thus, produced appreciable enhancement, that indicates the existence of such nucleophilic assistance also in the present system. However, the degree of enhancement is much smaller than that of the iodide salt. Furthermore, lithium and potassium iodides exhibited the same effect as that of sodium iodide. Therefore, the distinctively large enhancement caused by the iodide salts should be attributed mostly to the in situ generation of allyl iodide as suggested previously.[5]

Thus, we expected that the iodide ion might work in a catalytic amount by assuming rapid exchange of the halide ions in the reaction system. It was found indeed the case, although heating was required in some cases particularly for those with **2b** (runs 3, 5 and 12).

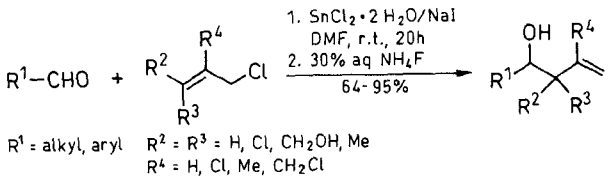
Under the optimized conditions, some representative aldehydes were allylated with **2a,b** or propargyl bromide in high yield (Table 2, entries 1–6). More importantly,

Table 1. Acceleration of the Allylation of Benzaldehyde (**1**) with Allyl Bromide and Chloride (**2a** and **2b** respectively) and Tin(II) Chloride Dihydratyte by Sodium Iodide[a]

	Molar Equivalent			Reaction Conditions			Material Balance (%)[b]		
Run	Allyl Halide	$SnCl_2 \cdot 2H_2O$	NaI	Solvent	Temp., °C	Time, h	yield of **3**	Recov. of **1**	Total
1	1.05 (**2a**)	1.2	none	DMF	r.t.	20	9	85	94
2	1.05 (**2a**)	1.2	1.2	DMF	r.t.	2	92	0	92
3	1.2 (**2a**)	1.2	0.2	DMF	r.t.	6	96[c]	2	98
4	1.2 (**2a**)	1.2	none	DMF	60	5	44	52	96
5	1.2 (**2a**)	1.2	0.02	DMF	60	5	87	10	97
6	1.05 (**2a**)	1.5	1.5	EtOH	r.t.	3	93	0	93
7	1.05 (**2a**)	1.5	1.5	MeCN[d]	r.t.	6	97	0	97
8	1.05 (**2a**)	1.5	1.5	THF	r.t.	20	97	0	97
9	1.05 (**2a**)	1.2	1.5	CH_2Cl_2	r.t.	24	8	85	93
10	1.1 (**2b**)	1.5	1.5	DMF	r.t.	20	98	0	98
11	1.2 (**2b**)	1.2	none	DMF	80	24	1	94	95
12	1.2 (**2b**)	1.2	0.2	DMF	80	24	93	3	96

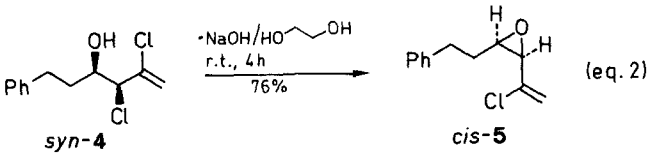
[a] Reactions were done in a stoppered flask at room temperature or in a sealed flask at higher temperatures without particular exclusion of the air, unless otherwise indicated.
[b] Estimated by GC based on the amount of **1** charged.
[c] Isolated in 93% yield; bp 130–135°C/14 Torr (bath temperature) (Lit.[13] bp 111–112°C/13 Torr).
[d] Performed under Ar atmosphere resulting in dark brown color development and a lower yield of **3** without exclusion of the air in this particular solvent.

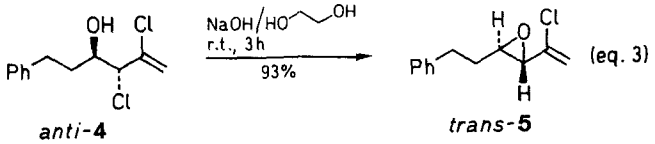
this procedure enables the use of a variety of allylic chlorides (entries 7–14).



