

## Bis-Silyloxydienes from Diketones

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Functionalized 1,3-dienes are useful intermediates in synthesis. Oxy-functionalized dienes are a potential means of introducing carbonyl functions by cycloaddition, e.g. by the Diels–Alder reaction. In a recent paper<sup>1</sup> we described an efficient procedure for the synthesis of silyl dienol ethers from vinylic ketones. The method is to treat the carbonyl compound with lithium bromide and chlorotrimethylsilane in dry tetrahydrofuran followed by the addition of triethylamine. In this paper we show that the method can be applied to the synthesis of bis-silyloxy dienes from 1,2- and 1,3-diketones. The following substrates have been studied: 2,3-butanedione (**1a**), 2,3-pentanedione (**2a**), 3-methyl-1,2-cyclopentanedione (**3a**), 2,4-pentanedione (**4a**), 2-acetylcyclohexanone (**5a**), 1-phenyl-1,3-butanedione (**6a**), and 1,3-cyclohexanedione (**7a**).

## Methods and results

The experimental procedure was as given in Ref. 1. The reactions were monitored by capillary GLC. Yields obtained in preparative-scale runs (ca. 50 mmol) are given in Table 1.

Table 1. Products and yields obtained.

Starting ketone	Products <sup>a</sup>	Yield <sup>b</sup> %
<b>1a</b>	<b>1b</b>	84
<b>2a</b>	<b>2b</b>	93
<b>3a</b>	<b>3b</b>	93
<b>4a</b>	<b>4b</b>	93
<b>5a</b>	<b>5b, 5c</b>	93
<b>6a</b>	<b>6b</b>	94
<b>7a</b>	<b>7b</b>	62 <sup>c</sup>

<sup>a</sup>For the identification of products, see Fig. 1. <sup>b</sup>Yields refer to isolated, distilled products. <sup>c</sup>Quantitative yield by GLC. The product could not be isolated by aqueous work-up owing to extremely rapid hydrolysis. See the Experimental for non-aqueous work-up.

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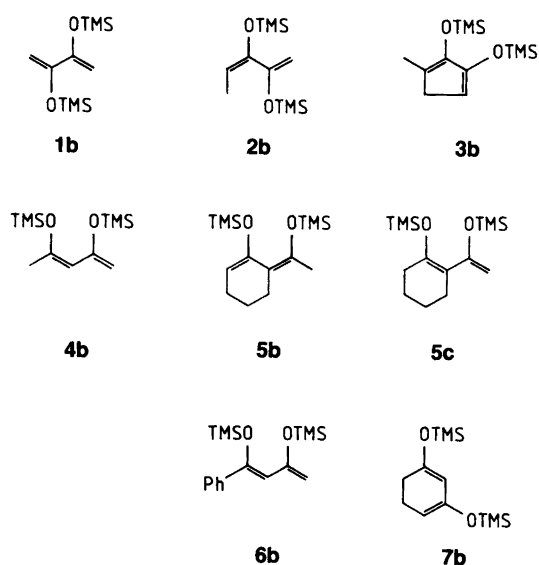


Fig. 1. Bis-silyloxy dienes prepared. For **2b** only one stereoisomer was observed; we were not able to determine whether it was *E* or *Z*. The products **4b** and **6b** showed the following *E/Z* ratios: **4b** (50:50), **6b** (95:5). The product from **5a** was an 80:20 mixture of the regioisomers **5b** and **5c**. Stereoisomers of **5b** were not determined.

## Discussion

The procedure described in this paper gives improved yields compared with previously described methods. The synthesis of 2,3-bis(trimethylsilyloxy)butadiene (**1b**) illustrates this: a two-step synthesis from dimethyl succinate via an acyloin condensation to 1,2-bis(trimethylsilyloxy)cyclobutene and thermal ring opening afforded a 64% yield.<sup>2</sup> Direct silylation of **1a** by trimethylsilyl triflate<sup>3</sup> afforded a 69% yield, and a similar procedure with trimethylsilyl triflate generated *in situ*<sup>4</sup> afforded 64%. Silylation of **1a** with chlorotrimethylsilane under basic conditions ( $\text{NaN}[\text{SiMe}_3]_2$ ) afforded only a 20% yield.<sup>5</sup>

Syntheses of **4b–7b** by treatment of the parent ketones with chlorotrimethylsilane and sodium bromide in acetonitrile have been described.<sup>6</sup> The yields reported for **4b** and **7b** by this procedure are similar to our results. The yields of **5b** and **6b** are improved by our method. In view of this, we

conclude that the method described in this paper is superior to those previously described.

