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-bromoallyltrimethylsilane and 2-bromoallyldimethylamine, is an excellent synthetic equivalent of the 2,2′-biallyl diradical which is hard to prepare by other routes.[1] 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.[2]

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

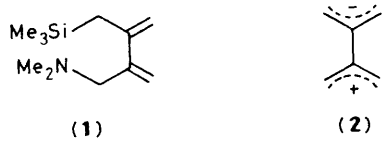
First, (**1**) was treated with methyl iodide to give the corresponding ammonium salt (**3**) in almost quantitative yield. The isolated (**3**) reacted with a variety of nucleophiles (**4**) such as lithium enolates and sodium derivatives of active methylene compounds in the presence of a catalytic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

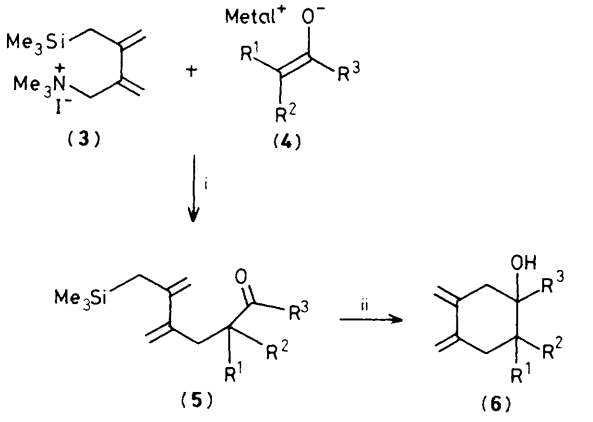
The allylation products (**5**) thus obtained were conveniently annulated with an aid of a catalytic amount of tetra-n-butylammonium fluoride (TBAF)[6] to give 3,4-dimethylenecyclohexanols (**6**) (Scheme 1). The results are summarized in Table 1. This method provides a convenient and interesting route 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.

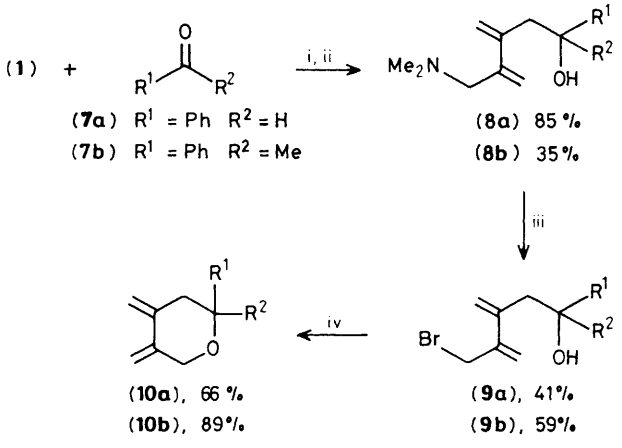
1,2-Dimethylenecyclohexanes (**6**) and their oxa analogues (**10**) are expedient reagents for cycloaddition reactions owing to their s-*cis* structure as reported previously,[1] and (**6d**) reacts with dimethyl fumarate to give the tricyclic compound (**11**) stereospecifically under mild condition (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, $Pd(PPh_3)_4$, THF; ii, TBAF, THF.



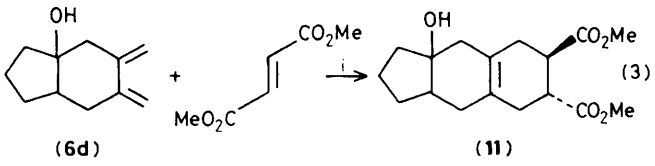
Scheme 2. *Reagents:* i, TBAF, THF, 40 °C, 5—15 h; ii, 0.01 M NaOH–MeOH, room temp., 1 day; iii, 1 M BrCN, CH_2Cl_2, 0 °C—room temp., 12 h; iv, NaH, THF, room temp., 1 day.

† A typical procedure is as follows: The ammonium iodide (**3**) (0.6 mmol) was mixed with $Pd(PPh_3)_4$ (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^nLi 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_2SO_4), and evaporation, followed by preparative t.l.c. on silica gel gave the product.

Table 1. Conversions of (**3**) into (**5**) and (**6**).[a]

Nucleophile (**4**)	Product R[1]	R[2]	R[3]	% Yield (**5**)[b]	(**6**)[c]
$NaCH(CO_2Et)_2$ (**4a**)	H	CO_2Et	OEt	71(25)[d]	—[e]
$NaCHCO_2Et$ COPh (**4b**)	H	CO_2Et	Ph	68(9)[d]	63
$NaCHCO_2Me$ COMe (**4c**)	H	CO_2Me	Me	85(13)[d]	52
OLi (**4d**)	H	$-[CH_2]_3-$		68	84
OLi (**4e**)	H	$-[CH_2]_4-$		79(8)[d]	81
Me, OLi (**4f**)	Me	$-[CH_2]_4-$		74	—[e]
OLi, Me (**4g**)	H	$-[CH_2]_3CHMe-$		70	—[e]
OLi, Ph (**4h**)	H	H	Ph	34(29)[d]	—[e]

[a] Products were isolated by t.l.c. and all new compounds gave satisfactory spectral data and elemental analysis. [b] Conditions: (**3**) (0.6 mmol), (**4**) (1.0—3.5 mmol), $Pd(PPh_3)_4$ (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**). [c] Conditions: TBAF (15 mol %), THF, 50 °C, 20 h. [d] The yield of the product of bisallylation at the active methylene site is shown in parentheses. [e] The reaction was not conducted.



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

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