

Efficient Synthesis of Cyclopentadienone Derivatives by the Reaction of Carbon Dioxide with 1,4-Dilithio-1,3-dienes

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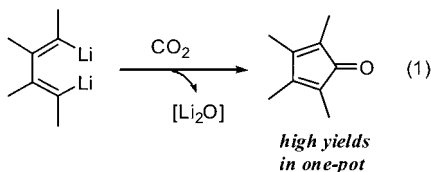
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One-pot reaction of carbon dioxide with 1,4-dilithio-1,3-diene derivatives afforded cyclopentadienone derivatives bearing various substituents in high yields within several minutes.

Introduction

Carbon dioxide has long been the focus of attention for numerous chemical disciplines from several points of view and has been recognized as a potential source of carbon in the synthetic chemistry and industry.¹ In this paper, we would like to report an efficient and selective synthetic method of cyclopentadienone derivatives from carbon dioxide and 1,4-dilithio-1,3-dienes, along with cleavage of one of the C=O double bonds (eq 1).



Reaction of carbon dioxide with organolithium compounds normally affords acids after hydrolysis.² Although formation of ketones is observed in many cases, they are usually unwanted side-reaction products.^{3–5} Cyclopentadienone compounds, which are useful reactive organic

intermediates, have a wide application in organic synthesis and in organometallic chemistry.^{6–8} However, known types of cyclopentadienone derivatives are very limited as a result of lack of efficient synthetic methods. In 1992, Zadel and Breitmaier reported a one-pot synthesis of unsymmetrical ketones from CO₂ and two organolithium compounds via an intermolecular reaction pattern.^{3e} To develop a practical method for the synthesis of cyclopentadienone derivatives by the well-known reaction of organolithium compounds with carbon dioxide, we applied the intramolecular reaction pattern using 1,4-dilithio-1,3-dienes. Cyclopentadienone derivatives with various substituents could be prepared in high yields in one-pot within several minutes.

Results and Discussion

1,4-Diiodo-1,3-diene derivatives are now readily available.⁹ Lithiation of 1,4-diiodo-1,3-diene derivatives affords 1,4-dilithio-1,3-dienes, which have been used as 1,4-dianion precursors for the preparation of main group metalloles.^{10,11} In our reaction, bubbling of CO₂ into a THF solution of 1,4-dilithio-1,3-dienes **2**, generated in situ from the reaction of corresponding diiodo compounds **1** with 2 equiv of *n*BuLi or 4 equiv of *t*-BuLi,^{9–11} afforded

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(1) Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063–2095. (b) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259–272. (c) Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207–2221. (d) *Carbon Dioxide Chemistry: Environmental Issues*; Paul, J., Pradier, C. M., Eds.; Royal Society of Chemistry: London, 1994. (e) Halmann, M. M. *Chemical Fixation of Carbon Dioxide. Methods for Recycling CO₂ into Useful Products*; CRC Press: Boca Raton, FL, 1993. (f) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, 1988.

(2) Wakefield, B. S. *Organolithium Methods*; Academic Press: San Diego, 1988; p 88. (b) Xu, B.; Ma, S. *Chin. J. Org. Chem.* **2000**, *20*, 54–63.

(3) Gilman, H.; Van Ess, P. R. *J. Am. Chem. Soc.* **1933**, *55*, 1258–1261. (b) Soloski, E. J.; Tamborski, C. J. *Organomet. Chem.* **1978**, *157*, 373–377. (c) Corey, J. Y.; McCarthy, W. Z. *J. Organomet. Chem.* **1984**, *271*, 319–326. (d) Katritzky, A. R.; Black, M.; Fan, W. *J. Org. Chem.* **1991**, *56*, 5045–5048. (e) Zadel, G.; Breitmaier, E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1035–1036.

(4) Carbonation of dilithium intermediates from reaction of diphenylacetylene with organolithium resulted in 2-phenyl-3-alkylindones in low yields (11–17%). See: (a) Mulvaney, J. E.; Gardlund, Z. G.; Gardlund, S. L. *J. Am. Chem. Soc.* **1963**, *85*, 3897–3898. (b) Mulvaney, J. E.; Gardlund, Z. G.; Gardlund, S. L.; Newton, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 476. (c) Rausch, M. D.; Klemann, L. P. *J. Am. Chem. Soc.* **1967**, *89*, 5732–5733.