## Experimental

**General techniques.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AC 80 spectrometer. Mass spectra were obtained using an HP GC/MSD 5830/5970 system. A Carlo-Erba Fractovap 4160 equipped with an FID was used to obtain high-resolution GLC. A capillary column, SE 54 25 m, 0.30 mm i.d. was used.

**Chemicals.** Tetrahydrofuran (THF) was distilled from sodium-benzophenone. Triethylamine was dried over potassium hydroxide and then percolated with a positive pressure of dry argon through a column of basic alumina (grade 1). Chlorotrimethylsilane was distilled under argon from calcium hydride. Lithium bromide was stored over phosphorus pentoxide in an argon-flushed desiccator. Starting diketones (Janssen) were distilled when necessary to obtain a purity of >98%.

**Synthesis of 2,3-bis(trimethylsilyloxy)butadiene.** Dry lithium bromide (17.37 g, 200 mmol) was placed in an oven-dried 250 ml Erlenmeyer flask containing a Teflon-coated magnetic stirring bar. The flask was heated to ca. 400°C with an electric heat gun. The flask was then sealed with a rubber septum while still hot and was allowed to cool under a stream of dry argon. Dry THF (60 ml) was then added to the flask by needle transfer directly from the solvent still. The mixture was stirred to dissolve all the lithium salt and then cooled to -15°C in an ice-salt bath, then successively treated with chlorotrimethylsilane (16.30 g, 150 mmol), 2,3-butadione (**1a**) (4.30 g, 50 mmol) and triethylamine (15.18 g, 150 mmol). The additions were made by needle transfer. The contents of the flask were stirred at -15°C for 1 h and then placed in an oil bath at 40°C where the reaction was allowed to proceed for 48 h. The mixture was then diluted with 100 ml of cold (0°C) pentane and poured into a 500 ml separatory funnel charged with 50 ml of saturated sodium chloride solution, 50 ml of saturated sodium hydrogen carbonate solution, 50 g of crushed ice, and an additional 50 ml of pentane. It was essential that all extractions and washings were carried out at low temperature and without delay. After the contents of the funnel had been shaken the aqueous layer was extracted with 2×100 ml of cold pentane. The combined pentane extracts were washed with cold brine (50 ml) and cold water (2×50 ml) and dried ( $\text{MgSO}_4$ ). The volatile compounds were evaporated under reduced pressure. The residual pale yellow oil was distilled, b.p. 84–86°C/8 mmHg, to yield **1b** as a colourless liquid (9.67 g, 84%).

The other compounds were prepared analogously.

**Non-aqueous work-up of product (7b).** The entire reaction mixture was evaporated to remove the solvent and excess reagents. The residue was triturated with hexane with cool-

ing to precipitate salts and then filtered. The filtrate was evaporated and the residue triturated with dry ether. Filtration, removal of solvent and distillation under reduced pressure afforded 7.94 g (62%) of **7b**, b.p. 104–106°C/7 mmHg (lit.,<sup>7</sup> 95–97°C/2 mmHg).

**Physical properties of compounds.** NMR spectra were recorded in  $\text{CDCl}_3$ . Mass spectra were taken at 70 eV and are reported as  $m/z$  (relative intensity/%) [assignment]. Reported boiling points refer to Kugelrohr temperature.

**2,3-Bis(trimethylsilyloxy)-1,3-butadiene (1b).** B.p. 84–86°C/8 mmHg (lit., 77–79°C/10 mmHg,<sup>2a</sup> 78–79°C/13–14 mmHg,<sup>4</sup> 74°C/12 mmHg, 83°C/25 mmHg).<sup>5</sup>  $^1\text{H}$  NMR:  $\delta$  4.82 (s, 2H), 4.32 (s, 2H), 0.21 (s, 18H) [Ref. 2(a), 3, 5].  $^{13}\text{C}$  NMR:  $\delta$  152.9, 92.7, -0.17 (Ref. 5). MS: 230 (31) [ $M^+$ ], 147 (35), 133 (18), 73 (100), 45 (45).

