Hydrogen Iodide Strategy for One-Pot Preparation of Allylic Azides, Nitriles, and Phenyl Sulfones from Allylic Alcohols

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Hydrogen iodide, HI, cleanly generated in situ from Me_3SiCl/NaI and water in acetonitrile under mild conditions, was found to be an attractive reagent for the conversion of allylic alcohols into allylic iodides which serve as good allylic cation equivalent. Thus, treatment of allylic alcohols with $Me_3SiCl/NaI/H_2O$, followed by the substitution with N_3^-, CN^-, and $PhSO_2^-$ ions in the same flask produced the corresponding allylic compounds bearing azide, cyano, and phenyl sulfonyl functionalities in fair yields. This method provides a useful procedure for the preparation of allylic compounds from easily available allylic alcohols.

Although the chlorotrimethylsialne/sodium iodide (Me_3SiCl/NaI) reagent is widely used in organic synthesis,[1,2] little attention has been given to this reagent as an immediate source of hydrogen iodide[3] which has synthetic possibilities not available from alternative hydrogen halides. For instance, hydrogen iodide is one of the strong proton acids ($pK_a = -10.7$).[4] Furthermore, iodide ion is a typical soft anion in the HSAB principle[5] and serves as a prominent nucleophile as well as a good leaving group in nucleophilic substitution reactions.[4]

Thus, HI, generated in situ from Me_3SiCl/NaI in the presence of water, smoothly added to a variety of olefins or alkynes to give the corresponding iodides in good yields.[6] For allylic alcohols, however, HI induces substitution reactions rather than addition reactions to form allylic iodides, which are conventionally prepared from sulfur compounds via several steps[7] or from allylic alcohols by the action of sodium iodide/boron trifluoride etherate,[8] in fair to good yields. In particular, it is important to note that the allylic iodides, prepared by this method, can be used without isolation for successive reactions in the same reaction flask.

In a previous paper, we have shown that the allylic iodides thus prepared are easily umpoled in the presence of zinc powder into an allylic anion equivalent, which subsequently undergoes Barbier-type reactions with carbonyl compounds to form homoallylic alcohols in a one-pot reaction.[9]

In the continuation of our study on the utilization of HI in synthetic processes, our attention has been directed to an alternative characteristic of allylic iodides, which serve as an allylic cation equivalent. This paper describes a convenient one-pot synthesis of allylic azides, cyanides, and phenyl sulfones via a facile conversion of allylic alcohols into allylic iodides with HI, generated in situ from $Me_3SiCl/NaI/H_2O$, followed by nucleophilic substitution with N_3^-, CN^-, and $PhSO_2^-$ ions under mild conditions.

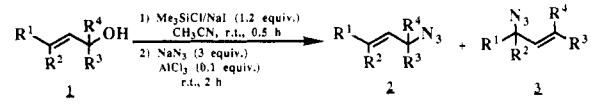
Table I. Azidation of Allylic Alcohols under Various Reaction Conditions

run[a]	substrate	catalyst	product (ratio: **2**/**3**)[b]	yield (%)[c]
1	**1a**	none	**2a** + **3a** (68:32)	32
2	**1a**	$AlCl_3$	**2a** + **3a** (64:36)	64 (70)
3	**1a**	ZnI_2	**2a** + **3a**	55
4	**1a**	$Pd(PPh_3)_4$	**2a** + **3a**	49
5	**1a**	$SnCl_2$	**2a** + **3a**	49
6	**1c**	$AlCl_3$	**2a** + **3a** (70:30)	57 (70)
7	**1d**	$AlCl_3$	**2d** + **3d**	34 (40)
8	**1e**	$AlCl_3$	**2e**	72 (90)
9	**1f**	$AlCl_3$	**2f**	63

[a] Substrate (10 mmol) was allowed to react with Me_3SiCl/NaI (12 mmol) in MeCN (30 mL) containing water at room temperature for 0.5 h, followed by NaN_3 (30 mmol) in the presence of catalyst (1 mmol) for additional 2 h. [b] The ratio was determined by VPC. [c] Isolated yields. The number in parentheses shows the yields when the resulting iodides were used in the azidation step.

