

## Novel One-pot Synthesis of 1-Iodo-1-trimethylsilyl 1,3-Dienes

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Iodine was added to 3-(trimethylsilyl)allylic phosphonium ylide regioselectively to give 3-iodo-3-trimethylsilyl allylic phosphonium ylide, which reacted with carbonyl compounds to give 1-iodo-1-trimethylsilyl 1,3-dienes with high stereoselectivity in good yield.

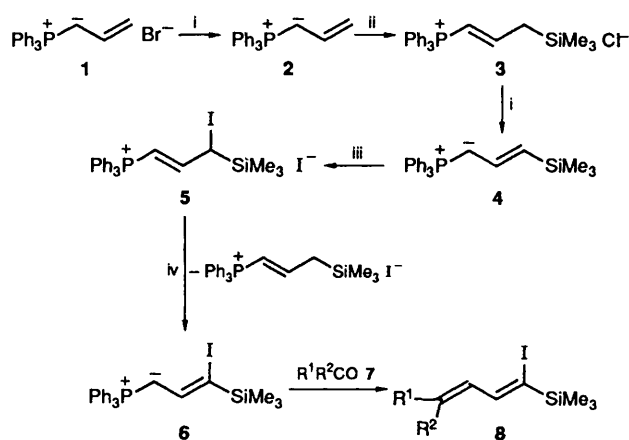
1,3-Dienes exist in a number of natural products such as leukotrienes and insect sex pheromones, and their synthesis is of current interest. Alkenyl iodides have been used as electrophiles in carbon-carbon bond-forming reactions, such as coupling with organometallic reagents catalysed by transition metals with high stereoselectivity,<sup>1</sup> and in the synthesis of trisubstituted alkenes.<sup>2</sup> Silylated alkenes<sup>3</sup> and 1,3-dienes<sup>4</sup> are also used widely in the synthesis of functionalised alkenes and 1,3-dienes, and are nucleophilic in nature. Therefore, either an iodo or a silyl group in the same molecule can be converted into other functional groups without interference from each other.<sup>5</sup> 1-Iodo-1-trimethylsilylalkenes have attracted some attention in organic synthesis.<sup>6</sup> However, the synthesis of a 1-iodo-1-trimethylsilyl 1,3-diene has not been reported previously.

The synthesis of vinyl iodides by a Wittig reaction is possible<sup>7</sup> but is sometimes limited because reactive Wittig reagents cannot be directly halogenated, and also because halogen-metal exchange often occurs when iodo-substituted phosphonium salts are treated with phenyl- or butyl-lithium.<sup>8</sup> It was recently reported that deprotonation has been accomplished in this situation by using sodium hexamethyldisilazide as a base.<sup>9</sup> Allylic phosphonium ylides react with carbonyl compounds at the 1-position<sup>10</sup> and with electrophiles such as  $\text{ClCO}_2\text{Me}$ ,<sup>11</sup>  $\text{Me}_3\text{SiCl}$ ,<sup>12</sup>  $\text{CF}_3\text{CO}_2\text{Et}$ <sup>13</sup> and  $\beta$ -keto  $\alpha,\beta$ -unsaturated esters<sup>14</sup> at the 3-position. When the substituent is bulky the reaction still occurs, but at the 1-position.<sup>15</sup> For example, the reaction of 3-(trimethylsilyl)allylidene(triphenyl)phosphorane with carbonyl compounds occurs at the 1-position.<sup>12</sup> Attempts to prepare 3-iodoallyl ylides *via* the addition of iodine to allylidene(triphenyl)phosphorane for the synthesis of a dienyl iodide failed. Since a silyl group is able to stabilise a carbanion, 3-silyl allylic ylides should be more stable, and could react with iodine to give a 3-iodo-3-trimethylsilyl allylic phosphonium ylide.