(5) For a review on the formation of ketones from reactions of carboxylic acids with organolithium reagents, see: Jorgenson, M. J. *Org. React.* **1970**, *18*, 1–97. See also: (a) Rubottom, G. M.; Kim, C. J. *Org. Chem.* **1983**, *48*, 1550–1552. (b) Ahn, Y.; Cohen, T. *Tetrahedron Lett.* **1994**, *35*, 203–206.

(6) Jikyo, T.; Eto, M.; Harano, K. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3463–3470.

(7) Gamba, A.; Gandolfi, R.; Oberti, R.; Sardone, N. *Tetrahedron* **1993**, *49*, 6331–6348. (b) Kawase, T.; Ohsawa, T.; Enomoto, T.; Oda, M. *Chem. Lett.* **1994**, 1333–1336. (c) Kumar, U.; Neenan, T. X. *Macromolecules* **1995**, *28*, 124–130. (d) Shibata, T.; Ohta, T.; Soai, K. *Tetrahedron Lett.* **1998**, *39*, 5785–5788. (e) Jikyo, T.; Eto, M.; Harano, K. *Tetrahedron* **1999**, *55*, 6051–6066.

(8) Eisch, J. J.; Aradi, A. A.; Han, K. I. *Tetrahedron Lett.* **1983**, *24*, 2073–2076. (b) Garlaschelli, L.; Malatesta, M. C.; Panzeri, S.; Albinati, A.; Ganazzoli, F. *Organometallics* **1987**, *6*, 63–72. (c) Pearson, A. J.; Shively, R. J., Jr.; Dubbert, R. A. *Organometallics* **1992**, *11*, 4096–4104. (d) Kirchner, K.; Mereiter, K.; Umfaher, A.; Schmid, R. *Organometallics* **1994**, *13*, 1886–1892. (e) Knolker, H.-J.; Baum, E.; Heber, J. *Tetrahedron Lett.* **1995**, *36*, 7647–7650. (f) Roers, R.; Rominger, F.; Braunweiler, C.; Gleiter, R. *Tetrahedron Lett.* **1998**, *39*, 7831–7834.

(9) For preparative methods for 1,4-diiodo-1,3-diene derivatives, see: (a) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829–2832. (b) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. K.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336–3346. (c) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870–2874. (d) Hill, J. E.; Balaich, G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911–2924. (e) Yamaguchi, S.; Jin, R.; Tamao, K.; Sato, F. *J. Org. Chem.* **1998**, *63*, 10060–10062. (f) Xi, C.; Huo, S.; Affi, T. H.; Hara, R.; Takahashi, T. *Tetrahedron Lett.* **1997**, *38*, 4099–4102.

Scheme 1

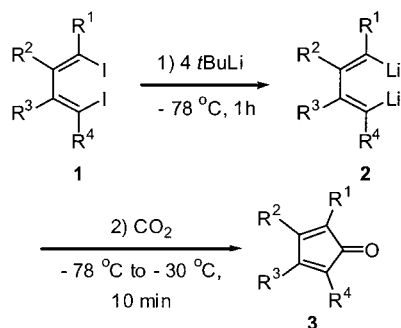


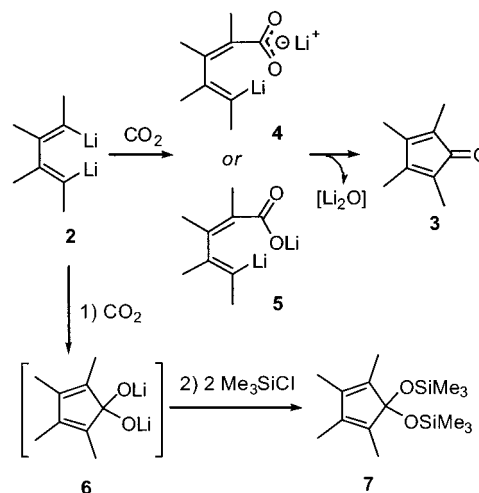
Table 1. Formation of Cyclopentadienone Derivatives by the Reaction of 1,4-Dilithio-1,3-diene Derivatives with Carbon Dioxide^a

Run	1,4-Dilithio-1,3-diene	Product	Yield/% ^b
1			92 (75)
2			90 (70)
3			80 (57)
4			(66)
5			90 (78)
6			84 (65)

^a Reaction conditions: the 1,4-dilithio-1,3-diene derivative was prepared in situ from the corresponding 1,4-diiodo-1,3-diene derivative (1.0 mmol) and *t*-BuLi (4.0 mmol) in THF (5 mL) at $-78\text{ }^{\circ}\text{C}$; carbon dioxide was bubbled into the 1,4-dilithio-1,3-diene solution for 1 min at $-78\text{ }^{\circ}\text{C}$, and then the mixture was stirred at $-30\text{ }^{\circ}\text{C}$ for 5 min under CO_2 . ^b GC yields. Isolated yields are given in parentheses.