Recently, Murahashi et al. have reported the palladium-catalyzed azidation of allylic acetates with azide ion and the conversion of the resulting allyl azides into amines on treatment with $PPh_3/NaOH$, without isolation.[10] In addition, the effectiveness of organic iodides in organic synthesis has been shown in the platinum-catalyzed carbonylation by Watanabe et al.[11]

To confirm the optimum conditions for the conversion of allylic alcohols into azides, (*E*)-2-hexen-1-ol (**1a**) was chosen as a model substrate and allowed to react under several reaction conditions (eq 1) (Table I).



(1)

1,2,3	R^1	R^2	R^3	R^4
a	n-C_3H_7	H	H	H
b	H	n-C_3H_7	H	H
c	H	H	n-C_3H_7	H
d	CH_3	CH_3	H	H
e	Ph	H	H	H
f	H	$-(CH_2)_3-$		H

The azidation of allylic alcohol **1a** was achieved by treating it with Me_3SiCl/NaI in acetonitrile containing

(1) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981, p 288.
(2) Schmidt, A. H. *Aldrichim. Acta* **1981**, *14*, 31.
(3) Conventionally, hydrogen iodide was prepared by the use of excess potassium iodide and 95% orthophosphoric acid at higher temperature (80 °C): Stone, H.; Schecher, H. *Organic Synthesis*; Wiley: New York, 1963; Collect. Vol. IV, p 543.
(4) Carey, F. A.; Sandberg, R. J. *Advanced Organic Chemistry*, 2nd ed., Part A; Plenum Press: New York, 1985; p 265.
(5) Ho, T. *Hard and Soft Acids and Bases Principle in Organic Synthesis*; Academic Press: New York, 1977; p 6.
(6) Irifune, S.; Kibayashi, T.; Ishii, Y.; Ogawa, M. *Synthesis* **1988**, 366.
(7) Sakurai, A.; Hayashi, T.; Hori, I.; Jindo, Y.; Oishi, T. *Synthesis* 1978, 370 and references cited therein.
(8) Vanker, T. D.; Trinadha, R. C. *Tetrahedron Lett.* **1985**, 2717.
(9) Kanai, T.; Irifune, S.; Ishii, Y.; Ogawa, M. *Synthesis* **1989**, 283.
(10) Murahashi, S.; Tanigawa, Y.; Imada, Y.; Taniguchi, Y. *Tetrahedron Lett.* **1986**, 227.
(11) Takeuchi, R.; Tsuji, Y.; Fujita, M.; Kondo, T.; Watanabe, Y. *J. Org. Chem.* **1989**, *54*, 1831.

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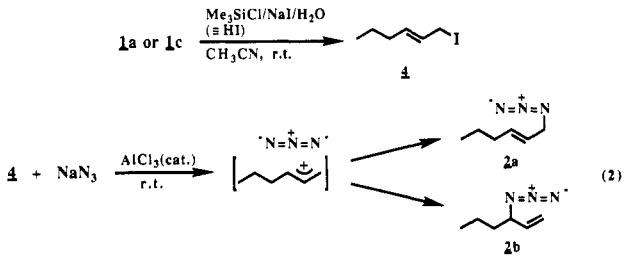
water[12] at room temperature for 0.5 h, followed by sodium azide under the influence of catalytic amounts of aluminum chloride ($AlCl_3$) for an additional 2 h, giving an approximately 2:1 regioisomeric mixture of (*E*)-1-azido-2-hexene (**2a**) and 3-azido-1-hexene (**3a**) in fair yields (64%).[13] In the absence of the catalyst, the substitution progressed sluggishly to give **2a** and **3a** in moderate yields (32%) even after 16 h, and the unchanged (*E*)-1-iodo-2-hexene resulted from **1a** was recovered. To compare the present approach with the conventional one,[3] **1a** was treated with KI and 95% orthophosphoric acid at room temperature. However, **1a** was recovered unchanged. The catalytic activity of ZnI_2, $Pd(PPh_3)_4$, and $SnCl_2$ was also examined, but their activities were low compared with that of $AlCl_3$.

