Subscriber access provided by American Chemical Society

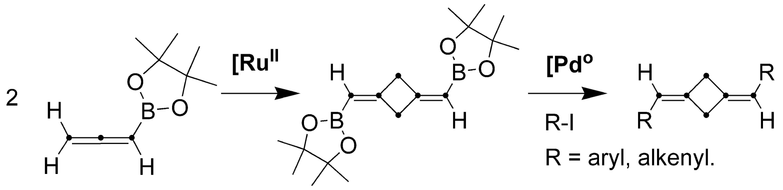
Communication

An Opened Route to 1,3-Dimethylenecyclobutanes via Sequential Ruthenium-Catalyzed [2 + 2] Cycloaddition of Allenyl Boronate and Palladium Suzuki Coupling

Emilio Bustelo, Carine Gurot, Alain Hercouet, Bertrand Carboni, Loc Toupet, and Pierre H. Dixneuf

J. Am. Chem. Soc., **2005**, 127 (33), 11582-11583• DOI: 10.1021/ja051930r • Publication Date (Web): 30 July 2005

Downloaded from http://pubs.acs.org on March 25, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Published on Web 07/30/2005

An Opened Route to 1,3-Dimethylenecyclobutanes via Sequential Ruthenium-Catalyzed [2 + 2] Cycloaddition of Allenyl Boronate and Palladium Suzuki Coupling

Emilio Bustelo,† Carine Guérot,† Alain Hercouet,† Bertrand Carboni,† Loïc Toupet,‡ and Pierre H. Dixneuf*,†

Institut de Chimie de Rennes, UMR 6509 Université de Rennes 1 − CNRS, Organométalliques et Catalyse, and UMR 6626 Université de Rennes 1 − CNRS, Groupe Matière Condensée et Matériaux, Campus de Beaulieu, 35042 Rennes, France

Received March 25, 2005; E-mail: pierre.dixneuf@univ-rennes1.fr

1,3-Dialkylidenecyclobutanes are key precursors for the formation of non-Kékulé hydrocarbon diradicals with triplet ground state: the 1,3-dialkylidenecyclobutane-2,4-diyls.[1,2] This transformation attracts interest because of the large positive bond enthalpy additivity deviation[3] and because diradicals have potential applications in material science[4] as paramagnetic building blocks for the formation of organic magnetic materials and polymers.[1,2] 1,3-Dimethylenecyclobutanes lead to 1,3-diradicals in low-temperature matrixes,[5] in gas phase with atomic oxygen anion,[6] and from bicyclo [1.1.0] butanes.[7]

However, their synthesis is not straightforward. The current preparation of the simplest member involves a six-step synthesis from allene and acrylonitrile.[8] The simplest access would result from [2 + 2] allene thermal cyclodimerization. However, it leads to a 1,2-isomer with small amounts of the 1,3-isomer (85:15).[9] Dimerization of substituted allenes gives mixtures of a number of dimers and oligomers.[10] Only some specific examples of substituted 1,3-dimethylenecyclobutanes are known, namely the 2,4-disulfone[11] and 1,3-bispyridinylidene derivatives.[7]

Recently, Ni(PPh$_3$)$_4$ was revealed to catalyze the [2 + 2] cycloaddition of electron-deficient allenes to give only conjugated 1,2-dimethylenecyclobutane isomers.[12]

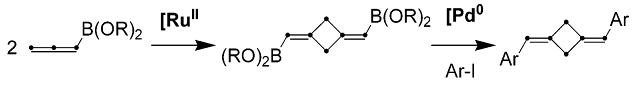
Among functional allenes, allenylboronates have never been involved in catalytic transformations despite their potential for formation of small cycle intermediates, with retention of the sp^2 C−B bond, allowing consecutive C−C bond formation. Our interest in regioselective catalytic oxidative couplings of functional alkynes and alkenes at electron-rich ruthenium precatalysts[13] led us to explore the allenylboronate reactivity.