Crotyl chloride gave a stereoisomeric mixture of the γ-adducts (entry 7) as observed previously in the related reaction with crotyl bromide.[3] Interestingly, the isomeric 3-chloro-1-butene was much less reactive (85% recovery under the same conditions), and it suggests that the substitution of such internal allylic chlorides by the iodide ion is much slower than that of the terminal ones under the reaction conditions. (*Z*)-4-Chloro-2-buten-1-ol reacted essentially in the same way as crotyl chloride irrespective of the presence of the hydroxy group (entry 9). Similar regio- and stereoselectivity has again been observed in the related palladium-catalyzed reaction of **1**, (*Z*)-2-butene-1,4-diol (or its derivatives), and tin(II) chloride.[4]

1,3-Dichloropropene and **1** gave a good yield of a diastereomeric mixture of internal allylic chlorides (entry 11), which did not significantly react further with the tin reagent as observed for 3-chloro-1-butene. The same product was obtained previously, only by using separately prepared 1-chloro-3-iodopropene, but in a lower yield.[3] 1,2,3-Trichloropropene also reacted in the same way to afford *syn*- and *anti*-chlorohydrins **4** (entry 12), which were easily separated by flash chromatography and converted to *cis*- and *trans*-α-chlorovinyloxiranes **5**, respectively (eq. 2 and 3). The stereochemical assignment was made by comparing the vicinal coupling constants of the oxiranes (J_{cis} = 4.2 Hz and J_{trans} = 2.0 Hz).[3] Relative ease of the cyclization reaction is compatible with this assignment: The conversion of *anti*-**4** to *trans*-**5** was complete within 3 hours, while that of *syn*-**4** to *cis*-**5** resulted in only 82% conversion after 4 hours.





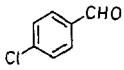
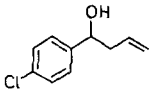
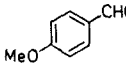
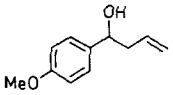
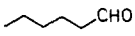
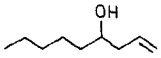
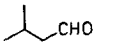
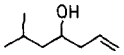
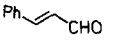
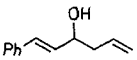
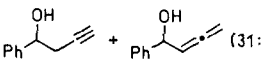
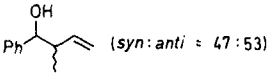
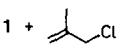
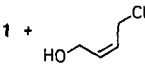
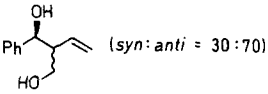
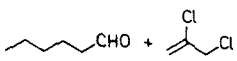
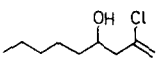
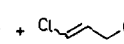
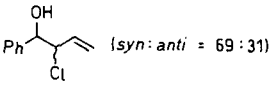
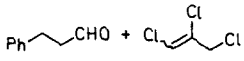
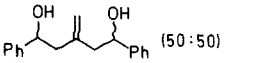
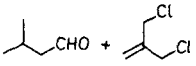
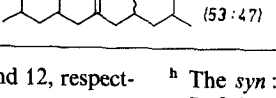
Finally, two examples with 3-chloro-2-chloromethylpropene (entries 13 and 14) indicate that this simple dichloride acquires synthetic value as an isobutene dianion equivalent[9,10] by this protocol.

In summary, the activation by the iodide ion extends the scope of the tin(II)-mediated Barbier-type aldehyde allylation, especially by enabling direct use of various allylic chlorides, under mild conditions.

Reactions were run in a stoppered flask at r.t. or in a sealed flask when heating was required. They were performed without exclusion of the air except for the reaction in MeCN, which was done under an Ar atmosphere. ^{1}H NMR (90 MHz) and ^{13}C NMR (22.6 MHz) spectra were recorded in $CDCl_3$ solutions. IR spectra were obtained for neat liquid films between NaCl plates, unless otherwise indicated. GC analyses for the conversion of **1** and the yield of **3** were performed with a column of Apiezon grease L on Celite 545 and with undecane as the internal standard. Flash chromatography was done with silica gel (230–400 mesh). Aldehydes, THF and Et_2O were distilled before use. The other solvents were used as purchased. All the allyl halides are commercially available except for (*Z*)-4-chloro-2-buten-1-ol. Two typical allylation procedures are described in the experimental, and the exact reaction conditions are given in Tables 1 and 2.

