New Cyclopentadienones from Sterically Demanding Inner Acetylenes and Dicobalt-octacarbonyl

Eckehard V. Dehmlow* and Andreas Winterfeldt

Fakultät für Chemie, Universität Bielefeld, Universitätsstraße 25, D-4800 Bielefeld 1

Z. Naturforsch. **44b**, 455–458 (1989); received December 5, 1988

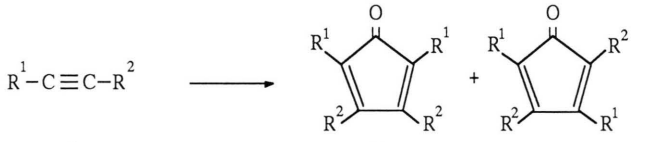
Alkyne-Carbon Monoxide Reaction, Metal Carbonyl Catalysis, Cyclopentadienones, Cycloalkanocyclopentadienones

Acetylenes carrying one bulky substituent can be transformed into symmetrically or asymmetrically substituted cyclopentadienones **2** or **3** when they are heated with $Co_2(CO)_8$ and carbon monoxide. Intramolecular cyclizations yielding compounds **5** are also possible.

We have shown recently that the $Co_2(CO)_8$ catalyzed reaction of bulky 1-alkynes with carbon monoxide yields substituted benzenes, cyclopentadienones, and/or novel 1-oxaspiro-[4.4]-nona-3,6,8-trien-2-ones [1]. In the present work these studies are extended to inner acetylenes carrying at least one sterically demanding substituent.

The alkynes are dissolved in petroleum ether and stirred initially with dicobalt octacarbonyl at room temperature, whereupon the usual formation of a complex [$Co_2(CO)_6$×alkyne] occurs. Subsequently, the mixture is heated under carbon monoxide. No benzene derivatives are formed with any of the bulky inner acetylenes (**1a–1n**).

(1-Adamantyl)-1-propyne (**1a**) gives, under these conditions, 2,5-di-(1-adamantyl)-3,4-dimethylcyclopentadienone (**2a**). The structure of **2a** follows from the ^{13}C-NMR-spectrum. This is symmetric and exhibits signals for the olefinic carbon atoms at 130 (singlet) and 149 ppm (multiplet, $^2J_{CH}$ = 5 Hz), indicating that the low field carbon atom carries the methyl group. It is known that the 2-position carbon atoms of tetrasubstituted cyclopentadienones give signals at higher fields than the C-3 atoms [2].



1 **2** **3**

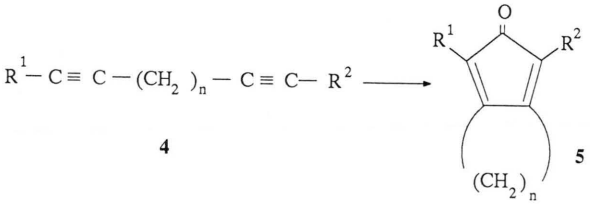
Alkyne **1**	R^1	R^2	Cyclopentadienones **2**	**3**
a	1-adamantyl	CH_3	+	–
b	mesityl	CH_3	+	+
c	mesityl	C_2H_5	+	+
d	1-adamantyl	C_2H_5	+	–
e	mesityl	$CH(CH_3)_2$	–	–
f	phenyl	$CH(CH_3)_2$	–	–
g	mesityl	$(CH_2)_7-CH_3$	+	+
h	mesityl	$(CH_2)_3-Si(CH_3)_3$	+	–
i	mesityl	$(CH_2)_4-Br$	+	–
j	1-adamantyl	$Si(CH_3)_3$	–	–
k	mesityl	$Si(CH_3)_3$	–	–
l	mesityl	$(CH_2)_4-CN$	–	–
n	mesityl	$C(CH_3)_2-OCH_3$	–	–

* Sonderdruckanforderungen an Prof. Dr. E. V. Dehmlow.

Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
0932–0776/89/0400–0455/$ 01.00/0

Mesityl-1-propyne (**1b**) and mesityl-1-butyne (**1c**), in contrast, give rise to two isomeric cyclopentadienones each, **2b** or **2c,** and **3b** or **3c,** respectively. (1-Adamantyl)-1-butyne (**1d**), however, gives only **2d.** Compounds with two relatively bulky substituents, such as 1-mesityl-3-methyl-1-butyne (**1e**) and even 3-methyl-1-phenyl-1-butyne (**1f**) cannot be transformed into cyclopentadienones. On the other hand, a single long chain R^2 in the alkyne **1g** (1-mesityl-1-decyne) allows the formation of compounds **2g** and **3g.**

Similarly, functionalized cyclopentadienones carrying trimethylsilyl or bromo groups at the far end of $(CH_2)_n$ side chains, compounds **2h** and **2i,** can be obtained. Interestingly, only symmetrically substituted derivatives are found in these cases. No such products are formed from various other alkynes **1j** to **1h,** carrying two bulky groups at the acetylene or a cyanide residue at the end of a $(CH_2)_n$ chain.



	n	R^1	R^2
a	3	mesityl	mesityl
b	4	mesityl	mesityl
c	5	mesityl	mesityl
d	6	*tert*-butyl	adamantyl(1)

Intramolecular couplings of diynes with bulky trimethylsilyl end groups were described by Volhardt and coworkers [3]. 1,ω-Dimesityl-1,ω-diynes **4a–4c** are transformed into the bicyclic compounds **5a–5c** under our conditions. This same type of conversion is possible also with an unsymmetrically substituted aliphatic diyne: 1-(1-adamantyl)-8-*tert*-butyl-1,7-octadiyne **4d** yields **5d.** In these reactions no intermolecular reaction products are observed.

These experiments show that a variety of substituted cyclopentadienones can be prepared by ring closure reactions of alkynes if the starting materials carry no more than one bulky group. Yields have not been optimized and could be improved. Limitations of the method are apparent if polar substituents are present on the acetylene.

Experimental

Melting points were measured with the apparatus after Dr. Tottoli (Büchi). They are not corrected. – Boiling points refer to air bath temperatures of a Kugelrohr distillation apparatus. – ^{13}C NMR spectra: AM 300 (Bruker) in $CDCl_3$, ^1H NMR: A 300 (Bruker) in $CDCl_3$, or WP 80 (Bruker) in $CDCl_3$.

General method for the preparation of the starting acetylenes

35 mol 1-adamantylacetylene (or mesitylacetylene) are dissolved in 25 ml THF and cooled to 0 °C. 40 mmol of butyl lithium in THF/petroleum ether are added dropwise at 0–5 °C, and the mixture is stirring for 30 min. Then 35 mmol of the appropiate alkyl halide are added, and the mixture is refluxed for 18 h. The mixture is poured into dilute hydrochloric acid and extracted with dichloromethane. After drying (Na_2SO_4), the solvent is removed and the residue is purified by distillation, crystallization, or chromatography. In this way the following new compounds are prepared:

1-Adamantyl-1-propyne (**1a**), m.p. 96 °C; ^{13}C NMR: δ 88.1, 74.1, 43.4, 36.5, 29.6, 28.2, 3.6. – MS: *m/z* 174 (M^+).

Mesityl-1-propyne (**1b**), m.p. 35 °C; ^1H NMR: δ 6.83 (s, 2H), 2.36 (s, 6H), 2.25 (s, 3H), 2.12 (s, 3H).

$C_{12}H_{14}$ (158,2)
Calcd C 91.08 H 8.92,
Found C 91.61 H 8.75.

Mesityl-1-butyne (**1c**), b.p. 60 °C/0.01 Torr; ^1H NMR: δ 6.83 (s, 2H), 2.49 (q, 2H), 2.37 (s, 6H), 2.25 (s, 3H), 1.26 (t, 3H).

$C_{13}H_{16}$ (172.3)
Calcd C 90.64 H 9.36,
Found C 90.29 H 9.37.

1-Adamantyl-1-butyne (**1d**), m.p. 49 °C; ^1H NMR: δ 2.16 (q, 2H), 1.93 (m, 3H), 1.83 (m, 6H), 1.67 (m, 6H), 1.10 (t, 3H).