Although the azidation resulted in about a 2:1 isomeric mixture of the rearranged products, **2a** and **3a**, a similar allylic rearrangement which affords a regioisomeric mixture has been observed in the substitution of 1-chloro-3-methyl-2-butene on treatment with azide ion.[14]

It is interesting to note that the azidation of 1-hexen-3-ol (**1c**) occurred in a manner similar to that of **1a** to give the same rearranged products **2a** and **3a**, whose ratio was almost the same as that from **1a**.

In the iodination of allylic alcohols by HI generated from $Me_3SiCl/NaI/H_2O$, the reaction involves the formation of a π-allylic cation intermediate and the subsequent nucleophilic attack of iodide ion from the less hindered side of the resulting π-allylic cation.[6] Therefore, the iodination of **1c** takes place via the same intermediate as that of **1a**. Consequently, **2a** and **3a** may be formed from **1a** and **1c** through an allylic rearrangement between the π-allylic cation and the azide ion (eq 2).



Similarly, the azidation of 3-methyl-2-buten-1-ol (**1d**) gave regioisomers **2d** and **3d** in somewhat lower yields. However, the reaction of 3-phenyl-2-propen-1-ol (**1e**) produced exclusively terminal azide, 1-azido-3-phenyl-2-propene (**2e**), without formation of the rearranged product. The following explanation may be advanced for this trend. The allylic cation on the C-3 position of **1e** is less reactive than that of the C-1 position, since the positive charge on the C-3 can be developed to some extent on the benzene ring through the conjugation. In addition, the negatively charged azide ion may attack with more difficulty at the C-3 carbon than the C-1 because of steric hindrance and the electrostatic repulsion between the azide ion and the benzene ring. Thus, terminal substitution will be favored. A cyclic alcohol, 2-cyclohexen-1-ol (**1f**), also underwent the azidation to give 1-azido-2-hexene (**2f**) in 63% yield.

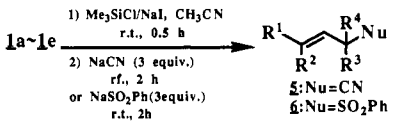
When (*E*)-1-iodo-2-hexene (**4**), isolated by simple workup after the iodination of **1a** with $Me_3SiCl/NaI/H_2O$,[15] was employed in the azidation step, the yield of **2a** and **3a** was found to be slightly improved.

Table II. Cyanation and Phenyl Sulfonylation of Allylic Alcohols

run[a]	substrate	nucleophile	product	yield (%)[b]
1	**1a**	NaCN	**5a**	65 (92)
2[c]	**1a**	NaCN	**5a**	46
3[c]	**1a**	$NaSO_2Ph$	**6a**	78
4	**1c**	NaCN	**5a**	61 (90)
5[c]	**1c**	$NaSO_2Ph$	**6a**	80
6	**1d**	NaCN	**5d**	47 (60)
7[c]	**1d**	$NaSO_2Ph$	**6d**	86
8	**1e**	NaCN	**5e**	30 (74)
9	**1b**	NaCN	**5a** + **5b** (80:20)[d]	62

[a] Substrate (10 mmol) was allowed to react with Me_3SiCl/NaI (12 mmol) in MeCN (30 mL) containing water at room temperature for 0.5 h, followed by nucleophile (30 mmol) at reflux for additional 2 h. [b] Isolated yields. The number in parentheses shows the yield when iodides were used. [c] Room temperature. [d] Isomeric ratio was determined by ^1H NMR.

In a similar manner to the azidation, the cyanation of allylic alcohols was successfully carried out (eq 3) (Table II).



5, 6	R^1	R^2	R^3	R^4
a	n-C_3H_7	H	H	H
b	H	n-C_3H_7	H	H
c	H	H	n-C_3H_7	H
d	CH_3	CH_3	H	H
e	Ph	H	H	H

Usually, the substitution of allylic halides with cyanide is best accomplished with dry powdered cuprous cyanide, derived from copper sulfate and sodium cyanide, rather than with alcholic alkali cyanides, with which side reactions such as isomerization and alcoholysis of the double bond are particularly bothersome.[16] However, the present conversion of allylic alcohols into allylic cyanides via in situ generation of allylic iodides could be performed satisfactorily by the use of an alkali cyanide such as sodium cyanide.