cyclopentadienone derivatives **3** in high yields in one pot (Scheme 1). These reactions were very fast and complete within 10 min at low temperature. Results are summarized in Table 1. 2,3,4,5-Tetrapropyl cyclopentadienone **3a**^{8b} and 2,3,4,5-tetrabutyl cyclopentadienone **3b** were formed in 92% and 90% yields, respectively. It is noteworthy that these compounds **3a** and **3b** are not stable. They gradually dimerized to form [4 + 2] cyclo-

Scheme 2



adducts quantitatively within 3 days even kept in the dark and cool.⁶

Unsymmetrically substituted cyclopentadienones could be also prepared in high yields in a similar procedure. Cyclopentadienones **3c–e** bearing silyl, phenyl, or alkyl groups were prepared in 80%, 66%, and 90% yield, respectively, from corresponding 1,4-diiodo-1,3-dienes. Indone is another type of important compound. By using this reaction, the indone derivative **3f** was formed in 84% yield.⁴ Compared with **3a** and **3b**, compounds **3c–f** are quite stable. No dimerization was observed after weeks.

Dilithiated ketals are usually turned to ketones after hydrolysis.^{5a} However, interestingly, without hydrolysis of the reaction mixture, cyclopentadienones **3** were already formed quantitatively, as demonstrated by the ¹³C NMR spectra of the reaction mixture. Thus, a proposed reaction mechanism is given in Scheme 2. One of the two alkenyllithium moieties reacts first with CO_2 to generate a lithium carboxylate **4** and/or **5**, which is then intramolecularly attacked by the remaining alkenyllithium moiety to afford cyclopentadienones **3** along with release of lithium oxide. It is noteworthy that, though the intermediacy of dilithiated ketals **6** cannot be excluded, no trimethylsilyl ketals **7** were observed when the reaction mixture was treated with chlorotrimethylsilanes.

Experimental Section

General. All reactions were conducted under a slightly positive pressure of dry, prepurified nitrogen using standard Schlenk line techniques when appropriate. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Tetrahydrofuran (THF) was refluxed and distilled from sodium/benzophenone ketyl under a nitrogen atmosphere. *n*-BuLi and *t*-BuLi were obtained from Kanto Chemicals Co. Ltd.

(10) For application of 1,4-dilithio-1,3-dienes as 1,4-dianion precursors for main group metalloles, see: (a) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215–263 and references therein. (b) Ashe, A. J., III; Kampf, J. W.; Al-Taweel, S. M. *J. Am. Chem. Soc.* **1992**, *114*, 372–374. (c) Ashe, A. J., III; Al-Ahmad, S.; Pilotek, S.; Puranik, D. B.; Elschenbroich, C.; Behrendt, A. *Organometallics* **1995**, *14*, 2689–2698. (d) Bankwitz, U.; Sohn, H.; Powell, D. R.; West, R. *J. Organomet. Chem.* **1995**, *499*, C7–C9. (e) Freeman, W. P.; Tilley, T. D.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 10457–10468. (f) Yamaguchi, S.; Jin, R.; Tamao, K. *J. Organomet. Chem.* **1998**, *559*, 73–80. (g) Reference 9f.

(11) Hoberg, H.; Richter, W. *J. Organomet. Chem.* **1980**, *195*, 355–362.

^1H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, in CDCl_3 unless stated otherwise. GC yields were determined using suitable hydrocarbons as internal standards. IR spectra were recorded as neat liquids. 1,4-Diiodo-1,3-diene derivatives (**1a–e**) and the diiodo compound **1f** were synthesized by the reported procedure.^{9f}

