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# Fritsch–Buttenberg–Wiechell Rearrangement in the Aliphatic Series

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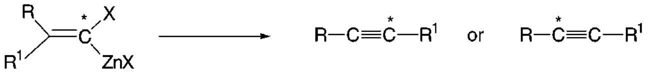
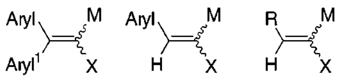
## ABSTRACT



**Substituted vinylidene zinc carbenoids undergo a Fritsch–Buttenberg–Wiechell rearrangement. The migratory aptitude of the two groups R/R$^1$ was studied by $^{13}$C labeling experiments and depends on the degree of substitution in R and R$^1$ groups and on the presence of an oxygen atom in the allylic position.**

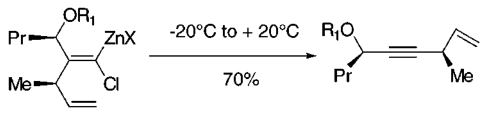
Vinylidene carbenoids of type **1**, **2**, or **3**[1] (Figure 1), derived from alkaline metals, are known to rearrange to alkynes (Fritsch−Buttenberg−Wiechell rearrangement)[2] in good yields. Recently, we have shown[3] that this rearrangement of zinc carbenoids of type **4** also leads to alkynes **5** in good yields (Scheme 1).



**1** **2** **3**

**Figure 1.** Carbenoids prone to rearrangement.

**Scheme 1**



**4** **5**

We have also demonstrated that the rearrangement from **4** to **5** occurs with complete retention of the starting configuration, although we had not proven the indentity of the migrating carbon.[3] In this paper, we address the latter question.

In diaryl-substituted systems of type **1**, it has been proven by $^{14}$C labeling that the major migrating group is the aryl moiety located *anti* to the halogen.[4] Such a stereoselectivity in the migration has been explained by large distortions of angles and elongation of the C−X bond as shown by X-ray diffraction in lithio and magnesio carbenoids.[5] However, in the case of **4**, the effect of the oxygen versus the vinyl substituent on the migrating atoms was uncertain. It has been

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[1] (a) Corey, E. J.; Fuchs, D. L. *Tetrahedron Lett.* **1972**, 3769−3772. (b) Harada, T.; Katsuhira, T.; Hara, D.; Kotani, Y.; Maejima, K.; Kaji, R.; Oku, A. *J Org. Chem.* **1993**, *58* 4897−4907. (c) Fischer, D. R.; Williamson, B. L.; Stang, P. J. *Synlett* **1992**, 535−536. (d) Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274−285. (e) Ben-Efraim, D. A. *The chemistry of carbon−carbon triple bond*, part 2; Wiley and Sons: New York, 1978; pp 773−776 and references therein. (f) Viehe, H. G. *Chemistry of acetylenes*; Marcel Dekker: New York, 1969; pp 117−134. (g) Moss, R. A.; Jones, M., Jr. *Carbenes*, Vol. II; Wiley and Sons: New York, 1975; p 44. (h) Erickson, K. L.; Wolinsky, J. *J. Am. Chem. Soc.* **1965**, *87*, 1142−1143. (i) Fienemann, H.; Köbrich, G. *Chem Ber*. **1974**, *107*, 2797−2803.

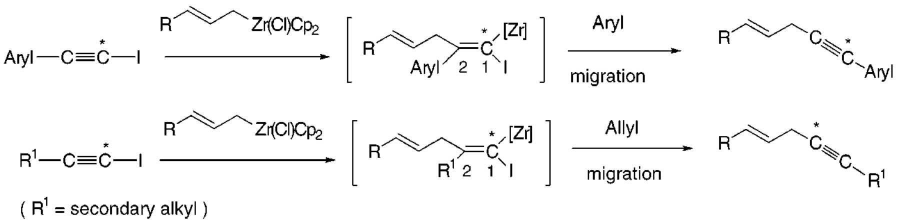
[2] Fritsch, P. *Liebigs Ann. Chem.* **1894**, *272*, 319−324. Buttenberg, W. P. *Liebigs Ann. Chem.* **1894**, *272*, 324−337. Wiechell, H. *Liebigs Ann. Chem.* **1894**, *272*, 337−344.

[3] Creton, I.; Rezaei, H.; Marek, I.; Normant, J. F. *Tetrahedron Lett.* **1999**, *40*, 1899−1902.