(*Z*)-4-Chloro-2-buten-1-ol:
This chloride was prepared more conveniently than by the previously reported procedure[11,12] by stirring (*Z*)-2-butene-1,3-diol (25 g)

Table 2. Allylation of Aldehydes via Iodide Ion-Promoted Stannylation of Allylic Bromides and Chlorides with Tin(II) Chloride Dihydrate

Entry	Reactants	Reaction Conditions[a]	Product(s) (Isomeric Ratio)[b]	bp (°C)/Torr[c] (bath temperature)	Molecular Formula[d] or Lit. bp (°C)/Torr	Yield (%)
1	 + **2a**	A		130–135/5	68/0.03[14]	95
2	 + **2a**	A		145–150/3	117–118/1.5[15]	83
3	 + **2b**	B		105–110/13	–[e]	87
4	 + **2a**	C		95–100/28	162–163/748[17]	93
5	 + **2a**	A		120–125/0.2	100/0.1[13]	87
6	**1** + 	D	 (31:69)	140–145/12	85–87/0.5[f,18]	84
7	**1** +  [9]	B	 (*syn*:*anti* = 47:53)	100–105/3	110/4[19]	89
8	**1** + 	B		105–110/3	95–100/12[20]	95
9	**1** + 	B	 (*syn*:*anti* = 30:70)	155–165/0.01	$C_{11}H_{14}O_2$ (178.2)	73[h]
10		B		100–105/13	$C_9H_{17}ClO$ (176.7)	92
11	**1** + 	B	 (*syn*:*anti* = 69:31)	125–130/3	–[i]	68
12	 E[j]	*syn*-**4** + *anti*-**4** (44:56)		180–185/1[k]	$C_{12}H_{14}Cl_2O$ (245.1)	64
13	**1** + 	E	 (50:50)	240–250/0.5-1	–[l]	84
14		E	 (53:47)	150–155/1	$C_{14}H_{28}O_2$ (228.4)	75[m]

[a] Conditions A-E refer to run numbers 2, 10, 8, 3 and 12, respectively, of Table 1.
[b] Isomeric ratio was estimated by ^{1}H NMR.
[c] Refers to bulb-to-bulb distillation.
[d] Satisfactory microanalyses obtained: C ± 0.45, H ± 0.29.
[e] n_D^{20} 1.4406 (Lit.[16] n_D^{20} 1.4409). Bp not reported in Ref. 16.
[f] Bp refers to the acetylenic alcohol.[18]
[g] The isomeric 3-chloro-1-butene is much less reactive under these conditions (85% recovery).
[h] The *syn* : *anti* ratio was estimated by the procedure reported in Ref. 4.
[i] ^{1}H NMR was compared with the literature data.[3]
[j] Reaction was carried out at 60 °C.
[k] Bp refers to the *anti*-isomer. The *syn*-isomer solidified; mp 64–65 °C.
[l] ^{1}H NMR was compared with the literature data.[9]
[m] The isomeric ratio was determined by ^{13}C NMR (see experimental section).

with conc. HCl (59 mL) at r.t. for 3 h and isolated by extraction (EtOAc and CH_2Cl_2), drying (Na_2SO_4), and distillation; yield: 23 g (52%), bp 78–83 °C/13 Torr (Lit.[11] bp 79–81 °C/11 Torr).

^{1}H NMR: δ = 1.5 (br s, 1 H), 3.8–4.5 (m, 4 H), 5.5–6.0 (m, 2 H).

2-Chloro-1-nonen-4-ol (Entry 10, Table 2); Typical Procedure:

To a magnetically stirred solution of hexanal (0.50 g, 5.0 mmol) and 2,3-dichloropropene (0.61 g, 5.5 mmol) in DMF (10 mL) was added successively $SnCl_2 \cdot 2H_2O$ (1.7 g, 7.5 mmol) and NaI (1.1 g, 7.5 mmol). Mild exothermic reaction was noted at the early stage. After stirring for 20 h at r.t., 30% aq NH_4F (10 mL) and Et_2O (20 mL) were added. The mixture was well stirred and separated. The aqueous phase was reextracted with Et_2O (20 mL). The Et_2O extracts were combined, washed with half-saturated aq NaCl (40 mL), and dried (Na_2SO_4). The product was isolated by flash chromatography (hexane/EtOAc) and purified by distillation; yield: 0.82 g (93%).

IR: ν = 3370 (OH), 1640 (C=C), 880 cm^{-1} (=CH_2).

^{1}H NMR: δ = 0.7–1.05 (m, 3 H), 1.05–1.8 [m, 9 H (1 H exchangeable with D_2O)], 2.46 (d, 2 H, J = 6.6 Hz), 3.7–4.2 (m, 1 H), 5.15–5.35 (m, 2 H).

2-Hydroxymethyl-1-phenyl-3-buten-1-ol (Entry 9, Table 2):

IR: ν = 3360 (OH), 1645 cm^{-1} (C=C).

