Generation of cyclobutadiene derivatives from 1-metallo-4-halobuta-1,3-diene derivatives

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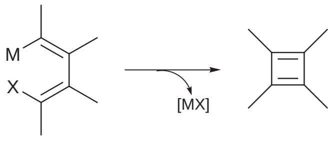
1-Zircona-4-halobuta-1,3-diene derivatives react in the presence of CuCl to produce cyclobutadiene derivatives which afford their dimers, or Diels–Alder adducts with dimethyl maleate or fumarate.

Cyclobutadiene is one of the most attractive molecules.[1] Several methods have been reported to generate cyclobutadiene derivatives,[1,2] such as (i) irradiation in argon matrix, (ii) preparation from diazo compounds or 3,4-dichlorocyclobutenes or (iii) dimerization of alkynes promoted by metal compounds. A conceptually new and simple method using intramolecular coupling of 1-metallo-4-halobuta-1,3-diene **1** can be considered as a preparative method for cyclobutadiene derivatives, as shown in eqn. (1). However, this simple method has not to the best of our knowledge been reported.

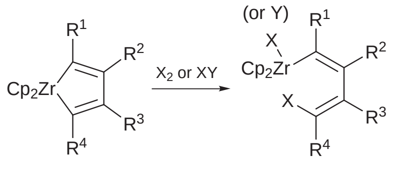


(1)

1 **2**

Here we report that 1-zircona-4-halobuta-1,3-diene derivatives afford *in situ* cyclobutadiene derivatives **2** in the presence of CuCl.

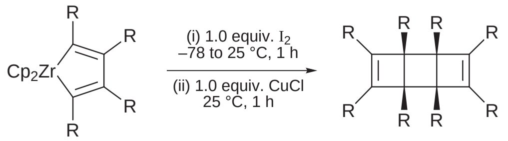
Recently, we reported the highly selective monohalogenation reaction of zirconacyclopentadienes **3** giving 1-zircona-4-halobuta-1,3-diene derivatives **4** [eqn. (2)].[3] Addition of 1 equiv. of CuCl to **4** in THF at room temperature afforded stereodefined tricyclo[4.2.0.0^{2,5}]octa-3,7-diene derivatives **5** within 1 h in good isolated yields (**5a**:‡ R = Et, 72%; **5b**: R = Me, 53%; **5c**:§ R = Pr, 78%) [eqn. (3)]. The ^{1}H and ^{13}C NMR spectra of **5b** were identical with those of authentic *syn*-**5b** prepared according to the literature procedure.[4]



(2)

3 **4**

$X_2 = I_2$; XY = NBS or NCS



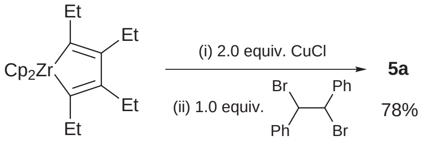
(3)

3

5a R = Et, 72%
b R = Me, 53%
c R = Pr, 78%

This result indicated that cyclobutadienes were formed *in situ* in this reaction. This reaction can be explained by intramolecular coupling between the 1,4 sp^2 carbon centers of **1** followed by dimerization of cyclobutadienes, as shown in Scheme 2.

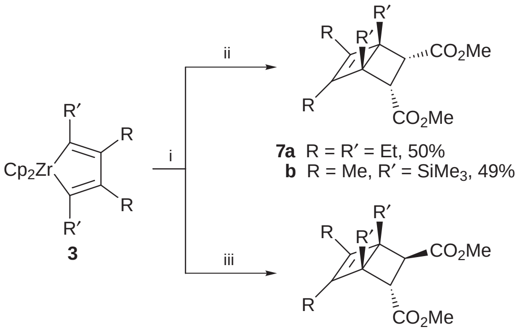
Alternatively, addition of 2 equiv. of CuCl to **3a** and monohalogenation of dicopper species **6**[5] formed *in situ* with 1 equiv. of stilbene dibromide also afforded **5a** in 78% yield along with the formation of 98% of stilbene [eqn. (4)].