1-Mesityl-3-methyl-1-butyne (**1e**), b.p. 40 °C/0.01 Torr; ^1H NMR: δ 6.83 (s, 2H), 2.85 (septet, 1H), 2.36 (s, 6H), 2.25 (s, 3H), 1.28 (d, 6H).

3-Methyl-1-phenyl-1-butyne (**1f**), b.p. 40 °C/0.01 Torr; ^1H NMR: δ 7.26 (m, 5H), 2.6 (m, 1H), 1.10 (d, 6H).

1-Mesityl-1-decyne (**1g**); ^1H NMR: δ 6.83 (s, 2H), 2.48 (t, 2H), 2.37 (s, 6H), 2.25 (s, 3H), 1.65–0.86 (m, 15H).

1-Mesityl-5-trimethylsilyl-1-pentyne (**1h**); ^{1}H NMR: δ 6.83 (s, 2H), 2.50 (t, 2H), 2.37 (s, 6H), 2.25 (s, 3H), 1.8–1.1 (m, 4H), $\approx$0.0 (s, 9H). – MS: *m/z* 258 (M^+).

$C_{17}H_{26}Si$ (258.5)
Calcd C 79.00 H 10.14,
Found C 79.09 H 9.72.

6-Bromo-1-mesityl-1-hexyne (**1i**), b.p. 95 °C/0.01 Torr; ^{1}H NMR: δ 6.84 (s, 2H), 3.48 (t, 2H), 2.55 (t, 2H), 2.37 (s, 6H), 2.26 (s, 3H), 2.20–1.66 (m, 4H).

1-Adamantyl-2-trimethylsilylethyne (**1j**), b.p. 80 °C/0.01 Torr; ^{1}H NMR: δ 1.86–1.66 (m, 15H), 0.11 (s, 9H). – MS (CI): *m/z* 233 ($M^+ + 1$).

$C_{15}H_{24}Si$ (232.4)
Calcd C 77.51 H 10.41,
Found C 77.21 H 10.15.

1-Mesityl-2-trimethylsilylethyne (**1k**), b.p. 60 °C/0.1 Torr; ^{1}H NMR: δ 6.84 (s, 2H), 2.38 (s, 6H), 0.25 (s, 9H). – MS (CI): *m/z* 217 ($M^+ + 1$).

$C_{14}H_{20}Si$ (216.4)
Calcd C 77.71 H 9.32,
Found C 77.70 H 9.09.

6-Cyan-1-mesityl-1-hexyne (**1l**), b.p. 90 °C/0.01 Torr; ^{1}H NMR: δ 6.84 (s, 2H), 2.6–2.4 (m, 4H), 2.36 (s, 6H), 2.26 (s, 3H), 1.9–1.8 (m, 4H).

1-Mesityl-3-methoxy-3-methyl-1-butyne (**1n**), b.p. 60 °C/0.01 Torr; ^{1}H NMR: δ 6.86 (s, 2H), 3.45 (s, 3H), 2.38 (s, 6H), 2.26 (s, 3H), 1.57 (s, 6H).

$C_{15}H_{20}O$ (216.3)
Calcd C 83.29 H 9.32,
Found C 83.14 H 9.32.

1,7-Dimesitylhepta-1,6-diyne (**4a**), m.p. 87 °C; ^{1}H NMR: δ 6.84 (s, 4H), 2.71 (t, 4H), 2.38 (s, 12H), 2.26 (s, 6H), 1.94 (quintet, 2H).

1,8-Dimesitylocta-1,7-diyne (**4b**), m.p. 78 °C; ^{1}H NMR: δ 6.84 (s, 4H), 2.57 (m, 4H), 2.37 (s, 12H), 2.26 (s, 6H), 1.84 (m, 4H).

1,9-Dimesitylnona-1,8-diyne (**4c**), m.p. 67 °C; ^{1}H NMR: δ 6.82 (s, 4H), 2.51 (m, 4H), 2.35 (s, 12H), 2.25 (s, 6H), 1.69 (m, 6H).

1-Adamantyl-1-tert-butylocta-1,7-diyne (**4d**), b.p. 100 °C/0.01 Torr; ^{1}H NMR: δ 2.16 (m, 4H), 1.93 (m, 3H), 1.83 (m, 6H), 1.66 (m, 6H), 1.55 (m, 4H), 1.20 (s, 9H). – MS: *m/z* 296 (M^+).

