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Cyclopropylidene Dianion Equivalent. Preparation of 1,1-Dilithio-2,2-diphenylcyclopropane

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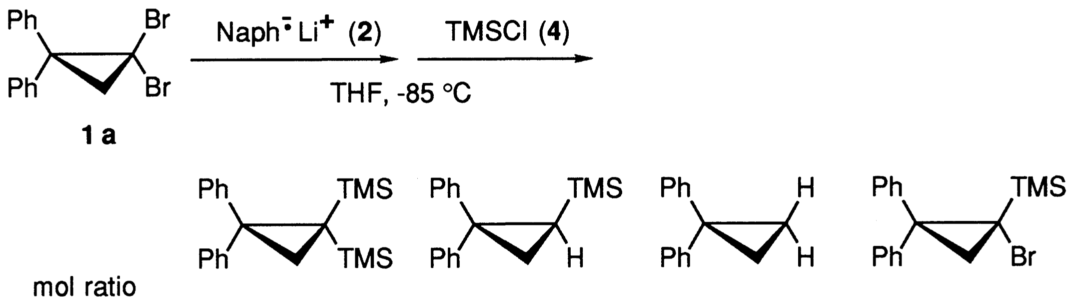
The title compound was prepared by the treatment of the corresponding 1,1-dibromocyclopropane with lithium naphthalene radical anion (Li-$C_{10}H_8$). Trapping of the dilithio compound by chlorotrimethylsilane provided evidence for its highly basic profile which can compete with silylation.

While the electrophilic nature of singlet carbenes, in general, has been disclosed in various reactions with nucleophiles, their electron accepting profile has scarcely appeared in literatures. In access to negatively double-charged carbene-type molecules, reports have gradually appeared where *gem*-dilithio-compounds were prepared by means of halogen-metal exchange or proton-abstraction reaction using alkyllithium reagents.[1] These compounds possessed more or less stabilizing groups such as carbonyl, cyano, sulfonyl,[2] nitro,[3] phenyl,[2,4] or alkylidene group[5] directly attached to the anionic center, whereas dilithio-compounds without stabilizing groups have suffered from difficulty in preparation. Recently, in place of using alkyllithium as the reagent, electron-transfer-type reductants have appeared effective for the purpose.[6]

On the basis of our preliminary study on the reduction of gem-dibromocyclopropanes[7] and somewhat sp^2-hybridized character of cyclopropane C-H bonds, we expected that cyclopropylidene dianion without directly-bound stabilizing groups could be generated. In this regard we would like to report here a novel generation of 1,1-dilithio-2,2-diphenylcyclopropane (**3a,** Scheme 1) from the corresponding dibromocyclopropane (**1a**) via its carbenoid by use of lithium naphthalene radical anion (Li-$C_{10}H_8$, **2**) as the electron source. The results unequivocally demonstrated the electron accepting ability of 1-bromo-1-lithio-2,2-diphenylcyclopropane (carbenoid).

To a deoxygenated dry THF solution of **2** (titrated,[8] 3.5-4.0 equiv. mol to **1a**) at -85 °C was added a THF solution of 1,1-dibromo-2,2-diphenylcyclopropane (**1a**, 0.28 mmol) over 1 min. At the end of addition, a deep-green color of the reductant **2** disappeared to give a light brown solution indicating that **2** was not present anymore. Immediately, to the decolorized solution was added chlorotrimethylsilane (**4**, 2.0 mmol) and products were determined and characterized by ^{1}H NMR and GLPC in comparison with independently prepared authentic compounds. Three products **5a**, **6a**, and **7a** were obtained but none of unreacted dibromide **1a** and bromo(trimethylsilyl)cyclopropane **8a** were detected (Eq. 1).[9] The low total yield (43%) of products **5a**, **6a**, and **7a** was due to the formation of a complex mixture of cyclopropanated dihydronaphthalenes which is a disadvantage of this type of reductant **2** generally encountered in the reduction of organic halides.

