A New Preparation of Methylenecyclopropanes Utilizing Trimethylsilyldiazomethane[†]

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Abstract: Reactions of aliphatic ketones with lithium trimethylsilyl-diazomethane in the presence of excess olefins afforded methylenecyclopropanes in moderate to good yields. The multiplicity of the alkylidene carbene intermediate in the reacting state has been revealed to be a singlet. © 1999 Elsevier Science Ltd. All rights reserved.

Alkylidene carbenes are attractive intermediates for organic synthesis.[1] We have already revealed that the reaction of lithium trimethylsilyldiazomethane (TMSC(Li)N$_2$) with carbonyl compounds proceeds smoothly to generate alkylidene carbenes[2] which undergo various types of reactions to give the homologous alkynes,[2a] aldehydes,[2b] and heterocycles such as 1,2-dihydrofurans,[2c] cyclohepta[b]pyrrol-2-ones,[2d] 3-pyrrolines,[2e] 2-pyrrolines[2f] depending upon substrates used. Our continued interest in the use of TMSC(Li)N$_2$ as an alkylidene carbene generator in organic synthesis led us to investigate the reactions of TMSC(Li)N$_2$ with aliphatic ketones and excess olefins. The multiplicity of alkylidene carbenes was also investigated.

We have found that aliphatic ketones react smoothly with TMSC(Li)N$_2$ in the presence of excess olefins to give the methylenecyclopropanes,[3] via the alkylidene carbene intermediate, as shown in Scheme 1.
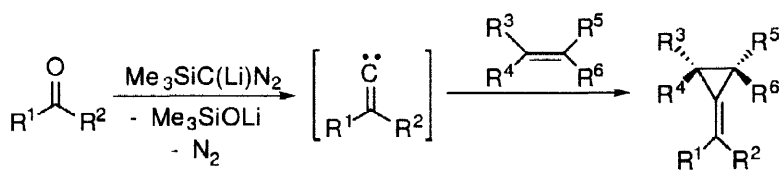
Scheme 1

[†] Dedicated with respect and deep appreciation to the memory of the late Sir Derek Barton whose sudden death is really a great loss to organic chemistry.

Preliminary experiments using 1,3-diphenylacetone (1a) and cyclohexene (2a) have revealed that (1) 1,2-dimethoxyethane (DME) seems to be a solvent of choice, (2) the preferred quantity of cyclohexene (2a) is 15 equivalents, and (3) the reaction carried out at -50 °C for 1 h and then at room temperature for 1 h proceeds most effectively. The results using the preferred reaction conditions are summarized in Tables 1 and 2. In Table 1, the results of the reaction using 1,3-diphenylacetone (1a) and various olefins (2) are shown. 1,3-Diphenylacetone (1a) and cyclohexene (2a) were converted smoothly into the corresponding methylenecyclopropane (3a) in 69% yield (entry 1). 1,5-Cyclohexadiene (2b) afforded the mono cycloaddition product (entry 2). The olefin bearing an allylic alkoxy group gave a complex mixture so that the desired product was obtained in low yield (entry 3). The olefins bearing directly attached alkoxy groups showed high reactivity to give the cycloaddition products in good yields (entries 4 and 5) while di and trisubstituted olefins were less reactive than monosubstituted ones (entries 6-9). In Table 2, various aliphatic

Table 1. Reaction of TMSC(Li)N$_2$ with 1,3-Diphenylacetone (1a) and Olefins (2).

Entry	Compd. No.	R^1,R^3,R^2,R^4	Product	Yield (%)[a]	Entry	Compd. No.	R^1,R^3,R^2,R^4	Product	Yield (%)[a]
1	2a	(cyclohexene)	3a	69	6	2f	n-Bu	3f	41
2	2b	(cyclooctene)	3b	52	7	2g	Ph	3g	50
3	2c	OMe	3c	29[b]	8	2h	Ph, Ph	3h	26
4	2d	EtO	3d	67	9	2i	Me, Me, Me	3i	35
5	2e	EtO, EtO	3e	62					

a) Isolated yield.   b) The ratio of exo/endo was not determined.

ketones including acyclic and cyclic ones (1) and 2a reacted to give the cycloaddition product in moderate to good yields. The reactivity of alkylidene carbenes seems to be quite dependent on the steric factor.[4] In the case of competitive reactions, 1,5-C-H insertion reaction[5a] and 1,2-rearrangement[5b] occurred preferentially.