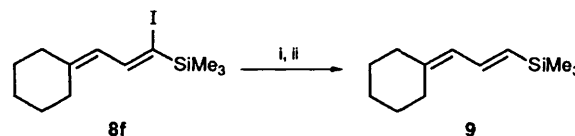
### Results and Discussion

Allylidene(triphenyl)phosphorane **2**, generated from the corresponding phosphonium bromide **1** and butyllithium, reacted with trimethylsilyl chloride. Deprotonation of the product **3** with another molecule of butyllithium gave 3-(trimethylsilyl)allylidene(triphenyl)phosphorane **4**. Iodine was added directly to 3-(trimethylsilyl)allylidene(triphenyl)phosphorane **4** at  $-78^\circ\text{C}$  to give the 3-iodopropenylphosphonium salt **5** regioselectively. Deprotonation of this product with another molecule of allylic phosphonium ylide **4** gave 3-iodo-3-(trimethylsilyl)allylidene(triphenyl)phosphorane **6**, which reacted with carbonyl compounds **7** to give 1-iodo-1-trimethylsilyl 1,3-dienes **8** in good yield and with high stereoselectivity (Scheme 1). In this case transylidation also occurred between phosphonium species **4** and **5** as reported in the literature.<sup>16</sup>

To identify the configuration of products **8**, an iodine/lithium exchange was performed. Compound **8f** was lithiated with butyllithium, followed by hydrolysis with dil. hydrochloric acid



Scheme 1 Reagents: i, BuLi; ii,  $\text{Me}_3\text{SiCl}$ ; iii,  $\text{I}_2$ ; iv, **4**



Scheme 2 Reagents and conditions: i, BuLi,  $-78^\circ\text{C}$ ; ii,  $\text{H}_3\text{O}^+$

Table 1 Preparation of 1-iodo-1-trimethylsilyl 1,3-dienes

<b>8</b>	$\text{R}^1$	$\text{R}^2$	Time (t/h)	Temp. ( $T/^\circ\text{C}$ )	Yield (%)	3E:3Z <sup>a</sup>
<b>a</b>	2,4- $\text{Cl}_2\text{C}_6\text{H}_3$	H	8	20	85	100:0
<b>b</b>	$n\text{-C}_6\text{H}_{13}$	H	8	20	71	78:22
<b>c</b>	$n\text{-C}_8\text{H}_{17}$	H	8	20	69	80:20
<b>d</b>	Me	Me	8	90	47	
<b>e</b>		$-\text{[CH}_2\text{]}_4-$	8	90	49	
<b>f</b>		$-\text{[CH}_2\text{]}_5-$	6	90	51	
<b>g</b>	Ph	Ph	10	90	54	
<b>h</b>	Ph	$n\text{-C}_3\text{F}_7$	8	90	64	28:72

<sup>a</sup> Estimated on the basis of NMR spectroscopy or GLC [FFAP capillary column (50 m  $\times$  0.3 mm) and oven temp.  $200^\circ\text{C}$ ].

to give the 1*E*-1,3-diene **9** (Scheme 2) exclusively as judged by its  $^1\text{H}$  NMR spectrum [ $\delta_{\text{H}}$  6.99 (1 H, dd,  $J$  18.2 and 10.6 Hz, 2-H), 5.97 (1 H, d,  $J$  10.6 Hz, 3-H) and 5.88 (1 H, d,  $J$  18.2 Hz, 1-H)]. It has been reported that iodine/lithium exchange occurs with retention of configuration.<sup>2</sup> Furthermore, a nuclear Overhauser enhancement (NOE) experiment on compound **8h** was performed, the NOE difference spectrum and NOESY spectrum showing that the trimethylsilyl group was *Z* with respect to 2-H. Therefore, the double bond in the 1-position in compounds **8** is in the *E* configuration.

Usually, allyl ylides show little stereoselectivity in Wittig reactions.<sup>15</sup> The good stereoselectivity of ylide **6** might be due to

anionic stabilisation by the trimethylsilyl group, making it a stabilised ylide.

Our results are shown in Table 1. All products were new and characterised by microanalyses, and IR, NMR and mass spectra. In this reaction, the aldehydes or ketones may be aliphatic or aromatic.