In contrast to the azidation, which necessitates the activation by $AlCl_3$ in the azidation step, the cyanation occurred in the absence of catalyst under refluxing acetonitrile. This may be attributed to the strong nucleophilicity of CN^- compared with that of N_3^-.[4] Furthermore, although the azidation was accompanied by an allylic rearrangement to form a regioisomeric mixture of azides, the cyanation took place only at the less hindered side of the allylic system to form terminal cyanides.

Allylic alcohols **1a** and **1c** were converted into the same cyanide, **5a**, in fair yields, since the same iodide **4** was formed from **1a** and **1c** in the iodination step. Unlike the azidation, the cyanation was markedly improved when the iodides isolated were used in the cyanation step.

The extension of the present method to phenyl sulfonylation provides a very useful procedure for the prepa-

(12) Commercially available acetonitrile without any dehydration was used. The same result was obtained when absolute acetonitrile was used, since the iodination of **1a** resulted in the simultaneous formation of water.

(13) The ^{13}C NMR spectrum of the reaction products indicated the formation of no product other than iodide and azides.

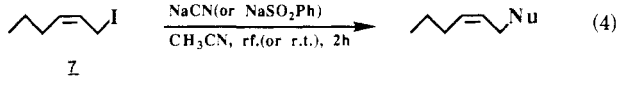
(14) (a) Patai, S., Ed. *The Chemistry of the Azide Group*; Interscience: New York, 1971; p 83. (b) Gagneux, A.; Winstein, S.; Young, W. G. *J. Am. Chem. Soc.* **1960**, *82*, 5956.

(15) After the reaction mixture was quenched with water, iodide was extracted with ether. Evaporation of ether gave almost pure iodide.[4]

(16) (a) Blatt, A. H., Ed. *Organic Syntheses*; Wiley: New York, 1956; Collect. Vol. I, p 46. (b) Wagner, R. B.; Zook, H. D. *Synthetic Organic Chemistry*; Wiley: New York, 1965; p 592.

ration of allylic sulfones under mild conditions. The reaction of **1a** with $Me_3SiCl/NaI/H_2O$ in acetonitrile, followed by sodium phenylsulfinate dihydrate at room temperature for 2 h gave regio- and stereoselectively (*E*)-2-hexenyl phenyl sulfone (**6a**) in 78% yield. For **1c** and **1d**, the reaction took place in a manner similar to cyanation to form **6a** and **6d**, respectively, in good yields. In general, allylic sulfones are prepared by the oxidation of the corresponding sulfides[17] or Pd(0)-catalyzed sulfonylation.[18]

In order to obtain information for the stereochemical outcome in the present substitution, (*Z*)-2-hexen-1-ol (**1b**) was subjected to cyanation. The treatment of **1b** with $Me_3SiCl/NaI/H_2O$, followed by NaCN, afforded a mixture of (*E*)- and (*Z*)-1-cyano-2-hexenes (**5a** and **5b**) in a ratio of 8:2. The *E*/*Z* ratio was found to depend on both the reaction time with $Me_3SiCl/NaI/H_2O$ and the content of water. For instance, when **1b** was treated with $Me_3SiCl/NaI/H_2O$ overnight at room temperature, only cyanide **6a** having the *E*-configuration was obtained. However, the same reaction on treatment with Me_3SiCl/NaI in the absence of water for 0.5 h gave a mixture of **5a** and **5b** (7:3).[19] Furthermore, the reaction of 1-iodo-2-hexene, consisting of *E*/*Z* = 7/3, with CN^- led to isomeric cyanides, **5a** and **5b**, whose ratio was almost the same as that of the original iodide. A normal S_N2 mechanism, therefore, may be involved in the cyanation step. Thus, (*Z*)-1-iodo-2-hexene (**7**), prepared independently, was subjected to the cyanation under the above-mentioned conditions to produce exclusively (*Z*)-1-cyano-2-hexene (**5b**) (91%) without formation of the corresponding *E* isomer **5a** (eq 4). The stereochemistry of



(4)

7

5b: Nu=CN(91%)
6b: Nu=SO_2Ph(89%)

the product **5b** strongly indicates that this nucleophilic substitution is of the S_N2 type, since the substitution takes place via a transition state having S_N1 or S_N2' character to produce partly *E* isomer **5a** through an allyl cationic intermediate. The substitution of **7** by $PhSO_2^-$ gave (*Z*)-2-hexenyl phenyl sulfone (**6b**) in 89% yield (eq 4).