Next we investigated the multiplicity of alkylidene carbene intermediates. Gilbert et al. had already reported that the alkylidene carbene derived from acetone and diethyl (diazomethyl)phosphonate (DAMP) reacted with cis-4-methyl-2-pentene to give the only cis adduct, but with trans-4-methyl-2-pentene to give the 5.9:1 mixture of trans and cis isomers.[6] They speculated that these results were due to the relative rate of cycloaddition reaction of cis- and trans-disubstituted alkenes with alkylidene carbenes since the trans alkene was contaminated with its cis isomer, and they concluded the reaction was stereoselective. Thus the stereochemistry of the additon of the alkylidene carbene derived from 1,3-diphenylacetone and TMSC(Li)N$_2$ was

Table 2. Reaction of TMSC(Li)N$_2$ with Aliphatic ketones (**1**) and Cyclohexene (**2a**).

Entry	Compd. No.	R^{1}COR^2	Product	Yield (%)[a]	Entry	Compd. No.	R^{1}COR^2	Product	Yield (%)[a]
1	**1b**		3ba	63	5	**1f**		3fa	54
2	**1c**		3ca	46	6	**1g**		3ga	57
3	**1d**		3da	52					
4	**1e**		3ea	63	7	**1h**	PhCH$_2$–N	3ha	63

a) Isolated yield.

investigated using *cis*- and *trans*-β-methylstyrenes,[7] as shown in Scheme 2. The reaction of 1,3-diphenylacetone with TMSC(Li)N$_2$ in the presence of *cis*-β-methylstyrene (**2j**) gave the only cis product (**3j**) in 47% yield. The trans isomer was not detected by ^{1}H NMR analysis. On the other hand, the cycloaddition reaction with *trans*-β-methylstyrene (**2k**) afforded 40% of methylenecyclopropanes, and very small amounts of cis isomer were found. The ratio of trans and cis isomers was determined to be 97.7:2.3 by ^{1}H NMR analysis. These results support Gilbert's speculation. *trans*-β-Methylstyrene seems to be more reactive than *trans*-4-methy-2-pentene due to less steric hindrance. Thus we believe that the multiplicity of alkylidene carbenes in the reacting state is in a singlet electronic state.
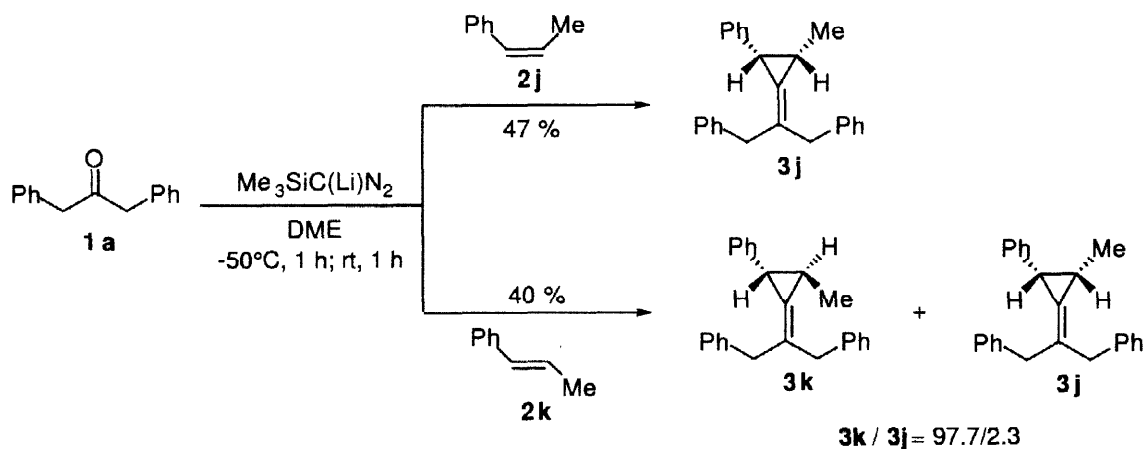
Scheme 2

In conclusion, the present method using commercially available TMSCHN$_2$ will provide a convenient and efficient preparation of methylenecyclopropanes from aliphatic ketones and olefins. The multiplicity of alkylidene carbene in the reacting state is determined to be a singlet.