In conclusion, this one-pot synthesis of 1-iodo-1-trimethylsilyl 1,3-dienes is performed under mild conditions with convenient work-up in good yields and high stereoselectivity and should be useful in the synthesis of functionalised 1,3-dienes.

## Experimental

All b.p.s and m.p.s are uncorrected. IR spectra of all products were obtained on a Perkin-Elmer 683 spectrometer.  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Varian XL-200 (200 MHz) spectrometer with  $\text{SiMe}_4$  and  $\text{CF}_3\text{CO}_2\text{H}$  (positive for upfield shifts) as external reference, respectively.  $J$ -Values are given in Hz. Mass spectra were run on a Finnigan-4021 spectrometer.

**General Procedure for the Preparation of 1-Iodo-1-trimethyl 1,3-Dienes.**—In a general procedure butyllithium (4 mmol) was added dropwise to a stirred suspension of phosphonium salt **1** (4 mmol) and dry tetrahydrofuran (THF) at  $0^\circ\text{C}$  under nitrogen. The mixture was stirred for 0.5 h to give a solution of ylide **2**, which was cooled to  $-78^\circ\text{C}$ ,  $\text{Me}_3\text{SiCl}$  (4 mmol) was added slowly, and a lot of solid was deposited. The mixture was stirred for a further 40 min at from  $-78$  to  $0^\circ\text{C}$ , recooled to  $-78^\circ\text{C}$ , and treated dropwise with butyllithium (4 mmol). After the mixture had been stirred for 1 h at from  $-78$  to  $0^\circ\text{C}$ , trimethylsilyllalylidene(triphenyl)phosphorane **4** was formed. Then a solution of iodine (2 mmol) in THF ( $5\text{ cm}^3$ ) was added slowly to the reaction mixture at  $-78^\circ\text{C}$ , and the mixture was warmed to  $20^\circ\text{C}$  and stirred for 1 h, to give 3-iodo-3-(trimethylsilyl)allylidene(triphenyl)phosphorane **6**. An aldehyde or a ketone **7** (2 mmol) was added to the mixture, which was then stirred for several hours at a certain temperature (see Table 1), and diethyl ether ( $40\text{ cm}^3$ ) was then added. The organic layer was washed with water to neutrality, and dried ( $\text{Na}_2\text{SO}_4$ ). Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel and elution with light petroleum ( $60$ – $90^\circ\text{C}$ ) to afford the product **8**.

4-(2,4-Dichlorophenyl)-1-iodo-1-(trimethylsilyl)buta-1,3-diene **8a** had b.p.  $112^\circ\text{C}/0.5\text{ mmHg}$  (Found: C, 39.8; H, 3.8.  $\text{C}_{13}\text{H}_{15}\text{Cl}_2\text{ISi}$  requires C, 39.32; H, 3.81%);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1570, 1240 and 990;  $\delta_{\text{H}}(200\text{ MHz}; \text{CDCl}_3)$  0.25 (9 H, s,  $\text{SiMe}_3$ ), 6.92 (1 H, dd,  $J$  8.2 and 18.0, 3-H), 7.20–7.54 (4 H, m, 3 ArH and 4-H) and 7.57 (1 H, d,  $J$  8.2, 2-H);  $m/z$  396 ( $\text{M}^+$ , 18%), 269 ( $\text{M}^+ - \text{I}$ , 50) and 73 ( $\text{SiMe}_3^+$ , 100).

1-Iodo-1-(trimethylsilyl)deca-1,3-diene **8b** had b.p.  $90^\circ\text{C}/0.5\text{ mmHg}$  (Found: C, 46.8; H, 7.2.  $\text{C}_{13}\text{H}_{25}\text{ISi}$  requires C, 46.43; H, 7.49%);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1615, 1240 and 960;  $\delta_{\text{H}}(200\text{ MHz}; \text{CDCl}_3)$  0.25 (9 H, s,  $\text{SiMe}_3$ ), 0.97 (3 H, t,  $J$  7.0, Me), 1.37 (8 H, m,  $[\text{CH}_2]_4$ ), 1.94–2.44 (2 H, m, 5-H) and 5.54–7.04 (3 H, m, 2-, 3- and 4-H);  $m/z$  336 ( $\text{M}^+$ , 19%), 321 ( $\text{M}^+ - \text{CH}_3$ , 5), 209 ( $\text{M}^+ - \text{I}$ , 15) and 73 ( $\text{SiMe}_3^+$ , 100).