We wish to report the first direct access to rigid 1,3-dimethylenecyclobutane derivatives via an original head-to-head [2 + 2] cyclodimerization of allenyl boronate, catalyzed by a ruthenium catalyst. Although global yields are still moderate, consecutive palladium-catalyzed C−C couplings open a route to *substituted* 1,3-dimethylenecyclobutanes (Scheme 1).

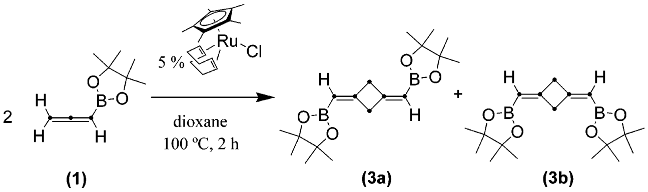
The allenyl boronate **1**, CH$_2$=C=CHB(pin) (pin = pinacol),[12] was reacted in the presence of 5 mol % of [Cp*RuCl(COD)] (**2**) in refluxing dioxane at 100 °C. The reaction proceeds in 2 h to reach the full conversion of the allene, affording [2 + 2] cyclodimerization products (Scheme 2).

GC mass of the crude product confirms the formation of two isomeric products **3a** + **3b** (m/z = 332) in a 2:1 ratio, corresponding to the double mass of the starting allenyl boronate. NMR analysis shows the existence of dimethylenecyclobutane structures, a result of the regioselective head-to-head dimerization of **1** by [2 + 2] coupling of the terminal double bonds.

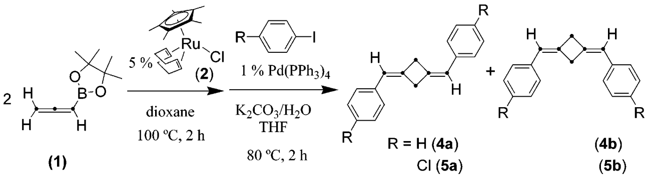
Scheme 1



Scheme 2



Scheme 3



The isolated yield of **3a** + **3b** varies between 40 and 60%. Decomposition of **3a** + **3b** with concomitant release of pinacol is always observed, hindering the separation of the two isomers. In search of more stable products, we reacted the mixture of **3a** + **3b** with iodobenzene in the presence of Pd(PPh$_3$)$_4$ under Suzuki reaction conditions.

To prevent yield loss during workup and overcome the low stability of boronate dimers **3a** + **3b**, both reactions were carried out sequentially in one-pot: first the ruthenium catalysis to prepare the dimeric product was performed, and then the palladium catalyst, aryl iodide, and a base were added.

Taking advantage of the good stability of pinacol boronate esters in water, we employed an aqueous solution of K$_2$CO$_3$ as a base, with catalyst Pd(PPh$_3$)$_4$ (1%) and phenyl iodide in THF. After heating for 2 h at 80 °C, ^{1}H NMR analysis of the reaction mixture showed the presence of the two phenyl-substituted isomers **4a** + **4b** (Scheme 3). Recrystallization allowed us to isolate the major isomer **4a** in 34% global yield.

The X-ray structure of **4a** was determined, establishing the 1,3-dialkylidenecyclobutane nature with an *E*,*E*-configuration of the two exocyclic double bonds (Figure 1).

The dimethylenecyclobutane framework is planar (torsion angles $C_{1'}C_2C_1C_3 = 179.2°$, $C_1C_2C_{1'}C_{2'} = 0.0°$), whereas the phenyl rings only slightly deviate from the planarity (torsion angle $C_4C_3C_1C_2$,

---

† CNRS, Organométalliques et Catalyse.
‡ CNRS, Groupe Matière Condensée et Matériaux.