Experimental

General.

Melting points were determined on a YANAGIMOTO micro melting point apparatus. Infrared (IR) spectra were measured on a SHIMADZU FTIR-8100 spectrometer. Nuclear magnetic resonance (NMR) spectra were measured on a EX-270 or GSX-400 spectrometer in deuterio solvent using tetramethylsilane or CHCl$_3$ as an internal standard. Mass spectra were obtained on a JEOL LMS-DX 300 spectrometer. Analytical TLC was performed on a silica gel plate (Merck Art. 5715). Column chromatography was carried out on silica gel BW-820 MH or BW 200 (purchased from Fuji Davison Co.). 1,2-Dimethoxyethane (DME) was dried by distillation from benzophenone ketyl.

Preparation of Methylenecyclopropanes (3) General Procedure: n-Butyllithium (1.59 M in hexane solution, 0.6 mmol) was added dropwise to a solution of TMSCHN$_2$[8] (1.75 M in hexane solution, 0.6 mmol) in DME (2 ml) at -50 °C under argon, and then stirred for 30 min. A solution of ketone (1) (0.5 mmol) and olefin (2) (7.5 mmol) in DME (1 ml) was added dropwise at -50 °C. The mixture was stirred at -50 °C for 1 h, and then at room temperature for 1 h. After being quenched with cold water, the mixture was extracted with hexane. The organic extracts were dried over MgSO$_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (BW-820 MH) to give methylenecyclopropane (3).

2-(7′-Bicyclo[4.1.0]heptylidene)-1,3-diphenylpropane (3a) Prepared from **1a** (105 mg, 0.5 mmol) and **2a** (616 mg, 7.5 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 15 g, hexane) to give **3a** (99 mg, 69%) as a colorless oil. The product (**3a**) solidified in a freezer; m.p. 35-37 °C (hexane); IR v_{max}^{neat} cm^{-1} 3061, 3027, 2973, 2926, 1603, 1493, 1453, 1329, 1076, 1030, 749; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.18-1.30 (4H, m), 1.45-1.60 (4H, m), 1.65-1.80 (2H, m), 3.38 (4H, s), 7.13-7.70 (10H, m); Anal. calcd for C$_{22}$H$_{24}$: C, 91.61; H, 8.39. Found: C, 91.58; H, 8.44.

2-(9′-Bicyclo[6.1.0]non-4′-enylidene)-1,3-diphenylpropane (3b) Prepared from **1a** (105 mg, 0.5 mmol) and **2b** (811 mg, 7.5 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 40 g, hexane → hexane:Et$_2$O=50:1) to give **3b** (81 mg, 52%) as a colorless oil; IR v_{max}^{neat} cm^{-1} 3061, 3027, 2928, 1601, 1495, 1455, 1076, 1030,749; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.39-1.69 (4H, m), 1.86-2.11 (4H, m), 2.24-2.34 (2H, m), 3.35 (4H, s), 5.60-5.72 (2H, m), 7.12-7.33 (10H, m); High-resolution MS calcd for C$_{24}$H$_{26}$: 314.2034. Found: 314.2026.

2-(2′-Methoxy-7′-bicyclo[4.1.0]heptylidene)-1,3-diphenylpropane (3c) Prepared from **1a** (105 mg, 0.5 mmol) and **2c** (840 mg, 7.5 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 40 g, hexane → hexane:Et$_2$O=50:1), and then by preparative thin layer chromatography (Merck Art 5717, hexane: Et$_2$O=30:1) to give **3c** (46 mg, 29%) as a pale yellow oil; IR v_{max}^{neat} cm^{-1} 3085, 3061, 3027, 2973, 2932, 1601, 1495, 1453, 1092, 750; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.02-1.18 (1H, m), 1.25-1.40 (2H, m), 1.43-1.60 (2H, m), 1.67-1.73 (3H, m), 3.20-3.24 (1H, m), 3.30 (3H, s), 3.40 (4H, s), 7.12-7.33 (10H, m); Anal. calcd for C$_{23}$H$_{26}$O · 1/3H$_2$O: C, 85.14; H,8.28. Found: C, 85.34; H, 8.19.