(4)

3a

Cyclobutadiene derivatives **2** formed *in situ* by this method were trapped with dimethyl maleate and dimethyl fumarate.[1,2,6] As expected, bicyclic compounds, dimethyl 1,4,5,6-tetraethylbicyclo[2.2.0]hex-5-ene-2-*endo*,3-*endo*-dicarboxylate **7a**[6] and its analogue **7b**, dimethyl 1,4,5,6-tetraethylbicyclo[2.2.0)hex-5-ene-2-*endo*,3-*exo*-dicarboxylate **8a** and its analogues **8b** and **8c**[6] were formed in fairly good yields from dimethyl maleate and dimethyl fumarate, respectively (Scheme 1). The stereochemistry of **7** and **8** was determined by comparison of their NMR data with those of authentic **7a** and **8c** prepared according to the literature.[6] Other bicyclohexene derivatives **9** were also formed *via* the same procedures as described above.[7]

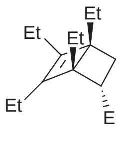


3

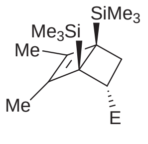
7a R = R′ = Et, 50%
b R = Me, R′ = SiMe$_3$, 49%

8a R = R′ = Et, 52%
b R = Me, R′ = SiMe$_3$, 49%
c R = R′ = Me, 36%

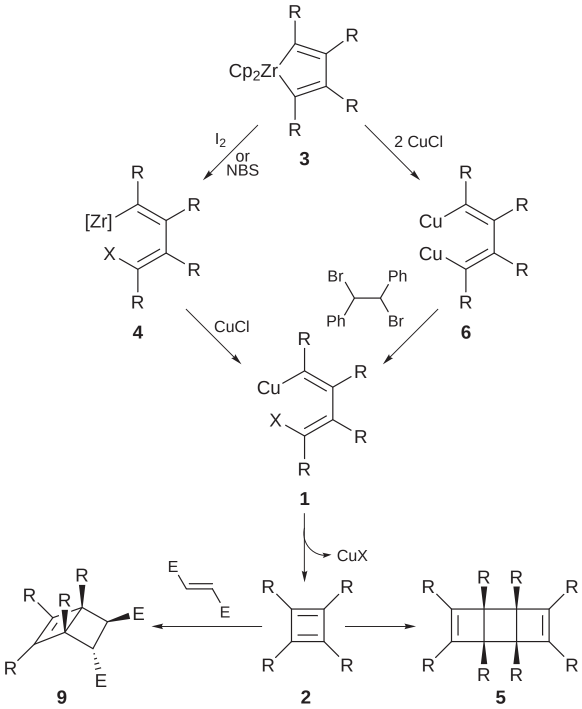
Scheme 1 *Reagents and conditions*: i, NBS (1 equiv.), 0 to 25 °C, 1 h; ii, dimethyl maleate (2 equiv.), CuCl (1 equiv.), 0 °C. 12 h; iii, dimethyl fumarate (2 equiv.), CuCl (1 equiv.), 0 °C, 12 h



9a E = CO$_2$Me, 71%
b E = CN, 61%



9c E = CO$_2$Me, 50%
d E = CN, 55%



Scheme 2

The formation of **7**, **8** and **9** supports the *in situ* generation of cyclobutadiene derivative **2**.[1,6,7] The reactions described here are summarized in Scheme 2.

Further investigations towards practical application of this simple method in organic synthesis are in progress.

Notes and References

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‡ *Selected data* for **5a**: δ_{H}(CDCl$_3$, Me$_4$Si) 0.94 (t, *J* 7.5, 12 H), 1.06 (t, *J* 7.6, 12 H), 1.58–1.66 (m, 4 H), 1.67–1.75 (m, 4 H), 1.83–1.92 (m, 4 H), 2.03–2.17 (m, 4 H); δ_{C}(CDCl$_3$, Me$_4$Si) 12.06, 13.18, 20.50, 21.89, 53.35, 144.97.

§ *Selected data* for **5c**: δ_{H}(CDCl$_3$, Me$_4$Si) 0.87–0.91 (m, 24 H), 1.31–1.57 (m, 24 H), 1.72–1.79 (m, 4 H), 1.95–2.02 (m, 4 H); δ_{C}(CDCl$_3$, Me$_4$Si) 14.95, 15.55, 20.86, 22.01, 31.31, 31.72, 53.04, 144.07.

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