Typical Procedure for the Preparation of Cyclopentadienone Derivatives from Corresponding Diiodo Compounds. To a THF (5 mL) solution of 1,4-diiodo-1,3-butadiene (1.0 mmol) at -78°C was added *t*-BuLi (4.0 mmol, 1.6 M in pentane). After this reaction mixture was stirred at -78°C for 1 h, CO_2 was bubbled for 1 min. The mixture was then stirred for 5 min under a slightly positive pressure of CO_2 at -30°C . The above reaction mixture was quenched with 3 N HCl and extracted with ether. The extract was washed with water, NaHCO_3 , water, and brine and dried over MgSO_4 . The solvent was then evaporated in vacuo to give a brown oil, which was purified by column chromatograph (silica gel, hexane/ CH_2Cl_2 = 1:1) to afford **2,3,4,5-tetrapropyl cyclopentadienone (3a)** as an orange liquid in 75% isolated yield (186 mg).^{8b} GC yield of 92% of **3a** was determined using dodecane as the internal standard. IR (neat): 1716 cm^{-1} ($\text{C}=\text{O}$). ^1H NMR (C_6D_6): δ 0.81–0.91 (m, 12H), 1.30–1.38 (m, 4H), 1.45–1.55 (m, 4H), 2.05–2.16 (m, 8H). ^{13}C NMR (C_6D_6): δ 14.38, 14.42, 22.76, 23.23, 25.41, 28.41, 126.22, 154.56, 203.86. HRMS calcd for $\text{C}_{17}\text{H}_{28}\text{O}$ 248.2140, found 248.2145.

2,5-Bis(trimethylsilyl)-3,4-dibutyl Cyclopentadienone (3c). Orange liquid, isolated yield 57% (192 mg), GC yield 80%. IR (neat): 1700 cm^{-1} ($\text{C}=\text{O}$). ^1H NMR: δ 0.40 (s, 18H), 0.92 (t, J = 6.2 Hz, 6H), 1.33–1.48 (m, 8H), 2.40 (t, J = 7.3 Hz, 4H). ^{13}C NMR: δ 0.06, 13.86, 23.18, 28.05, 32.87, 128.21, 172.85, 211.12. HRMS calcd for $\text{C}_{19}\text{H}_{36}\text{OSi}_2$ 336.2305, found 336.2317.

2,4-Dibutyl-3,5-diphenyl Cyclopentadienone (3d). Reddish liquid, isolated yield 66% (227 mg). IR (neat): 1690 cm^{-1} ($\text{C}=\text{O}$). ^1H NMR: δ 0.57 (t, J = 6.9 Hz, 3H), 0.75 (t, J = 6.9 Hz, 3H), 0.80–1.53 (m, 8H), 2.12 (t, J = 6.9 Hz, 2H), 2.42 (t,

J = 6.9 Hz, 2H), 7.22–7.43 (m, 10H). ^{13}C NMR: δ 13.39, 13.75, 22.41, 22.66, 22.84, 26.69, 29.90, 31.62, 125.00, 127.05, 127.85, 128.07, 128.17, 128.35, 128.46, 129.30, 131.72, 134.17, 153.47, 158.28, 202.53. HRMS calcd for $\text{C}_{25}\text{H}_{28}\text{O}$ 344.2140, found 344.2145.

2,3-Dipropyl-4-butyl-5-trimethylsilyl Cyclopentadienone (3e). Orange liquid, isolated yield 78% (228 mg), GC yield 90%. IR (neat): 1678 cm^{-1} ($\text{C}=\text{O}$). ^1H NMR: δ 0.16 (s, 9H), 0.83–0.98 (m, 9H), 1.23–1.48 (m, 8H), 2.03 (t, J = 6.8 Hz, 2H), 2.20 (t, J = 8.1 Hz, 2H), 2.33 (t, J = 7.5 Hz, 2H). ^{13}C NMR: δ 0.13, 13.89, 14.31, 14.47, 22.70, 22.75, 23.16, 25.25, 27.84, 28.85, 32.55, 122.94, 130.25, 154.88, 173.60, 207.91. HRMS calcd for $\text{C}_{18}\text{H}_{32}\text{OSi}$ 292.2222, found 292.2231.

2,3-Dibutyl-1-indone (3f). Light green liquid, isolated yield 65% (157 mg), GC yield 84%. IR (neat): 1718 cm^{-1} ($\text{C}=\text{O}$). ^1H NMR: δ 0.81–0.91 (m, 6H), 1.23–1.55 (m, 8H), 2.17 (t, J = 7.5 Hz, 2H), 2.45 (t, J = 7.5 Hz, 2H), 6.93–7.29 (m, 4H). ^{13}C NMR: δ 13.88 (2 CH_3), 22.58, 22.75, 22.99, 25.97, 29.94, 31.42, 118.90, 121.59, 127.79, 131.11, 133.08, 134.75, 145.64, 157.71, 198.50. HRMS calcd for $\text{C}_{17}\text{H}_{22}\text{O}$ 242.1671, found 242.1679.

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Supporting Information Available: Characterization data for **3b** and ^1H and ^{13}C NMR spectra for compounds **3a–f**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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