

## 2-Dimethylaminomethyl-3-trimethylsilylmethylbuta-1,3-diene as a Synthetic Equivalent of 2,2'-Biallyl Zwitterionic Species

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The title compound reacts with nucleophiles followed by electrophiles in tandem or in the reverse order smoothly to give 1,2-dimethylenecyclohexanes and their oxa analogues; thus this reagent acts as the synthetic equivalent of 2,2'-biallyl zwitterionic species.

We have previously reported that 2-dimethylaminomethyl-3-trimethylsilylmethylbuta-1,3-diene (**1**), readily prepared by the Grignard cross-coupling reaction of 2-bromoallyl-trimethylsilane and 2-bromoallyldimethylamine, is an excellent synthetic equivalent of the 2,2'-biallyl diradical which is hard to prepare by other routes.<sup>1</sup> During our studies on the synthetic applications of this reagent, we have now found that the reagent (**1**) is useful for the introduction of both nucleophiles and electrophiles into the 2,2'-biallyl skeleton, thus acting formally as the synthetic equivalent of the zwitterion (**2**) of 2,2'-biallyl.<sup>2</sup>

Reagent (**1**) includes an allylic silane unit which acts as the nucleophilic part<sup>3</sup> and an allylic amine which would form an electrophilic unit after quaternization with an alkyl halide.<sup>4</sup> Therefore we studied the reaction of (**1**) with both nucleophilic and electrophilic reagents stepwise by two methods.

First, (**1**) was treated with methyl iodide to give the corresponding ammonium salt (**3**) in almost quantitative yield. The isolated (**3**) reacted with a variety of nucleophiles (**4**) such as lithium enolates and sodium derivatives of active methylene compounds in the presence of a catalytic amount of tetrakis-(triphenylphosphine)palladium(0)<sup>5</sup> to afford the corresponding substitution products (**5**) regioselectively in good yield. †

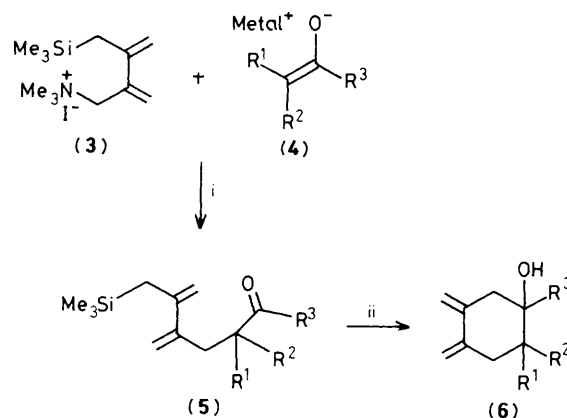
The allylation products (**5**) thus obtained were conveniently annulated with an aid of a catalytic amount of tetra-n-butylammonium fluoride (TBAF)<sup>6</sup> to give 3,4-dimethylenecyclohexanols (**6**) (Scheme 1). The results are summarized in Table 1. This method provides a convenient and interesting route to vicinal exocyclic methylenecyclohexane derivatives which are hard to get by other methods.

The inverse route involving (**2**) (Scheme 2) leads to 3,4-dimethylenetetrahydropyrans (**10**) in good yield.

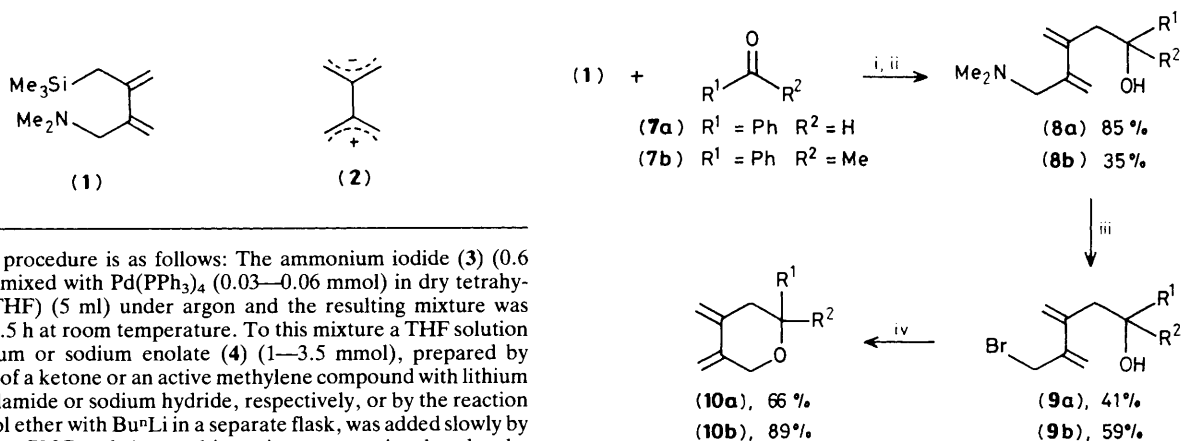
1,2-Dimethylenecyclohexanes (**6**) and their oxa analogues (**10**) are expedient reagents for cycloaddition reactions owing

to their *s-cis* structure as reported previously,<sup>1</sup> and (**6d**) reacts with dimethyl fumarate to give the tricyclic compound (**11**) stereospecifically under mild condition (benzene, 40 °C, 10 h) in excellent yield (Scheme 3).