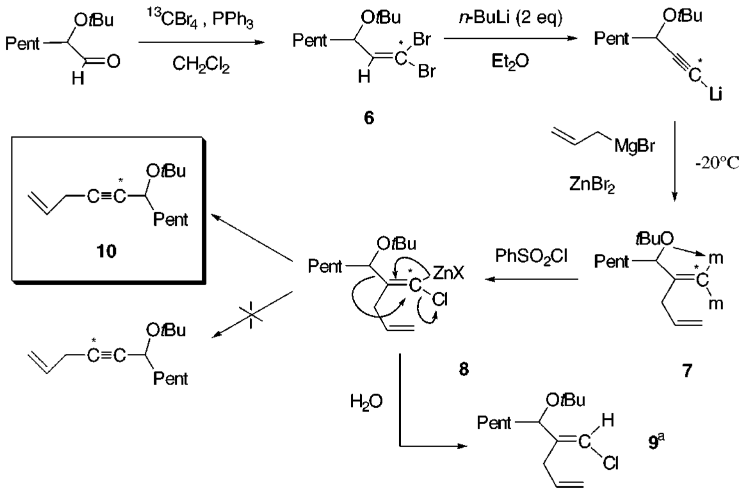
[4] (a) Bothner-By, A. A. *J. Am. Chem. Soc*. **1955**, *77*, 3293−3296. (b) Curtin, D. Y.; Flynn, E. W.; Nystrom, R. F. *J. Am. Chem. Soc.* **1958**, *80*, 4599−4601.

10.1021/ol991117z CCC: $19.00

**Scheme 2**



**Scheme 3**



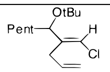
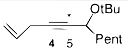
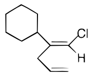
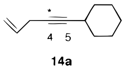
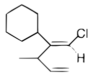
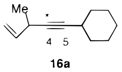
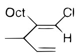
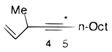
[a] This hydrolytic experiment was made from unlabeled compound **6**.

shown recently[6] that $^{13}$C-labeled vinylidene zirconium−iodo carbenoids bearing an aryl and an allyl moiety on C(2) undergo the aryl migration preferentially, whereas those bearing an alkyl and an allyl moiety on C(2) behave differently (Scheme 2), indicating the exclusive migration of the allyl group when the alkyl $R^1$ group is secondary, whereas both groups migrate if $R^1$ is primary, although in this case the exact geometry of the intermediate carbenoid could not be ascertained.

To further examine an alkyl versus an allyl migration, we prepared labeled **6** from α-*tert*-butoxyheptanal and $^{13}CBr_4$ (Scheme 3). **6** was converted to 1-lithio-3-*tert*-butoxy-1-octyne which was submitted in situ to carbometalation,[7] affording the vinylidene *gem*-bismetallic **7**.

From previous experiments[8] on the corresponding unlabeled starting material, we knew that chlorination of the intermediate vinyl bismetallic **7** by $PhSO_2Cl$ gave **8** stereoselectively, the nonchelated C−ZnX bond being cleaved more readily than the other, and we were pleased to find ($^{13}$C NMR) that the unique enyne **10** was formed by increasing the temperature (Table 1, entry 1), indicating the exclusive migration of the alkoxymethine moiety located *trans* to the chlorine in **8**.

**Table 1.** Fritsch−Buttenberg−Wiechell Rearrangement of Vinylic Chloro Carbenoids

| Entry | Hydrolyzed carbenoid[a] | | E/Z ratio | Rearranged enynes[b] | | Product ratio | Major migrating group |
|---|---|---|---|---|---|---|---|
| 1 |  | **9** | 100 / 0 |  | **10** | - | alkoxy-methine |
| 2 |  | **13** | 33 / 66 | <br>**14a** | + **14b** | **14a** / **14b** = 92/8 | allyl |
| 3 |  | **15** | 66 / 33 | <br>**16a** | + **16b** | **16a** / **16b** = 86/14 | 2-butenyl |
| 4 |  | **17** | 66 / 33 | **18a** + <br>**18b** | | **18a** / **18b** = 33/66 | n-octyl |

[a] Only the major chloroolefin obtained upon hydrolysis of the carbenoid intermediate is represented. [b] Only the major enyne is represented.

The generality of this process was then studied with systems devoid of any chelating heteroatom, and we looked

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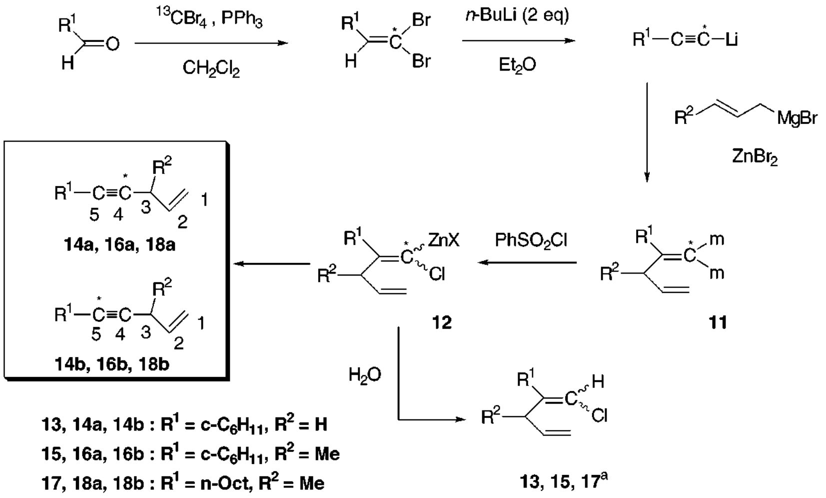
(5) Boche, G.; Marsh, M.; Müller, A.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1032−1033. Boche, G.; Harms, K.; Marsch, M.; Müller, A. *J. Chem. Soc. Chem. Commun.* **1994**, 1393−1394. For an excellent review, see: Braun, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 430−451.