^{1}H NMR: δ = 1.7 (t, 1 H, J = 5.4 Hz, exchangeable with D_2O), 2.3–2.9 [m, 2 H (1 H exchangeable with D_2O)], 3.5–3.9 [m, 2 H, changing to two doublets centered at 3.55 and 3.75 ppm (both

J = 5.8 Hz) of 71:29 area ratio on addition of D_2O], 4.65–4.95 [m, 1 H, changing to d at 4.8 ppm (J = 5.9 Hz) on addition of D_2O], 4.95–5.4 (m, 2 H), 5.4–6.1 (m, 1 H), and 7.25 (br s, 5 H).

syn- and _anti_-4,5-Dichloro-1-phenyl-5-hexen-3-ols (_syn_- and _anti_-4) (Entry 12, Table 2); Typical Procedure:

A solution of 3-phenylpropanal (0.67 g, 5.0 mmol), 1,2,3-trichloropropene (0.87 g, 6.0 mmol), $SnCl_2 \cdot 2H_2O$ (1.35 g, 6.0 mmol) and NaI (0.15 g, 1.0 mmol) in DMF (10 mL) was prepared and sealed in a 50 mL round-bottomed flask equipped with a magnetic stirring bar. The mixture was heated to 60 °C for 24 h with stirring and worked up as described for 2-chloro-1-nonen-4-ol to give a mixture of the diastereomeric products. On flash chromatography (hexane/EtOAc, 95:5–88:12), syn-**4** was eluted first. It solidified when the solvent was evaporated; yield: 0.35 g (28%); mp 64–65 °C.

$C_{12}H_{14}Cl_2O$	calc.	C 58.79	H 5.76	Cl 28.93
(245.1)	found	58.95	5.77	28.77

IR (KBr): ν = 3435, 3380 (OH), 1630 (C=C), 910 cm^{-1} (=CH_2).

^1H NMR: δ = 1.5–2.1 (m, 2 H), 2.3 (br s, 1 H), 2.5–3.1 (m, 2 H), 3.9 (dt, 1 H, J = 4.7, 6.9 Hz), 4.4 (d, 1 H, J = 6.9 Hz), 5.43, 5.58 (2d, 1 H each, J = 1.8 Hz), 7.0–7.4 (m, 5 H).

^{13}C NMR: δ = 31.7, 35.0, 69.5, 71.7, 117.5, 126.0, 128.4, 138.2, 141.2.

Successively eluted was _anti_-**4**. This was further purified by distillation; yield: 0.44 g (36%); bp 180–185 °C/1 Torr (bath temperature).

$C_{12}H_{14}Cl_2O$	calc.	C 58.79	H 5.76	Cl 28.93
(245.1)	found	58.34	5.76	29.00

IR: ν = 3570, 3425 (OH), 1630 (C=C), 905 cm^{-1} (=CH_2).

^1H NMR: δ = 1.5–2.4 [m, 3 H (1 H exchangeable with D_2O)], 2.4–3.1 (m, 2 H), 3.8–4.1 (m, 1 H), 4.4 (d, 1 H, J = 7.1 Hz), 5.50–5.63 (2 d, 1 H each, J = 1.8 Hz), 7.0–7.4 (m, 5 H).

^{13}C NMR: δ = 31.7, 34.1, 66.6, 71.7, 118.0, 126.0, 128.4, 138.2, 141.3.

2,10-Dimethyl-6-methyleneundecane-4,8-diol (Entry 14, Table 2):

By using the same procedure as above, but heating at 80 °C, the reaction of 3-methylbutanal (0.90 g, 10.5 mmol), 3-chloro-2-chloromethyl-1-propene (0.63 g, 5.0 mmol), $SnCl_2 \cdot 2H_2O$ (2.8 g, 12.5 mmol), and NaI (0.38 g, 2.5 mmol) in DMF (15 mL) gave the diol; yield: 0.85 g (75%).

IR: ν = 3350 (OH), 1645 (C=C), 895 cm^{-1} (=CH_2).

^1H NMR: δ = 0.94 (d, 12 H, J = 6.4 Hz), 1.0–1.5 (m, 4 H), 1.5–2.0 [m, 4 H (2 H exchangeable with D_2O)], 2.0–2.4 (m, 4 H), 3.7–4.0 (m, 2 H), 5.0 (br s, 2 H).