Thus, (**1**) is an important reagent for tandem annulations to prepare polycyclic compounds which are useful precursors for the synthesis of a variety of naturally occurring compounds, and antibiotic, and antitumour agents.



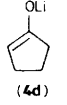
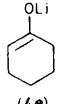
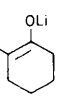
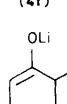
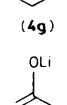
Scheme 1. Reagents: i, Pd(PPh<sub>3</sub>)<sub>4</sub>, THF; ii, TBAF, THF.



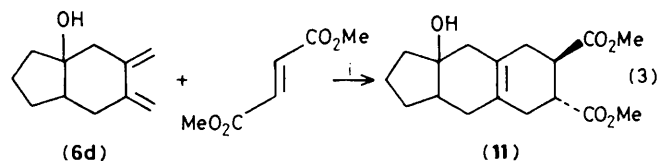
Scheme 2. Reagents: i, TBAF, THF, 40 °C, 5–15 h; ii, 0.01 M NaOH–MeOH, room temp., 1 day; iii, 1 M BrCN, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C–room temp., 12 h; iv, NaH, THF, room temp., 1 day.

† A typical procedure is as follows: The ammonium iodide (**3**) (0.6 mmol) was mixed with Pd(PPh<sub>3</sub>)<sub>4</sub> (0.03–0.06 mmol) in dry tetrahydrofuran (THF) (5 ml) under argon and the resulting mixture was stirred for 0.5 h at room temperature. To this mixture a THF solution of the lithium or sodium enolate (**4**) (1–3.5 mmol), prepared by metallation of a ketone or an active methylene compound with lithium di-isopropylamide or sodium hydride, respectively, or by the reaction of a silyl enol ether with Bu<sup>n</sup>Li in a separate flask, was added slowly by a syringe at –78 °C and the resulting mixture was stirred under the conditions in footnote b of Table 1. After hydrolysis, the organic layer was separated. Ether extraction, washing with brine, drying (Na<sub>2</sub>SO<sub>4</sub>), and evaporation, followed by preparative t.l.c. on silica gel gave the product.

**Table 1.** Conversions of (3) into (5) and (6).<sup>a</sup>

Nucleophile (4)	Product			% Yield	
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	(5) <sup>b</sup>	(6) <sup>c</sup>
NaCH(CO <sub>2</sub> Et) <sub>2</sub> (4a)	H	CO <sub>2</sub> Et	OEt	71(25) <sup>d</sup>	— <sup>e</sup>
NaCHCO <sub>2</sub> Et   COPh (4b)	H	CO <sub>2</sub> Et	Ph	68(9) <sup>d</sup>	63
NaCHCO <sub>2</sub> Me   COMe (4c)	H	CO <sub>2</sub> Me	Me	85(13) <sup>d</sup>	52
 (4d)	H	—[CH <sub>2</sub> ] <sub>3</sub> —		68	84
 (4e)	H	—[CH <sub>2</sub> ] <sub>4</sub> —		79(8) <sup>d</sup>	81
 (4f)	Me	—[CH <sub>2</sub> ] <sub>4</sub> —		74	— <sup>e</sup>
 (4g)	H	—[CH <sub>2</sub> ] <sub>3</sub> CHMe—		70	— <sup>e</sup>
 (4h)	H	H	Ph	34(29) <sup>d</sup>	— <sup>e</sup>

<sup>a</sup> Products were isolated by t.l.c. and all new compounds gave satisfactory spectral data and elemental analysis. <sup>b</sup> Conditions: (3) (0.6 mmol), (4) (1.0–3.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (5–10 mol %), THF, room temp.–reflux, 2–4 h for sodium derivatives (4a–c); –78 °C room temp., 12–15 h for lithium derivatives (4d–h). <sup>c</sup> Conditions: TBAF (15 mol %), THF, 50 °C, 20 h. <sup>d</sup> The yield of the product of bisallylation at the active methylene site is shown in parentheses. <sup>e</sup> The reaction was not conducted.

**Scheme 3.** Conditions: i, Benzene, 50 °C, 10 h, 84%.

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