In conclusion, the treatment of allylic alcohols with $Me_3SiCl/NaI/H_2O$, followed by N_3^-, CN^-, and $PhSO_2^-$, offers a convenient method for the preparation of allylic azides, cyanides, and phenyl sulfones, which are valuable starting materials in organic syntheses.

The same strategy will be useful for the preparation of a wide variety of allylic compounds. The extension and application of this method are now in progress in our laboratory.

Experimental Section

The structures of all compounds were supported by their IR (JASCO Model A-202 spectrometer), ^1H, and ^{13}C NMR (JEOL GSX-400 and Hitachi R-90H spectrometers in $CDCl_3$ using TMS as internal standard). VPC analysis was carried out Shimadzu GC-12A chromatograph employing a thermal conductivity detector and a 3 mm × 3 m stainless column packed with PEG-20M (5%) or Silicon OV-7 (5%) on Chromosorb W. Flash chromatography was performed on silica gel (eluent: hexane–ethyl acetate 8–9.5:2–0.5).

General Procedure for One-Pot Preparation of Allylic Compounds. Azidation. To an efficiently stirred solution of NaI (1.8 g, 12 mmol) in CH_3CN (15 mL) were slowly added Me_3SiCl (1.5 mL, 12 mmol) and then the appropriate allylic alcohol (10 mmol); the mixture was allowed to react at room temperature for 0.5 h. To the stirred mixture was added $AlCl_3$ (0.13 g, 1 mmol) and NaN_3 (1.95 g, 30 mmol). After the solution was stirred for 2 h, the reaction was quenched with water (10 mL) and the mixture extracted with ether (3 × 15 mL). The ether layer was washed with 10% $Na_2S_2O_3$ solution (15 mL) and dried over $MgSO_4$. After evaporation of the ether, products were isolated by column chromatography on silica gel by eluting successively with a mixed solvent of hexane and ethyl acetate (8–9.5:2–0.5).

Cyanation and Phenyl Sulfonylation. The cyanation and phenyl sulfonylation could be carried out in a manner similar to that of the azidation. Both substitutions were performed in the absence of catalyst.

Preparation of (*Z*)-1-Iodo-2-hexene (1). To a solution of (*Z*)-2-hexen-1-ol (**1b**) (0.5 g, 5 mmol) in CH_3CN (10 mL) were added pyridine (0.39 g, 5 mmol) and methanesulfonyl chloride (0.80 g, 7 mmol). The mixture was stirred at room temperature for 4 h and quenched with water (10 mL). The product was extracted with ether. The ether extracts were washed with 10% $Na_2S_2O_3$ solution (10 × 3 mL), dried over $MgSO_4$, filtered, and evaporated to give (*Z*)-2-hexenyl methanesulfonate. To a solution of the resulting (*Z*)-2-hexenyl methanesulfonate (0.36 g, 2 mmol) in CH_3CN (10 mL) was added NaI (0.90 g, 6 mmol); the mixture was stirred at room temperature for 1 h. The reaction mixture was treated as above to give almost pure (*Z*)-1-iodo-2-hexene (**7**) (59%).

General Procedure for Two-Step Preparation of Allylic Compounds. After the same treatment of **1a** with $Me_3SiCl/NaI/H_2O$ as above, the reaction was quenched with water (10 mL); the mixture was extracted with ether (3 × 30 mL). The ether extracts were washed with 10% $Na_2S_2O_3$ (3 × 30 mL) and dried over $MgSO_4$. Evaporation of ether gave almost pure iodide **4** (75%).

To a stirred solution of **4** (1.8 g, 8.3 mmol) in acetonitrile (15 mL) at room temperature was added an appropriate nucleophile (25 mmol) in the presence of $AlCl_3$ (0.1 equiv) (for only azidation). The mixture was allowed to react under refluxing (for cyanation) or room temperature (for phenyl sulfonylation). The isolation of the products was carried out in the same manner as above. The products were identified by ^{13}C NMR, ^1H NMR, and IR.