1-Iodo-1-(trimethylsilyl)dodeca-1,3-diene **8c** had b.p.  $100^\circ\text{C}/0.5\text{ mmHg}$  (Found: C, 48.9; H, 7.9.  $\text{C}_{15}\text{H}_{29}\text{ISi}$  requires C, 49.44; H, 8.02%);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1615, 1240 and 960;  $\delta_{\text{H}}(200\text{ MHz}; \text{CDCl}_3)$  0.25 (9 H, s,  $\text{SiMe}_3$ ), 0.98 (3 H, t,  $J$  7.0, Me), 1.33 (12 H, m,  $[\text{CH}_2]_6$ ), 2.00–2.40 (2 H, m, 5- $\text{H}_2$ ), 5.50–7.00 (3 H, m, 2-, 3- and 4-H);  $m/z$  364 ( $\text{M}^+$ , 22%), 349 ( $\text{M}^+ - \text{CH}_3$ , 2), 237 ( $\text{M}^+ - \text{I}$ , 11) and 73 ( $\text{SiMe}_3^+$ , 100).

1-Iodo-4-methyl-1-(trimethylsilyl)penta-1,3-diene **8d** had b.p.  $70^\circ\text{C}/0.5\text{ mmHg}$  (Found: C, 39.0; H, 6.1.  $\text{C}_9\text{H}_{17}\text{ISi}$  requires C, 38.58; H, 6.11%);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1620 and 1238;  $\delta_{\text{H}}(200\text{ MHz}; \text{CDCl}_3)$  0.23 (9 H, s,  $\text{SiMe}_3$ ), 1.82 (6 H, s,  $=\text{CMe}_2$ ), 6.14 (1 H, d,  $J$

10.0, 3-H) and 7.38 (1 H, d,  $J$  10.0, 2-H);  $m/z$  280 ( $\text{M}^+$ , 54%), 265 ( $\text{M}^+ - \text{CH}_3$ , 54), 153 ( $\text{M}^+ - \text{I}$ , 100) and 73 ( $\text{SiMe}_3^+$ , 55).

3-Cyclohexylidene-1-iodo-1-(trimethylsilyl)propene **8e** had b.p.  $80^\circ\text{C}/0.5\text{ mmHg}$  (Found: C, 43.6; H, 6.25.  $\text{C}_{11}\text{H}_{19}\text{ISi}$  requires C, 43.14; H, 6.25%);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1680, 1620 and 1240;  $\delta_{\text{H}}(200\text{ MHz}; \text{CDCl}_3)$  0.25 (9 H, s,  $\text{SiMe}_3$ ), 1.80 (4 H, m), 2.40 (4 H, m), 6.20 (1 H, d,  $J$  10.0, 3-H) and 6.77 (1 H, d,  $J$  10.0, 2-H);  $m/z$  306 ( $\text{M}^+$ , 57%), 291 ( $\text{M}^+ - \text{CH}_3$ , 41), 179 ( $\text{M}^+ - \text{I}$ , 100) and 73 ( $\text{SiMe}_3^+$ , 65).

3-Cyclohexylidene-1-iodo-1-(trimethylsilyl)propene **8f** had b.p.  $100^\circ\text{C}/0.5\text{ mmHg}$  (Found: C, 45.2; H, 6.8.  $\text{C}_{12}\text{H}_{21}\text{ISi}$  requires C, 45.00; H, 6.61%);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1679, 1610 and 1230;  $\delta_{\text{H}}(200\text{ MHz}; \text{CDCl}_3)$  0.25 (9 H, s,  $\text{SiMe}_3$ ), 1.53 (6 H, m), 5.90 (1 H, d,  $J$  10.0, 3-H), 2.17 (4 H, m) and 6.75 (1 H, d,  $J$  10.0, 2-H);  $m/z$  320 ( $\text{M}^+$ , 1%), 193 ( $\text{M}^+ - \text{I}$ , 1) and 73 ( $\text{SiMe}_3^+$ , 100).