General method for the conversion of alkynes with carbon monoxide and dicobalt-octacarbonyl

4.2 mmol $Co_2(CO)_8$ and 9.5 mmol alkyne are dissolved in 15 mmol petroleum ether (b.p. 80–100 °C) and stirred for 1 h at room temperature. Under these conditions the formation of a complex occurs. Thereafter the mixture is refluxed under a slight CO pressure at 120 °C bath temperature for 4 to 18 h. After cooling and diluting with dichloromethane, the solution is filtered, concentrated, and chromatographed over silica gel using petroleum ether/ether 20:1 to 10:1 as eluent.

2,5-Diadamantyl-3,4-dimethylcyclopentadienone (**2a**), m.p. 209 °C, 5% yield; ^{13}C NMR: δ 204.5 (s), 149.4 (q, J = 5 Hz), 130.2 (s), 41.5 (t, J = 130 Hz), 36.9 (t, J = 124 Hz), 36.4 (s), 28.6 (d, J = 131 Hz), 13.4 (q, J = 127 Hz). – IR: 1695 cm^{-1}.

$C_{27}H_{36}O$ (376.6)
Calcd C 86.12 H 9.64,
Found C 86.33 H 9.78.

3,4-Dimethyl-2,5-dimesitylcyclopentadienone (**2b**) (first fraction of chromatography), m.p. 174 °C, 22% yield; ^{1}H NMR: δ 6.88 (s, 4H), 2.28 (s, 6H), 2.11 (s, 12H), 1.89 (s, 6H). – ^{13}C NMR: δ 200.5, 153.4, 137.3, 137.1, 128.1, 128.0, 126.9, 21.1, 20.3, 12.7. – IR: 1702 cm^{-1}.

$C_{25}H_{28}O$ (344.5)
Calcd C 87.16 H 8.19,
Found C 86.96 H 8.24.

2,4-Dimethyl-3,5-dimesitylcyclopentadienone (**3b**) (second fraction of chromatography), m.p. 155 °C, 2% yield; ^{1}H NMR δ 6.94 (s, 2H), 6.90 (s, 2H), 2.32 (s, 3H), 2.29 (s, 3H), 2.20 (s, 6H), 2.12 (s, 6H), 1.58 (s, 3H), 1.48 (s, 3H). – ^{13}C NMR: δ 202.1, 155.8, 153.4, 137.6, 137.4, 137.2, 135.3, 129.9, 128.1, 126.3, 124.2, 21.1, 20.3, 19.8, 13.4, 8.1. – IR: 1702 cm^{-1}.

$C_{25}H_{28}O$ (344.5)
Calcd C 87.16 H 8.19,
Found C 87.31 H 8.38.

3,4-Diethyl-2,5-dimesitylcyclopentadienone (**2c**) (first fraction of chromatography), m.p. 146 °C, 12% yield; ^{1}H NMR: δ 6.88 (s, 4H), 2.29 (q, 4H), 2.28 (s, 6H), 2.12 (s, 12H), 1.02 (t, 6H). – IR: 1705 cm^{-1}.

$C_{27}H_{32}O$ (372.6)
Calcd C 87.05 H 8.66,
Found C 86.97 H 8.54.

2,4-Diethyl-3,5-dimesitylcyclopentadienone (**3c**) (second fraction of chromatography), 22% yield; ^{1}H NMR: δ 6.94 (s, 2H), 2.32 (s, 3H), 2.29 (s, 3H), 2.23 (s, 6H), 2.14 (s, 6H), 2.02 (q, 2H), 1.89 (q, 2H), 0.90 (t, 3H), 0.63 (t, 3H). – IR: 1700 cm^{-1}. – MS: *m/z* 372 (M^+).

2,5-Diadamantyl-3,4-diethylcyclopentadienone (**2d**), m.p. 149 °C, 6% yield; ^{1}H NMR: δ 2.40 (q, 4H), 2.00 (m, 18H), 1.73 (m, 12H), 1.09 (t, 6H). – IR: 1695 cm^{-1}.

$C_{29}H_{40}O$ (404.6)
Calcd C 86.08 H 9.96,
Found C 85.73 H 9.91.