(*E*)-1-Azido-2-hexene (2a): IR (NaCl) 3310, 2900, 2100, 1670, 1240, 970 cm^{-1}; ^1H NMR ($CDCl_3$) 5.54 (dt, 1 H, *J* = 14.6 and 7.3 Hz), 5.50 (dt, 1 H, *J* = 14.6 and 7.3 Hz), 3.70 (d, 2 H, *J* = 7.3 Hz), 2.06 (q, 2 H), 1.43 (m, 2 H), 0.92 (t, 3 H); ^{13}C NMR ($CDCl_3$) 136.8 (d), 122.8 (d), 52.9 (t), 34.3 (t), 22.2 (t), 13.5 (q).

3-Azido-1-hexene (3a): IR (NaCl) 3310, 2900, 2100, 1670, 1240, 970 cm^{-1}; ^1H NMR ($CDCl_3$) 5.75 (dt, 1 H), 5.27 (d, 2 H), 3.81 (q, 1 H), 2.08 (q, 2 H), 1.50 (m, 2 H), 0.94 (t, 3 H); ^{13}C NMR ($CDCl_3$) 135.9 (d), 117.7 (t), 64.8 (d), 36.4 (t), 19.1 (t), 13.7 (q).

1-Azido-3-methyl-2-butene (2d): IR (NaCl) 3290, 2900, 2100, 1650, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) 5.34 (t, 1 H), 3.75 (d, 2 H), 1.81 (s, 3 H), 1.72 (s, 3 H); ^{13}C NMR ($CDCl_3$) 139.4 (s), 117.2 (d), 48.1 (t), 25.9 (q), 18.0 (q).

1-Azido-1,1-dimethyl-2-propene (3d): IR (NaCl) 3290, 2900, 2100, 1650, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) 5.86 (t, 1 H), 5.20 (d, 2 H), 1.34 (s, 6 H); ^{13}C NMR ($CDCl_3$) 136.1 (d), 120.1 (t), 37.6 (s), 26.0 (q), 23.2 (q).

1-Azido-3-phenyl-2-propene (2e): IR (NaCl) 3300, 2950, 2100, 1650, 1470, 1230, 970 cm^{-1}; ^1H NMR ($CDCl_3$) 7.25–7.42 (m, 5 H), 6.65 (d, 1 H, *J* = 15.6 Hz), 6.25 (dt, 1 H, *J* = 15.6 and 6.6 Hz), 3.94 (d, 2 H, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$) 135.8 (s), 134.3 (d), 128.5 (d), 128.0 (d), 126.5 (d), 122.3 (d), 52.9 (t).

1-Azido-2-cyclohexene (2f): IR (NaCl) 3030, 2930, 2100, 1650, 1500, 1260, 900; ^1H NMR ($CDCl_3$) 6.00 (dt, 1 H), 5.71 (dd, 1 H), 3.88 (q, 1 H), 1.89 (q, 2 H), 1.75 (m, 2 H), 1.62 (q, 2 H); ^{13}C NMR ($CDCl_3$) 132.6 (d), 124.6 (d), 55.9 (d), 28.7 (t), 24.8 (t), 19.2 (t).

(*E*)-1-Cyano-2-hexene (5a): IR (NaCl) 2900, 2250, 1450, 1700, 1380 cm^{-1}; ^1H NMR ($CDCl_3$) 5.75 (dt, 1 H, *J* = 14.6 and 7.3 Hz), 5.38 (dt, 1 H, *J* = 14.6 and 7.3 Hz), 3.08 (d, 2 H, *J* = 7.3 Hz), 2.03

(17) Cope, A.; Morrison, D. E.; Field, L. *J. Am. Chem. Soc.* **1950**, *72*, 59.

(18) (a) Inomata, K.; Yamamoto, T.; Kotake, H. *Chem. Lett.* **1981**, 1357. (b) Julia, M.; Nel, M.; Saussine, L. *J. Organomet. Chem.* **1979**, *181*, C17.