1-Iodo-4,4-diphenyl-1-(trimethylsilyl)buta-1,3-diene **8g** had m.p.  $119$ – $120^\circ\text{C}$  (Found: C, 56.5; H, 5.4.  $\text{C}_{19}\text{H}_{21}\text{ISi}$  requires C, 56.44; H, 5.23%);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1240 and 860;  $\delta_{\text{H}}(200\text{ MHz}; \text{CDCl}_3)$  0.23 (9 H, s,  $\text{SiMe}_3$ ), 6.60–7.00 (2 H, m, 2- and 3-H) and 7.10–7.53 (10 H, m);  $m/z$  404 ( $\text{M}^+$ , 13%), 389 ( $\text{M}^+ - \text{CH}_3$ , 2), 227 ( $\text{M}^+ - \text{I}$ , 16) and 73 ( $\text{SiMe}_3^+$ , 100).

5,5,6,6,7,7-Heptafluoro-1-iodo-4-phenyl-1-(trimethylsilyl)-hepta-1,3-diene **8h** had b.p.  $108^\circ\text{C}/0.5\text{ mmHg}$  (Found: C, 38.9; H, 3.2.  $\text{C}_{16}\text{H}_{16}\text{F}_7\text{ISi}$  requires C, 38.72; H, 3.25%);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1330, 1210 and 970;  $\delta_{\text{H}}(200\text{ MHz}; \text{CDCl}_3)$  0.26 (9 H, s,  $\text{SiMe}_3$ ), 6.40 [1.20 H, d,  $J$  10.0, 2-H (1Z, 3E)], 6.70 [0.72 H, d,  $J$  10.0, 2-H (1Z, 3Z)] and 6.90–7.50 (6 H, m, ArH and 3-H);  $\delta_{\text{F}}$  3.3 (3 F, m), 28.0 [0.56 F, s, (1Z, 3E)], 33.3 [1.44 F, 2, (1Z, 3Z)] and 47.3 (2 F, m);  $m/z$  496 ( $\text{M}^+$ , 15%), 481 ( $\text{M}^+ - \text{CH}_3$ , 2), 369 ( $\text{M}^+ - \text{I}$ , 3), 277 ( $\text{M}^+ - \text{F} - \text{ISiMe}_3$ , 83) and 73 ( $\text{SiMe}_3$ , 100).

**Preparation of 3-Cyclohexylidene-1-(trimethylsilyl)propene 9.**—Butyllithium (1 mmol) was added dropwise to a stirred solution of 3-cyclohexylidene-1-iodo-1-(trimethylsilyl)propene **8f** (0.32 g, 1 mmol) in dry THF ( $4\text{ cm}^3$ ) at  $-78^\circ\text{C}$  under nitrogen. The reaction solution was stirred for 0.5 h at  $-78^\circ\text{C}$  and was then hydrolysed with  $2\text{ mol dm}^{-3}$  HCl (2 drops), and diethyl ether ( $20\text{ cm}^3$ ) was added. The organic layer was washed with water to neutrality and dried ( $\text{Na}_2\text{SO}_4$ ). Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel and elution with light petroleum ( $60$ – $90^\circ\text{C}$ ) to afford the title product **9** in 93% yield, b.p.  $68^\circ\text{C}/0.5\text{ mmHg}$ ;  $\delta_{\text{H}}$  6.99 (1 H, dd,  $J$  18.2 and 10.6, 2-H), 5.97 (1 H, d,  $J$  10.6, 3-H), 5.88 (1 H, d,  $J$  18.2, 1-H), 1.02–2.60 (10 H, m) and 0.25 (9 H, s,  $\text{SiMe}_3$ ).

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