10.1021/ja051930r CCC: $30.25 © 2005 American Chemical Society

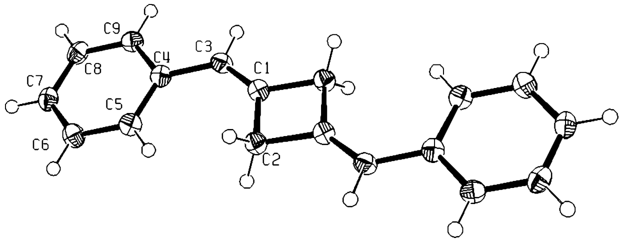
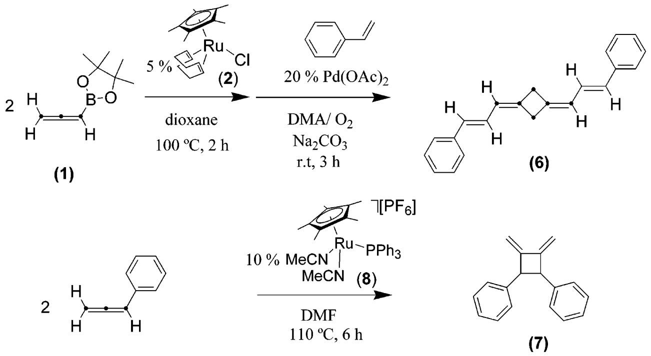


Figure 1. ORTEP drawing of the molecular structure of **4a**.

Scheme 4



3.3°). This is in agreement with the early studies on gas-phase electron diffraction of 1,3-dimethylenecyclobutane.[8]

The theoretical and chemical interest of these species (1,2- and 1,3-dimethylenecyclobutane) has recently led to prediction of its structural and spectroscopic properties.[14] Bond angles and lengths of the phenyl-substituted compound **4a** are in good agreement.

Some insight into the nature of the minor isomer **4b** was gained by NMR. ^{1}H and ^{13}C{^{1}H} NMR data of **4b** only differ from **4a** in the nonequivalence of the cyclobutane CH_2 signals. The lack of a symmetry plane perpendicular to the molecular plane supports a 1,3-(*Z*,*Z*)-dimethylenecyclobutane structure, discarding the presence of the 1,2-isomer.[12]

The Suzuki reaction of **3a** + **3b** with *p*-chloroiodobenzene gives the corresponding *p*-chloro-substituted dimers **5a** + **5b**. The major isomer **5a** was isolated by recrystallization in 25% global yield (Scheme 3).

Other Pd-catalyzed C−C coupling reactions are feasible. The recently reported oxygen-promoted Pd(II) catalysis for cross-coupling of alkenylboronic compounds and olefins was attempted.[15] Compounds **3a** + **3b** were reacted with styrene in the presence of $Pd(OAc)_2/O_2$ and Na_2CO_3 in DMA for 3 h at room temperature, giving 1,3-dipropenylidenecyclobutane **6** (only one isomer was isolated) as a red solid in 15% global yield (Scheme 4).

Thus, although yields are moderate, the sequential ruthenium/palladium catalysis allows us to introduce aryl or alkenyl groups to reach a new family of 1,3-dimethylenecyclobutanes.

Allene MeCH═C═CHB(pin) (pin = pinacol) was treated under the same conditions as **1**, giving a complex mixture of stereoisomers. The introduction of substituents on the allene carbon chain is known to modify both reactivity and selectivity.[12]

The ability of [Cp*RuCl(COD)] **2** to dimerize allene **1** to give 1,3-dimethylenecyclobutane contrasts well with the codimerization of allene with unsaturated ketones by [CpRuCl(COD)]/$CeCl_3$, which involves the substituted allene double bond.[16]

The observed allene dimerization regioselectivity benefits from both pinacol boronate and bulky C_5Me_5 group nature. A direct access to **4a** from phenylallene dimerization catalyzed by **2** gives a mixture of **4a**, **4b**, and 1,2-diphenyl-3,4-dimethylenecyclobutane **7**[17] (in 2:1:3 ratio), showing a lack of regioselectivity (head-to-head versus tail-to-tail coupling) with respect to allenyl boronate **1**.