(19) Olah has reported that cinnamyl alcohol is converted by using TMS/NaI reagent into the corresponding iodide, but the stereochemistry of the reaction is not described: Olah, G. A.; Narang, S. C.; Balaram Gupta, B. G.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247.

(q, 2 H), 1.43 (m, 2 H), 0.93 (t, 3 H); ^{13}C NMR ($CDCl_3$) 136.0 (d), 117.2 (d), 116.9 (s), 34.2 (t), 22.0 (t), 20.4 (t), 13.6 (q).

(*Z*)-1-Cyano-2-hexene (5b): ^{1}H NMR ($CDCl_3$) 5.69 (dt, 1 H, J = 10.6 and 7.3 Hz), 5.40 (dt, 1 H, J = 10.6 and 7.0 Hz), 3.10 (d, 2 H, J = 7.0 Hz), 2.04 (q, 2 H), 1.42 (m, 2 H), 0.93 (t, 3 H); ^{13}C NMR ($CDCl_3$) 135.7 (d), 116.9 (d) 116.6 (s), 29.2 (t), 22.1 (t), 15.5 (t), 13.6 (q).

1-Cyano-3-methyl-2-butene (5d): IR (NaCl) 2950, 2250, 1670, 1450, 1380 cm^{-1}; ^{1}H NMR ($CDCl_3$) 5.16 (t, 1 H), 3.03 (d, 2 H), 1.76 (s, 3 H), 1.67 (s, 3 H); ^{13}C NMR ($CDCl_3$) 138.5 (s), 118.4 (s), 111.7 (d), 25.3 (t), 17.9 (q), 16.3 (q).

1-Cyano-3-phenyl-2-propene (5e): IR (NaCl) 3000, 2250, 1650, 1450, 1380 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.25–7.39 (m, 5 H), 6.74 (d, 1 H, J = 15.4 Hz), 6.06 (dt, 1 H, J = 15.4 and 6.6 Hz), 3.30 (d, 2 H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) 135.5 (s), 134.4 (d), 128.5 (d), 128.1 (d), 126.3 (d), 117.2 (s), 116.7 (d), 20.6 (t).

(*E*)-2-Hexenyl Phenyl Sulfone (6a): IR (NaCl) 2920, 1450, 1370, 1310, 1140, 1090, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.53–7.87 (m, 5 H), 5.51 (dt, 1 H, J = 14.6 and 7.3 Hz), 5.40 (dt, 1 H, J = 14.6 and 7.3 Hz) 3.75 (d, 2 H, J = 7.3 Hz), 1.97 (q, 2 H), 1.28 (m, 2 H), 0.81 (t, 3 H); ^{13}C NMR ($CDCl_3$) 141.4 (d), 138.3 (s), 133.4 (d), 128.8 (d), 128.3 (d), 115.9 (d), 60.1 (t), 34.5 (t), 21.8 (t), 13.5 (q).

(*Z*)-2-Hexenyl Phenyl Sulfone (6b): IR (NaCl) 2960, 1450, 1300, 1140, 1090, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.20–7.90 (m, 5 H), 5.62 (dt, 1 H, J = 9.1 and 7.3 Hz), 5.42 (dt, 1 H, J = 9.1 and 7.7 Hz), 3.85 (d, 2 H, J = 7.7 Hz), 1.71 (q, 2 H), 1.14 (m, 2 H), 0.74 (t, 3 H); ^{13}C NMR ($CDCl_3$) 139.2 (d), 138.7 (s), 133.5 (d), 128.9 (d), 128.4 (d), 115.2 (d), 55.2 (t), 29.2 (t), 22.0 (t), 13.5 (q).

3-Methyl-2-butenyl Phenyl Sulfone (6d): IR (NaCl) 2950, 1450, 1380, 1310, 1150, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.53–7.88 (m, 5 H), 5.19 (t, 1 H), 3.79 (d, 2 H), 1.71 (s, 3 H), 1.30 (s, 3 H); ^{13}C NMR ($CDCl_3$) 142.7 (s), 138.6 (s), 133.4 (d), 128.8 (d), 128.2 (d), 110.3 (d), 56.1 (t), 25.7 (q), 17.7 (q).