^{13}C NMR: δ = 22.0, 22.1, 23.1, 23.2, 24.4, 24.5, 44.4, 45.1, 46.4, 67.3, 68.0, 114.7, 114.8, 143.9, 144.3 (all the peaks were observed in pairs except for the one at 46.4 ppm which was apparently broader than the others, and the average of the peak hight ratios of these pairs was 53:47).

1-Phenyl-2,3-butadien-1-ol and 1-Phenyl-3-butyn-1-ol (Entry 6, Table 2):

Although a mixture of these alcohols has been prepared previously,[5] complete spectral data have not been given. Here, these isomeric products from the reaction of **1** and propargyl bromide were isolated by GC. The major product was the allenic alcohol.

IR: ν = 3370 (OH), 1960 (C=C=C), 850 cm^{-1} (=CH_2).

^1H NMR: δ = 2.2 (d, 1 H, J = 3.7 Hz, exchangeable with D_2O), 4.8, 5.15–5.6 (2 m, 2 H each), 7.2–7.5 (m, 5 H).

The minor product was the acetylenic alcohol.

IR: ν = 3400 (OH), 3295 (=C–H), 2120 cm^{-1} (weak, C=C).

^1H NMR: δ = 2.05 (t, 1 H, J = 2.5 Hz), 2.4 (d, 1 H, J = 3.7 Hz, exchangeable with D_2O), 2.65 (dd, 2 H, J = 6.3, 2.5 Hz), 4.7–5.0 [m, 1 H, changing to t (J = 6.3 Hz) at 4.85 ppm on addition of D_2O], 7.2–7.5 (m, 5 H).

***cis*-2-(1'-Chloroethenyl)-3-(2'-phenylethyl)oxirane (*cis*-5):**

To a stirred solution of _syn_-**4** (0.30 g, 1.24 mmol) in ethylene glycol (5 mL) was added crushed solid NaOH (0.054 g, 1.36 mmol) under cooling in a water bath (ca. 15 °C). After stirring for 4 h at r.t. water (20 mL) was added. The product was then extracted with hexane (2 × 15 mL) and Et_2O (20 mL), and the extracts were combined and dried (Na_2SO_4). ^1H NMR spectrum of the crude product indicated the clean formation of _cis_-**5** as well as the existence of unreacted _syn_-**4** (18 mol-%). The _cis_-oxirane was isolated by flash chromatography (hexane/Et_2O, 98:2) and purified by bulb-to-bulb distillation, bp 145–150 °C (bath temperature); yield: 0.20 g (76%).

$C_{12}H_{13}ClO$	calc.	C 69.06	H 6.28	Cl 16.99
(208.7)	found	69.16	6.29	17.11

IR: ν = 1640 (C=C), 895 (=CH_2).

^1H NMR: δ = 1.6–2.0 (m, 2 H), 2.8 (dd, 2 H, J = 7.2, 8.4 Hz), 3.15 (dt, 1 H, J = 4.2, 6.2 Hz), 3.55 (d with further fine splitting, 1 H, J = 4.2, < 1 Hz), 5.4 (br s with fine splitting, 2 H, J < 1 Hz), 7.0–7.4 (m, 5 H).

^{13}C NMR: δ = 28.4, 32.3, 57.6, 58.2, 113.4, 126.1, 128.3, 128.4, 135.0, 140.9.

***trans*-2-(1'-Chloroethenyl)-3-(2'-phenylethyl)oxirane (*trans*-5):**

The same procedure as above was used, but with a reaction time of 3 h, resulting in the complete conversion of _anti_-**4** (0.36 g, 1.48 mmol) to _trans_-**5**, which was purified by bulb-to-bulb distillation, bp 140–145 °C/1 Torr (bath temperature); yield: 0.26 g (93%).

$C_{12}H_{13}ClO$	calc.	C 69.06	H 6.28	Cl 16.99
(208.7)	found	68.89	6.22	17.15

IR: ν = 1630 (C=C), 890 cm^{-1} (=CH_2).

^1H NMR: δ = 1.7–2.1 (m, 2 H), 2.6–2.9 (m, 2 H), 3.05 (dt, 1 H, J = 2.0, 5.6 Hz), 3.2 (d, 1 H, J = 2.0 Hz), 5.35 (d, 1 H, J = 1.5 Hz), 5.46 (br s with fine splitting, 1 H, J < 1 Hz), 7.0–7.4 (m, 5 H).

^{13}C NMR: δ = 32.0, 33.2, 58.5, 59.1, 114.0, 126.1, 128.3, 128.5, 137.8, 140.7.

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