The formation of both disilylated and monosilylated cyclopropane (**5a** and **6a**, respectively), to the most extent, can be rationally explained in terms of silylation of dilithiocyclopropane intermediate (**3a**), the dianion equivalent (Scheme 1). A possible incorporation of metal/halogen exchange reaction between bromo(lithio)cyclopropane **10a** and bromo(silyl)cyclopropane (**8a**), which might produce lithio(silyl)-cyclopropane (**11a**) followed by second silylation or protonation to give **5a** or **6a** (Scheme 1, *route b*), was ruled out by the negative outcome of an independent reaction between **10a** and **8a**. Therefore, most of **5a** arose apparently from the direct trapping of **3a** with chlorosilane **4** (*route a*).

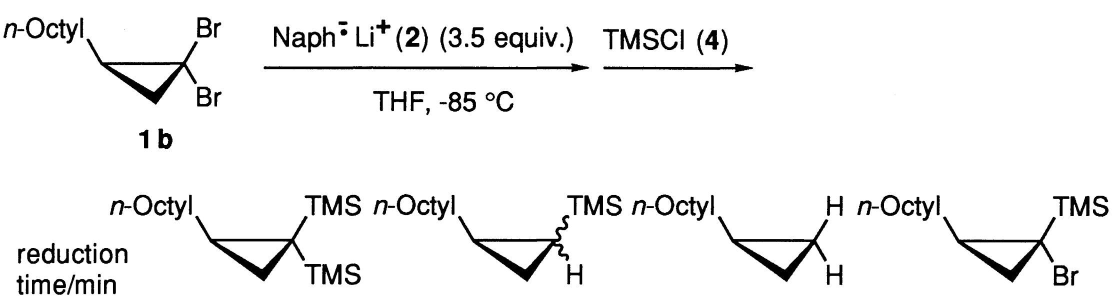


(1)

mol ratio 2 / 1a	5a	6a	7a	8a
3.5	8.3%	25%	3.6%	0%
4.0	9.3%	28%	6.0%	0%

Silylcyclopropane **6a** was formed by the silylation of anion intermediate **9a** which arose from **3a** after single protonation. 1,1-Diphenylcyclopropane (**7a**) was formed mainly from **3a** by double protonation with the solvent (THF) or naphthalene[10] and this was verified by the formation of **7a**-d_2 (1.5%) in the reaction carried out in THF-d_8.[11]

Attempts at reductive dilithiation of 1,1-dibromo-2-octylcyclopropane (**1b**) to generate its 1,1-dilithio derivative **3b**, however, gave different results. Similar treatment of **1b** with **2** (3.5 equiv., titrated) at -85 °C did not show the decoloration of the reductant solution even 40 min after the addition, indicating that some amount of **2** still remained. To this reaction mixture was added chlorosilane **4** and the product mixture was analyzed by ^{1}H NMR and GLPC in comparison with the authentic compounds. It turned out that disilylcyclopropane (**5b**) was not formed and, instead, 1-octylcyclopropane (**7b**, 1.9%), silylcyclopropane (**6b**, 5.7%), and bromo(silyl)-cyclopropane (**8b**, 31%) were produced (Eq. 2).[12] Essentially the same results were obtained when the reaction was quenched with **4** after the reduction for 1.5 min. Again, the low product yield (total 39%) was due to the same reason described for **1a** (*vide ante*).