2-(1′-Ethoxycyclopropylidene)-1,3-diphenylpropane (3d) Prepared from **1a** (105 mg, 0.5

mmol) and 2d (541 mg, 7.5 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 15 g, hexane:Et$_2$O=50:1) to give 3d (93 mg, 67%) as a yellow oil; IR v_{max}^{neat} cm^{-1} 3085, 3061, 3029, 2975, 1603, 1495, 1455, 1331, 1152, 1103, 1048, 1030, 752; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.16-1.29 (2H, m), 1.22 (3H, t, J=6.9 Hz), 3.39 (2H, ABq, J=14.5 Hz), 3.49 (2H, s), 3.59 (2H, q, J=7.3 Hz), 3.75 (1H, d, J=3.3 Hz), 7.10-7.31 (10H, m); High-resolution MS calcd for C$_{20}$H$_{22}$O: 278.1671. Found: 278.1669.

2-(1′,1′-Diethoxycyclopropylidene)-1,3-diphenylpropane (3e)   Prepared from 1a (105 mg, 0.5 mmol) and 2e[9] (871 mg, 7.5 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 20 g, hexane:Et$_2$O=50:1) to give 3e (99 mg, 62%) as a colorless oil; IR v_{max}^{neat} cm^{-1} 3085, 3061, 3029, 2977, 2928, 1765, 1603, 1495, 1455, 1181, 1115, 1049, 749; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.24 (6H, t, J=7.1 Hz), 1.48 (2H, s), 3.34 (2H, s), 3.54 (2H, s), 3.69-3.81 (4H, m), 7.08-7.32 (10H, m); High-resolution MS calcd for C$_{22}$H$_{26}$O$_2$: 322.1933. Found: 322.1938.

2-(1′-n-Butylcyclopropylidene)-1,3-diphenylpropane (3f)   Prepared from 1a (105 mg, 0.5 mmol) and 2f (631 mg, 7.5 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 15 g, hexane) to give 3f (60 mg, 41%) as a colorless oil; IR v_{max}^{neat} cm^{-1} 3085, 3063, 3029, 2959, 2924, 1603, 1495, 1455, 1076, 1030, 752; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 0.67-0.75 (1H, m), 0.88 (3H, t, J=6.9 Hz), 1.12-1.25 (2H, m), 1.34-1.40 (4H, m), 1.43-1.57 (2H, m), 3.36 (2H, s), 3.39 (2H, s), 7.11-7.30 (10H, m); Anal. calcd for C$_{22}$H$_{26}$: C, 90.98; H, 9.02. Found: C,90.81; H,9.08.

2-(1′-Phenylcyclopropylidene)-1,3-diphenylpropane (3g)   Prepared from 1a (105 mg, 0.5 mmol) and 2g (781 mg, 7.5 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 35 g, hexane → hexane:Et$_2$O=50:1) to give 3g (77 mg, 50%) as a colorless oil; IR v_{max}^{neat} cm^{-1} 3085, 3061, 3027, 2967, 2913, 1603, 1493, 1453, 1433, 1075, 1030, 752; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.22 (1H, dd, J=4.5, 8.1 Hz), 1.72 (1H, t, J=8.4 Hz), 2.63 (1H, dd, J=4.5, 8.4 Hz), 3.35 (2H, s), 3.47 (2H, ABq, J=14.4 Hz), 6.99-7.33 (15H, m); High-resolution MS calcd for C$_{24}$H$_{22}$: 310.1721. Found: 310.1722.