**2,3-Bis(trimethylsilyloxy)-1,3-pentadiene (2b).** B.p. 98–100°C/10 mmHg.  $^1\text{H}$  NMR:  $\delta$  5.38 (q, 1H,  $J$  7.1 Hz), 4.63 (s, 1H), 4.25 (s, 1H), 1.62 (t, 3H,  $J$  7.1 Hz), 0.22 (s, 18H).  $^{13}\text{C}$  NMR:  $\delta$  153.6, 147.0, 105.5, 91.7, 11.3, 0.48, -0.12. MS: 244 (26) [ $M^+$ ], 229 (24), 147 (85), 73 (100), 45 (52).

**1-Methyl-2,3-bis(trimethylsilyloxy)-1,3-cyclopentadiene (3b).** B.p. 62–65°C/0.1 mmHg.  $^1\text{H}$  NMR 4.85 (t, 1H,  $J$  2.1 Hz), 2.47 (d, 2H,  $J$  2.1 Hz), 1.70 (s, 3H), 0.13 (s, 9H), 0.08 (s, 9H).  $^{13}\text{C}$  NMR:  $\delta$  152.6, 146.5, 117.6, 99.9, 35.6, 12.9, 1.5, 0.7. MS: 256 (49) [ $M^+$ ], 167 (18), 147 (16), 73 (100), 45 (38).

**2,4-Bis(trimethylsilyloxy)-1,3-pentadiene (4b).** B.p. 100–102°C/9 mmHg (lit.,<sup>6</sup> 78°C/0.5 mmHg).  $^1\text{H}$  NMR:  $\delta$  *E*-isomer: 5.18 (s, 1H), 4.12 (s, 1H), 4.06 (s, 1H);  $\delta$  *Z*-isomer: 4.75 (d, 1H,  $J$  0.7 Hz), 4.68 (s, 1H), 4.29 (d, 1H,  $J$  0.7 Hz);  $\delta$  *E*+*Z* isomers, not assigned: 1.99 (s, 3H), 1.82 (s, 3H), 0.25 (s, 9H), 0.22 (s, 9H), 0.19 (s, 9H), 0.18 (s, 9H) (Ref. 6). MS 244 (7) [ $M^+$ ], 229 (70), 147 (62), 73 (100), 45 (61).

**1-Trimethylsilyloxy-6-(1-trimethylsilyloxyethylidene)-1-cyclohexene (5b).** B.p. 102–104°C/9 mmHg (lit.,<sup>6</sup> 102°C/0.5 mmHg).  $^1\text{H}$  NMR:  $\delta$  4.85 (t, 1H,  $J$  3.9 Hz), 1.5–2.4 (m, 9H), 0.18 (s, 18H) (Ref. 6). MS 284 (31) [ $M^+$ ], 269 (62), 147 (34), 73 (100), 45 (41).

**1-Trimethylsilyloxy-2-(1-trimethylsilyloxyvinyl)-1-cyclohexene (5c).** B.p. see **5b**;  $^1\text{H}$  NMR:  $\delta$  4.50 (s, 1H), 4.36 (s, 1H), 1.5–2.4 (m, 8H), 0.18 (s, 18H) (Ref. 6); MS: 284 (26) [ $M^+$ ], 269 (92), 147 (48), 73 (100), 45 (41).

**1-Phenyl-1,3-bis(trimethylsilyloxy)-1,3-butadiene (6b).** B.p. 96–99°C/0.07 mmHg (lit.,<sup>6</sup> 124°C/0.5 mmHg).  $^1\text{H}$  NMR:  $\delta$  *E*-isomer: 7.3–7.6 (m, 5H), 5.59 (d, 1H,  $J$  1.3 Hz), 5.04 (s, 1H), 4.58 (d, 1H,  $J$  1.3 Hz), 0.34 (s, 9H), 0.22 (s, 9H) (Ref. 6);  $\delta$  *Z*-isomer: 7.3–7.6 (m, 5H), 5.70 (s, 1H), 4.29

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(s, 1 H), 4.24 (s, 1 H), 0.10 (s, 9 H), 0.01 (s, 9 H) (Ref. 6). MS: 306 (40) [ $M^+$ ], 305 (100), 147 (18), 73 (94), 45 (38).

*1,3-Bis(trimethylsilyloxy)-1,3-cyclohexadiene (7b)*.  $^1\text{H}$  NMR:  $\delta$  4.9 (d, 1 H,  $J$  1.5 Hz), 4.55 (dt, 1 H,  $J$  1.5 Hz, 3.9 Hz), 2.05–2.40 (m, 4 H), 0.22 (s, 9 H), 0.18 (s, 9 H) (Ref. 6). MS: 256 (45) [ $M^+$ ], 255 (30), 147 (13), 73 (100), 45 (49).

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