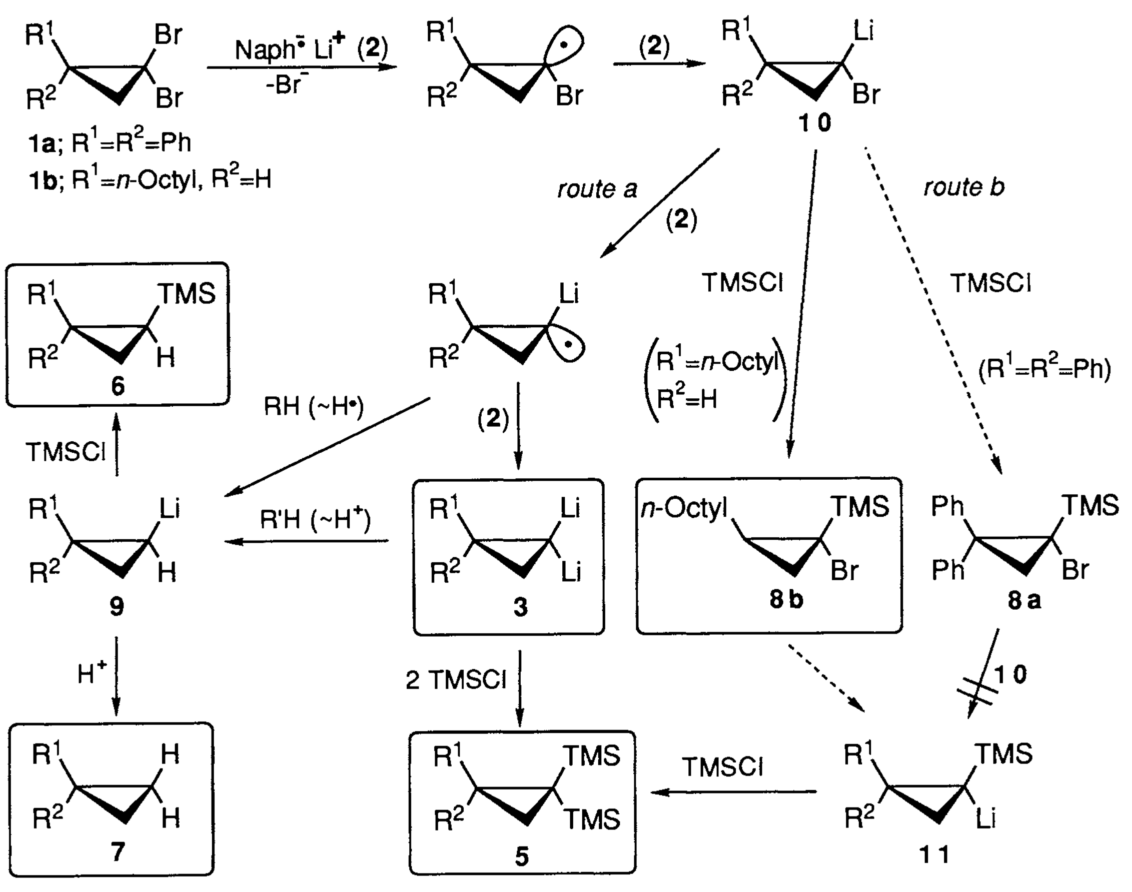


(2)

reduction time/min				
1.5	**5b** (0%)	**6b** (7.8%)	**7b** (3.2%)	**8b** (28%)
40	(0%)	(5.7%)	(1.9%)	(31%)

The formation of unnegligible amount of **8b** indicates that bromo(lithio)cyclopropane **10b** survived intact or was reduced only at a very slow rate in the presence of reductant **2**. This is a remarkable difference in reactivity from that of **10a** which easily produced dilithio-compound **3a** under the same conditions. The difference can be interpreted in terms of substituent effect. Since the octyl group is a poor carbanion stabilizing substituent, further reduction of **10b** is suppressed in comparison with **10a** where the phenyl groups, though not directly bound to the carbanion center, stabilize the charge inductively.

Scheme 1 summarizes the possible reduction pathway of gem-dibromocyclopropanes **1** with reductant **2**. Explicitly the key step is the reduction of intermediate bromo(lithio)cyclopropane **10**: while small amounts of **7b** and **6b** were produced from **1b**, further reduction of octyl-substituted bromo(lithio)-intermediate **10b** is kinetically less favored and, therefore, **10b** survived much longer than **10a** in the presence of **2**. Nevertheless, dilithio-compound **3b** may be formed to a minor extent and, being a highly basic dianion, it is protonated by the solvent to form monoanion **9b** before the electrophile **4** is added. In contrast, dilithio-compound **3a** is not so basic as **3b** that it undergoes both protonation by the solvent and silylation with **4** competitively.