2-(1′,1′-Diphenylcyclopropylidene)-1,3-diphenylpropane (3h)   Prepared from 1a (105 mg, 0.5 mmol) and 2h (1.352 g, 7.5 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 40 g, hexane → hexane:Et$_2$O=50:1) to give 3h (51 mg, 26%) as a yellow viscous oil; IR v_{max}^{neat} cm^{-1} 3085, 3063, 3029, 2959, 2924, 1603, 1495, 1455, 750; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.90 (2H, s), 3.40 (2H, s), 3.61 (2H, s), 6.86-6.90 (2H, m), 7.12-7.32 (18H, m); High-resolution MS calcd for C$_{30}$H$_{26}$: 386.2034. Found: 386.2036.

2-(1′,1′,2′-Trimethylcyclopropylidene)-1,3-diphenylpropane (3i)   Prepared from 1a (105 mg, 0.5 mmol) and 2i (526 mg, 7.5 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 10 g, hexane) to give 3i (48 mg, 35%) as a colorless oil; IR v_{max}^{neat} cm^{-1} 3085, 3063, 3029, 2924, 1603, 1495, 1455, 1076, 1030, 750; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.01 (3H, d, J=5.9 Hz), 1.04 (3H, s), 1.13 (3H, s), 1.10-1.20 (1H, m), 3.30 (4H, s), 7.12-7.30 (10H, m); High-resolution MS calcd for C$_{21}$H$_{24}$: 276.1878. Found: 276.1870.

2-(7'-Bicyclo[4.1.0.]heptylidene)-4-phenylbutane (3ba) Prepared from **1b** (74 mg, 0.5 mmol) and **2a** (616 mg, 7.5 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 20 g, hexane) to give **3ba** (72 mg, 63%) as a colorless oil; IR v_{max}^{neat} cm^{-1} 3087, 3063, 3027, 2969, 2928, 1605, 1497, 1449, 1371, 1329, 1030, 745; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.07-1.26 (4H, m), 1.40-1.50 (2H, m), 1.57-1.73 (4H, m), 1.83 (3H, s), 2.43 (2H, t, J=8.1 Hz), 2.80 (2H, t, J=8.1 Hz), 7.14-7.30 (5H, m). Anal. calcd for C$_{17}$H$_{22}$: C, 90.20; H, 9.80. Found: C, 90.16; H, 9.87.

3-(7'-Bicyclo[4.1.0.]heptylidene)pentane (3ca) Prepared from **1c** (86 mg, 1 mmol) and **2a** (1.232 g, 15 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 15 g, hexane) to give **3ca** (75 mg, 46%) as a colorless oil; IR v_{max}^{neat} cm^{-1} 2965, 2930, 1460, 1449, 1372, 845; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.05 (6H, t, J=7.6 Hz), 1.14-1.26 (4H, m), 1.42-1.52 (2H, m), 1.60-1.85 (4H, m), 2.16 (4H, q, J=7.5 Hz). The spectral data of **3ca** was identical with those reported.[10]

7'-Bicyclo[4.1.0.]heptylidenecyclopentane (3da) Prepared from **1d** (84 mg, 1 mmol) and **2a** (1.232 g, 15 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 15 g, hexane) to give **3da** (84 mg, 52%) as a colorless oil; IR v_{max}^{neat} cm^{-1} 2928, 1449; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.18 (4H, p, J=3.2 Hz), 1.45-1.53 (2H, m), 1.64-1.74 (8H, m), 2.20-2.40 (4H, m); High-resolution MS calcd for C$_{12}$H$_{18}$: 162.1409. Found: 162.1423.

7'-Bicyclo[4.1.0.]heptylidenecyclohexane (3ea) Prepared from **1e** (98 mg, 1 mmol) and **2a** (1.232 g, 15 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 20 g, hexane) to give **3ea** (111 mg, 63%) as a colorless oil; IR v_{max}^{neat} cm^{-1} 2975, 2928, 1447, 1237, 1161, 1096; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.21-1.24 (4H, m), 1.43-1.62 (8H, m), 1.68-1.80 (4H, m), 2.13-2.31 (4H, m). The spectral data of **3ea** was identical with those reported.[10]

7'-Bicyclo[4.1.0.]heptylidenecycloheptane (3fa) Prepared from **1f** (112 mg, 1 mmol) and **2a** (1.232 g, 15 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 15 g, hexane) to give **3fa** (103 mg, 54%) as a colorless oil; IR v_{max}^{neat} cm^{-1} 2971, 2924, 1449, 857, 839; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.15-1.25 (4H, m), 1.43-1.79 (14H, m), 2.17-2.44 (4H, m); High-resolution MS calcd for C$_{14}$H$_{22}$: 190.1721. Found: 190.1728.