To obtain a better regioselectivity with phenylallene dimerization, the use of a more sterically hindered ruthenium site was attempted (Scheme 4). The reaction of phenylallene in the presence of 10 mol % $[Cp^*Ru(PPh_3)(MeCN)_2][PF_6]$ (**8**) in DMF at 110 °C for 6 h gave the tail-to-tail coupling compound **7**, isolated in 44% yield.

In conclusion, a new route to the previously inaccessible disubstituted 1,3-dimethylenecyclobutanes has been opened by sequential ruthenium/palladium catalysis from readily available materials by a simple experimental protocol. Ongoing studies aim to develop the functionalization of dimer **3** through the rich boron chemistry and search the access to new polymeric materials bearing rigid cyclobutane units.

Acknowledgment. We are grateful to the E.U. (COST D17) for support and for the "Marie Curie" Fellowship to E.B.

Supporting Information Available: Crystallographic data of **4a** and experimental procedures for all new compounds (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88.
(2) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 3927.
(3) (a) Zhang, D. Y.; Borden, W. T. *J. Mol. Struct.* **2000**, *556*, 151. (b) Misiolek, A. W.; Jackson, J. E. *J. Am. Chem. Soc.* **2001**, *123*, 4774. (c) Zhang, D. Y. *J. Phys. Org. Chem.* **2001**, *14*, 295. (d) Zhang, D. Y.; Borden, W. T. *J. Org. Chem.* **2002**, *67*, 3989.
(4) (a) Rajca, A. *Chem. Rev.* **1994**, *94*, 871. (b) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385. (c) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179. (d) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* **1988**, *21*, 114.
(5) (a) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 1774. (b) Dowd, P.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 2788.
(6) Hill, B. T.; Squires, R. R. *J. Chem. Soc., Perkin Trans.* **1998**, *2*, 1027.
(7) Horner, M.; Hünig, S. *J. Am. Chem. Soc.* **1977**, *99*, 6120. By photochemical [2 + 2] cyclodimerization of styrylpyridinium salts followed by deprotonation.
(8) With 37% overall yield. Caserio, F. F.; Parker, S. H.; Piccolini, R.; Roberts, J. D. *J. Am. Chem. Soc.* **1958**, *80*, 5507.
(9) (a) Blomquist, A. T.; Verdol, J. A. *J. Am. Chem. Soc.* **1956**, *78*, 109−112. (b) Borden W. T.; Reich, I. L.; Sharpe, L. A.; Weinberg, R. B. *J. Org. Chem.* **1975**, *40*, 2438.
(10) Murakami, M.; Matsuda, T. Cycloaddition of Allenes. In *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds., Wiley-VCH: Weinheim, Germany, 2004; pp 727−815.
(11) Braverman, S.; Freund, M.; Reisman, D.; Goldberg, I. *Tetrahedron Lett.* **1986**, 1297−1300. Obtained by butyllithium-promoted dimerization of γ,γ-dimethylallenyl phenyl sulfone.
(12) Saito, S.; Hirayama, K.; Kabuto, C.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 10776−10780.
(13) (a) Le Paih, J.; Derien, S.; Bruneau, C.; Demerseman, B.; Toupet, L.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2912. (b) Le Paih, J.; Monnier, F.; Dérien, S.; Dixneuf, P. H.; Clot, E.; Eisenstein, O. *J. Am. Chem. Soc.* **2003**, *125*, 11964.
(14) MP2, DFT (B3PW91), and RHF theoretical methods involving the 6-311++G** basic set: Rode, J. E.; Dobrowolki, J. C.; Jamroz, M. H.; Borowiak, M. A. *Vib. Spectrosc.* **2001**, *25*, 133.
(15) Yoon, C. H.; Yoo, K. S.; Yi, S. W.; Mishra, R. K.; Jung, K. W. *Org. Lett.* **2004**, *6*, 4037.
(16) Trost, B. M.; Pinkerton, A. B. *J. Am. Chem. Soc.* **1999**, *121*, 4068.
(17) Blomquist, A. T.; Meinwald, Y. C. *J. Am. Chem. Soc.* **1960**, *82*, 3619.

JA051930R