2,5-Dimesityl-3,4-dioctylcyclopentadienone (**2g**) (first fraction of chromatography), 14% yield; ^{1}H NMR: δ 6.87 (s, 4H), 2.27 (s, 6H), 2.11 (s, 12H), 2.3–2.0 (m, 4H), 1.5–0.8 (m, 30H). – IR: 1700 cm^{-1}. – MS: *m/z* 540 (M^+).

2,4-Dimesityl-3,5-dioctylcyclopentadienone (**3g**) (second fraction of chromatography), 5% yield; ^{1}H NMR: δ 6.92 (s, 2H), 6.88 (s, 2H), 2.32 (s, 3H), 2.28 (s, 3H), 2.22 (s, 6H), 2.13 (s, 6H), 2.5–2.0 (m, 4H), 1.5–0.8 (m, 30H). – IR: 1700 cm^{-1}. – MS: *m/z* 540 (M^+).

2,5-Dimesityl-3,4-di(3'-trimethylsilylpropyl)cyclopentadienone (**2h**), m.p. 128 °C, 5% yield; ^{1}H NMR: δ 6.87 (s, 4H), 2.27 (m, 10H), 2.11 (s, 12H), 1.4–0.4 (m, 8H), –0.11 (s, 18H). – IR: 1700 cm^{-1}. – MS: *m/z* 544 (M^+).

3,4-Di(4'-brombutyl)-2,5-dimesitylcyclopentadienone (**2i**), m.p. 179 °C, 1% yield; ^{1}H NMR: δ 6.88 (s, 4H), 3.32 (t, 4H, J = 6.5 Hz), 2.28 (m, 10H), 2.11 (s, 12H), 1.83 (m, 4H), 1.56 (m, 4H). – IR: 1695 cm^{-1}.

$C_{31}H_{38}Br_2O$ (586.5)
Calcd C 63.49 H 6.53,
Found C 63.49 H 6.52.

3,4-Cyclopentano-2,5-dimesitylcyclopentadienone (**5a**), m.p. 180 °C, 47% yield; ^{1}H NMR: δ 6.69 (s, 4H), 2.49 (t, 4H), 2.28 (s, 6H), 2.16 (s, 12H), 2.11 (q, 2H). – IR: 1690 cm^{-1}.

$C_{26}H_{28}O$ (356.5)
Calcd C 87.60 H 7.92,
Found C 87.69 H 8.13.

3,4-Cyclohexano-2,5-dimesitylcyclopentadienone (**5b**), m.p. 152 °C, 12% yield; ^{1}H NMR: δ 6.88 (s, 4H), 2.38 (m, 4H), 2.27 (s, 6H), 2.13 (s, 12H), 1.67 (m, 4H). – IR: 1700 cm^{-1}.

$C_{27}H_{30}O$ (370.5)
Calcd C 87.52 H 8.16,
Found C 87.11 H 8.05.

3,4-Cycloheptano-2,5-dimesitylcyclopentadienone (**5c**), m.p. 167 °C, 6% yield; ^{1}H NMR: δ 6.89 (s, 4H), 2.32 (m, 4H), 2.28 (s, 6H), 2.11 (s, 12H), 1.69 (m, 6H). – IR: 1700 cm^{-1}.

$C_{28}H_{32}O$ (384.6)
Calcd C 87.45 H 8.39,
Found C 87.05 H 8.93.

2-Adamantyl-5-tert-butyl-3,4-cyclohexanocyclopentadienone (**5d**), red oil, 49% yield; ^{1}H NMR: δ 2.7 (m, 4H), 2.1–1.5 (m, 19H), 1.21 (s, 9H). – ^{13}C NMR: δ 204.0, 149.2, 149.0, 129.4, 129.2, 41.4, 37.0, 36.6, 33.3, 30.6, 28.7, 27.2, 27.0, 22.8, 22.6. – IR: 1690 cm^{-1}.

$C_{23}H_{32}O$ (324.5) (could not be obtained totally pure)
Calcd C 85.13 H 9.94,
Found C 82.33 H 10.13.

This research was supported, in part, by Fonds der Chemischen Industrie.

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