4-(7'-Bicyclo[4.1.0.]heptylidene)cyclohexanone ethylene acetal (3ga)   Prepared from **1g** (156 mg, 1 mmol) and **2a** (1.232 g, 15 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 15 g, hexane:Et$_2$O=50:1 → 30:1) to give **3ga** (134 mg, 57%) as a colorless oil; IR v_{max}^{neat} cm^{-1} 2926, 1447, 1358, 1119, 1092, 1034, 943, 914; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.18-1.25 (4H, m), 1.50-1.60 (2H, m), 1.67-1.80 (8H, m), 2.31-2.44 (4H, m), 3.98 (4H, s); High-resolution MS calcd for C$_{15}$H$_{22}$O$_2$: 234.1620. Found: 234.1622.

4-(7'-Bicyclo[4.1.0.]heptylidene)-1-benzylpiperizine (3ha)   Prepared from **1h** (95 mg, 0.5 mmol) and **2a** (616 mg, 7.5 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 20 g, hexane:Et$_2$O=20:1) to give **3ha** (84 mg, 63%) as a colorless oil; IR v_{max}^{neat} cm^{-1} 3063, 3027, 2928, 1495, 1464, 1361, 1341, 1130,737; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.21-1.22 (4H, m), 1.50-1.56 (2H,

m), 1.66-1.77 (4H, m), 2.35-2.60 (8H, m), 3.53 (2H, s), 7.23-7.36 (5H, m); High-resolution MS calcd for $C_{19}H_{25}N$: 267.1987. Found: 267.1989.

2-(cis-1'-Methyl-2'-phenylcyclopropylidene)-1,3-diphenylpropane (3j)   Prepared from **1a** (105 mg, 0.5 mmol) and **2j** (886 mg, 7.5 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 35 g, hexane → hexane:Et2O=80:1) to give **3j** (76 mg, 47%) as a colorless oil. The *trans* isomer (**3k**) was not detected by ^1H NMR analysis; IR v_{max}^{neat} cm^{-1} 3083, 3061, 3027, 2923, 1601, 1495, 1453, 1088, 1075, 1030,749; ^1H NMR (CDCl3, 270 MHz) δ 0.79 (3H, d, J=6.4 Hz), 1.87-1.93 (1H, m), 2.86 (1H, d, J=9.1 Hz), 3.44 (2H, ABq, J=14.5 Hz), 3.47 (2H, ABq, J=14.8 Hz), 7.12-7.32 (15H, m); ^{13}C NMR (CDCl3) δ 11.3 (CH3), 18.4 (CH), 24.7 (CH), 40.1 (CH2), 40.5 (CH2), 125.7 (CH), 125.9 (CH), 126.0 (CH), 127.8 (CHx2), 128.0 (C), 128.2 (CHx2), 128.3 (CHx2), 128.9 (CHx2), 129.1 (CHx2), 129.2 (CHx2), 129.5 (C), 138.1 (C), 139.9 (C), 140.0 (C) ; High-resolution MS calcd for $C_{25}H_{24}$: 324.1878. Found: 324.1872.