(*Z*)-1-Iodo-2-hexene (7): IR (NaCl) 2960, 1460, 1150, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) 5.75 (dt, 1 H, J = 10.7 and 7.4 Hz), 5.48 (dt, 1 H, J = 10.7 and 8.8 Hz), 3.92 (d, 2 H, J = 8.8 Hz), 2.06 (q, 2 H) 1.45 (m, 2 H), 0.94 (t, 3 H); ^{13}C NMR ($CDCl_3$) 134.4 (d), 126.6 (d), 28.8 (t), 21.9 (t), 13.8 (q), 0.6 (t).

Registry No. **1a**, 928-95-0; **1b**, 928-94-9; **1c**, 4798-44-1; **1d**, 556-82-1; **1e**, 4407-36-7; **1f**, 822-67-3; **2a**, 120990-08-1; **2d**, 72422-42-5; **2e**, 68340-12-5; **2f**, 16717-84-3; **3a**, 126216-29-3; **3d**, 84466-88-6; **4**, 115977-54-3; **5a**, 100596-91-6; **5b**, 80639-55-0; **5d**, 4786-23-6; **5e**, 20068-10-4; **6a**, 98830-70-7; **6b**, 126216-30-6; **6d**, 15874-80-3; **7**, 115977-55-4; hydrogen iodide, 10034-85-2; (*Z*)-2-hexenyl methanesulfonate, 95351-72-7.

Synthesis and Reactions of (*E*)-1,4-Bis(silyl)-Substituted Enynes

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(*E*)-1,4-Bis(silyl)- and (*E*)-1,4-bis(disilanyl)but-1-en-3-ynes have been synthesized by the reaction of ethynyl-substituted mono- and disilanes with a catalytic amount of chlorotris(triphenylphosphine)rhodium(I) at room temperature in high yields. Similar reaction of 1-hexyne gave 2-butyloct-1-en-3-yne, while phenylacetylene afforded a mixture of 2,4-diphenylbut-1-en-3-yne and 1,4-diphenylbut-1-en-3-yne in low yields. The reaction of (*E*)-1,4-bis(methyldiphenylsilyl)but-1-en-3-yne (**2a**) with 1 equiv of methyllithium followed by methyl iodide gave (*E*)-1-(methyldiphenylsilyl)pent-1-en-3-yne. Similar treatment of 1,4-bis(1-phenyltetramethyldisilanyl)but-1-en-3-yne with methyllithium followed by hydrolysis produced 1-(1-phenyltetramethyldisilanyl)but-1-en-3-yne. The reaction of **2a** with methanol in the presence of a catalytic amount of sodium methoxide afforded 1-(methyldiphenylsilyl)but-1-en-3-yne, which reacted with hydrosilanes in the presence of a platinum catalyst to give (*E*,*E*)-1,4-bis(silyl)buta-1,3-dienes.

Introduction

The C–H bond activation of 1-alkynes by a transition-metal catalyst constitutes one of the most important methods of preparing enynes, which can be used in synthetic routes to many complex compounds including natural products. Many papers that deal with the transition-metal-catalyzed dimerization of 1-alkynes leading to enynes have been reported to date.[1-7] Most of the papers, however, are concerned with head-to-tail dimerization.

The head-to-head couplings with high yields of the enynes were observed when 1-alkynes were heated in benzene in the presence of a catalytic amount of chlorotris(triphenylphosphine)rhodium(I).[2] These couplings, however, are restricted to the 1-alkynes bearing a 3-hydroxy group. Recently, we have discovered that treatment of ethynyl-substituted mono- and disilanes with a catalytic amount of tetrakis(triphenylphosphine)palladium(0) at 100 °C in a sealed glass tube affords (*E*)-enynes arising from head-to-head coupling, as a single regioisomer.[8] We have now found that chlorotris(triphenylphosphine)rhodium(I), a more effective catalyst than the palladium complex, gives head-to-head dimers at room temperature in high yields. Here we report the regio- and stereospecific synthesis of (*E*)-1,4-bis(silyl)- and (*E*)-1,4-bis(disilanyl)butenynes and some reactions of (*E*)-1,4-bis(methyldiphenylsilyl)butenyne obtained from dimerization of ethynylmethyldiphenylsilane.

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