Scheme 1.

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9) Analytical data of products. **5a**: ^{1}H NMR(CCl_4) δ 0.00 (18H, s, used as the internal standard), 1.95 (2H, s), 7.40-7.95 (10H, m); ^{13}C NMR($CDCl_3$) δ 1.35, 9.61, 18.09, 43.78, 126.19, 128.07, 130.05, 146.05. Anal. Found: C, 74.46; H, 9.08. Calcd for $C_{21}H_{30}Si_2$: C, 74.48; H, 8.93. **6a**: ^{1}H NMR ($CDCl_3$) δ 0.00 (9H, s, used as the internal standard), 0.97 (1H, dd, J = 10.7 and 8.0 Hz), 1.50 (1H, dd, J = 10.7 and 3.9 Hz), 1.69 (1H, dd, J = 8.0 and 3.9 Hz), 7.32-7.65 (10H, m); ^{13}C NMR ($CDCl_3$) δ −1.59, 15.35, 17.69, 35.56, 125.53, 126.36, 127.44, 128.04, 130.61, 143.31, 148.08. Anal. Found: C, 81.24; H, 8.32. Calcd for $C_{18}H_{22}Si$: C, 81.14; H, 8.32. **7a**: ^{1}H NMR(CCl_4) δ 1.30 (4H, s), 7.15 (10H, m); ^{13}C NMR($CDCl_3$) δ 16.42, 29.83, 125.91, 128.24, 128.39, 145.71; HRMS Found: 194.1091. Calcd for $C_{15}H_{14}$: 194.1096 (M^+).
10) pK_a(C-H) of THF has not been reported yet. It could be estimated to be around 43 (but less than 46 of *c*-C_3H_6) by comparison of the reactivity of THF with CH_2=CH^- or Ar^- (pK_as of ethene and ArH = 43-44) which slowly abstracts proton from THF and with LDA (pK_a of *i*-Pr_2NH = 38) which remains intact in THF: A. Streitwieser, Jr., R. A. Caldwell, and W. R. Young, *J. Am. Chem. Soc.*, **91**, 529 (1969); A. Streitwieser, Jr., P. J. Scannon, and H. M. Niemeyer, *ibid.*, **94**, 7936 (1972).
11) A mixture of **7**-d_2 (1.5%), -d_1 (7%), and -d_0 (13%) was obtained in a mixed solvent (THF-d_8/h_8 = 4:1).
12) Analytical data of products. **6b**: ^{1}H NMR($CDCl_3$) δ −0.71 (1H, ddd, J = 9.9, 6.9, and 6.9 Hz), −0.09 (9H, s), 0.27 (1H, ddd, J = 9.9, 4.5, and 3.3 Hz), 0.34 (1H, ddd, J = 6.9, 6.9, and 3.3 Hz), 0.55-1.45 (18H, m); HRMS Found: 226.2134. Calcd for $C_{14}H_{30}Si$: 226.2118 (M^+). **7b**: ^{1}H NMR($CDCl_3$) δ −0.02 (2H, ddd, J = 5.4, 5.4, and 3.9 Hz), 0.38 (2H, ddd, J = 9.9, 5.4, and 3.9 Hz), 0.65-1.50 (18H, m). **8b**(unstable): ^{1}H NMR($CDCl_3$) δ 0.15 (9H, s), 0.63-1.65 (20H, m). **8b** is identical to that obtained in 85% yield from the reaction of **1b** with n-BuLi followed by the treatment with **4**. Also, an independent treatment of **8b** with n-BuLi followed by treatment with MeOH gave **6b** in 98% yield.

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