2-($trans$-1'-Methyl-2'-phenylcyclopropylidene)-1,3-diphenylpropane (3k)   Prepared from **1a** (105 mg, 0.5 mmol) and **2k** (886 mg, 7.5 mmol). The residue was purified by column chromatography on silica gel (BW-820 MH, 35 g, hexane → hexane:Et2O=80:1) to give **3k** (66 mg, 40%) as a colorless oil. The *cis* isomer (**3j**) was detected and the ratio of **3k/3j** was determined to be 97.7/2.3 by ^1H NMR analysis. The product (**3k**) solidified in a freezer; m.p. 56-58 ℃ (hexane); IR v_{max}^{neat} cm^{-1} 3085, 3061, 3027, 2924, 1603, 1495, 1453, 1088, 1075, 1044, 1030,749; ^1H NMR (CDCl3, 270 MHz) δ 1.15 (3H, d, J=5.9 Hz), 1.45-1.59 (1H, m), 2.18 (1H, d, J=3.3 Hz), 3.34 (2H, s), 3.45 (2H, s), 7.00-7.34 (15 H, m); ^{13}C NMR (CDCl3) δ 17.8 (CH3), 23.9 (CH), 28.5 (CH), 40.1 (CH2), 40.5 (CH2), 125.3 (CH), 125.8 (CH), 126.0 (CHx3), 128.1 (CHx2), 128.18 (CHx2), 128.25 (CHx2), 128.9 (C), 129.0 (CHx2), 129.2 (CHx2), 131.3 (C), 139.8 (C), 140.0 (C), 142.7 (C) ; High-resolution MS calcd for $C_{25}H_{24}$: 324.1878. Found: 324.1881.

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3. The preparation of methylenecyclopropanes from ketones and olefins had already been reported with respect to the study of the intermediate using diethyl (diazomethyl)phosphonate: Gilbert, J.C.; Weerasooriya, U.; Giamalva, D. *Tetrahedron Lett.* **1979**, *49*, 4619.

4. The reaction of t-butylmethylketone or diisopropylketone with TMSC(Li)N2 in the presence of

cyclohexene gave no desired product.

5. (a) The reaction of 1-phenyl-7-octen-3-one (11) with TMSC(Li)N$_2$ gave the 1,5-C-H insertion product (4), 1-phenethyl-3-vinylcyclopentene.
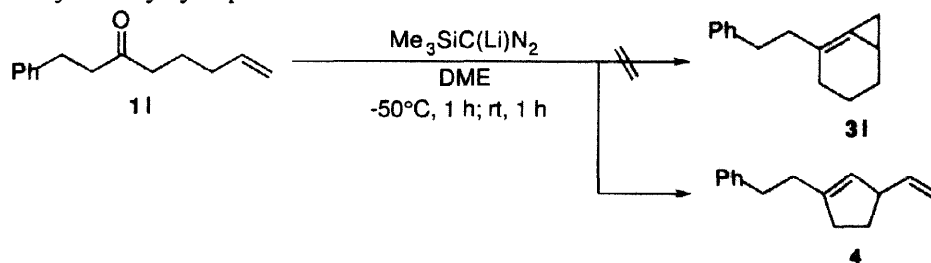
For the example of intramolecular [2+2] cycloaddition reaction, see: Köbrich, G.; Baumann, M. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 52. For the example of 1,5-C-H insertion reaction using TMSC(Li)N$_2$, see: Ohira, S.; Okai, K.; Moritani, T. *J. Chem. Soc., Chem. Commun.* **1992**, 721.

(b) The reaction of acetophenone (1m) with TMSC(Li)N$_2$ in the presence of cyclohexene gave the 1,2-rearrangement product (5), 1-phenyl-1-propyne, see ref. 2a.
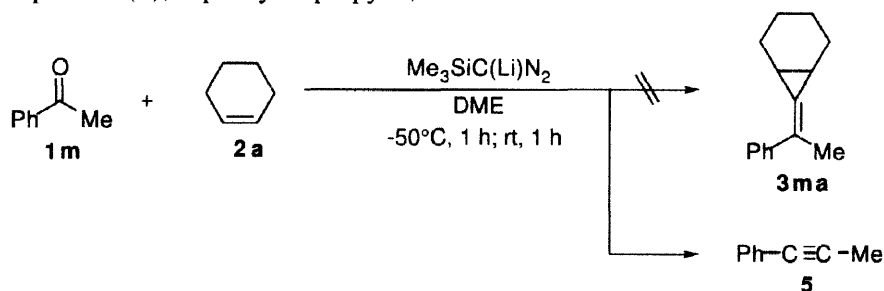
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7. ^{1}H NMR analysis showed the purity of *cis-* and *trans*-β-methylstyrene was respectively >98.9%, and each olefin contained its isomer.

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