[6] Yamanoi, S.; Matsumoto, T.; Suzuki, K. *Tetrahedron Lett.* **1999**, *40*, 2793−2796.

[7] For a review on the carbometalation reaction, see: Marek, I.; Normant, J. F., *Metal-Catalysed cross-coupling reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; pp 271−337.

[8] Creton, I.; Marek, I.; Normant, J. F. *Synthesis* **1996**, 1499−1508.

**Scheme 4**



[a] These hydrolytic experiments were made from the corresponding unlabeled dibromoalkenes.

at the competitive migration of a secondary or a primary alkyl versus an allyl or 2-butenyl group (Scheme 4).

First, labeled, metalated cyclohexylacetylene was prepared from cyclohexanecarboxaldehyde and $^{13}CBr_4$ as above and submitted to allylzincation. The monochlorination of the bimetallic species **11** ($R^1 = c\text{-}C_6H_{11}$, $R^2 = H$) gave the carbenoid **12** which upon warming delivered the two alkynes **14a** and **14b** in a 12/1 ratio (Table 1, entry 2). However, this ratio is not related to the geometry of the intermediate **12**, as the hydrolysis of the corresponding unlabeled compound led to a mixture of chlorovinyl derivatives **13** (*E/Z* = 1/2).

$^{13}C$ NMR studies on unlabeled **14** allowed us to discriminate C(4) and C(5) via a long-range H−C COSY experiment and thus determine the identity of **14a** and **14b**. The major enyne corresponds to a migration of the allyl moiety, but shows that this happens whatever its initial position, *cis* or *trans* to chlorine. Thus, the total stereoselectivity observed from **8** to **10** is related to the presence of the allylic alkoxy moiety.

The competition between a cyclohexyl and a 2-butenyl group was then considered (Table 1, entry 3). Lithiated cyclohexylacetylene leads to the corresponding chlorovinyl educts **15** (*E/Z* = 2/1), whereas the Fritsch−Buttenberg−Wiechell rearrangement performed on the labeled 1-alkyne shows a predominance of the 2-butenyl migration of 6/1 (lower than allyl migration). Finally, the competition between a primary *n*-octyl and a 2-butenyl group (Table 1, entry 4) showed that from a *E/Z* = 2/1 ratio in **17** the migration of the *n*-octyl group prevails by 2/1: the primary *n*-octyl group, although predominantly *cis* to Cl in **17** (as determined on the unlabeled product), migrates better than the secondary cyclohexyl in **15**. It must be noted that no allylic rearrangement of the 2-butenyl moiety is observed as no linear enyne (tetradec-2-en-5-yne) is detected. Thus, the migrating aptitude of the 2-butenyl group is related more to its substitution order than to its allylic character.

The migrating aptitude of the groups can be classified as follows: alkoxymethine > *n*-octyl >(?) allyl > 2-butenyl > cyclohexyl. Unfortunately, the experiment corresponding to the symbol (?) above cannot be made, because with *n*-alkyl acetylides ($RCH_2C{\equiv}CH$) the allylmetalation does not stop, as is documented,[9] at the desired vinyl bismetallic but instead goes on to the trismetallic derivative $RCH_2(allyl)_2CCM_3$. This relation between substitution and migration seems to be in good agreement with the migration order observed in the "Fritsch−Buttenberg−Wiechell type" rearrangement of true alkylidene carbenes as reported recently. [10]

In summary, the Fritsch−Buttenberg−Wiechell rearrangement in the aliphatic series for zinc carbenoids depends on the migrating aptitude of the groups, whatever the configuration of the carbenoid. Only in the case of allylic ether (**8**) was the selective migration of the alkoxymethine moiety *trans* to chlorine observed.

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**Supporting Information Available:** General experimental procedures, including spectroscopic and physical data, for the preparation of $^{13}C$-labeled dibromoalkenes and compounds **10**, **14**, **16**, and **18** via the tandem alkynyllithium formation−allylzincation−Fritsch-Buttenberg-Wiechell rearrangement. This material is available free of charge via the Internet at http://pubs/acs/org.

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(9) Frangin, Y.; Gaudemar, M. *Bull. Soc. Chim. Fr.* **1976**, 1173. Gaudemar, M. *C. R. Acad. Sci. Paris Ser. C* **1971**, *273*, 1669. Frangin, Y.; Gaudemar, M. *C. R. Acad. Sci. Paris Ser. C* **1974**, *278*, 885.

(10) Graf von der Schulenburg, W.; Hopf, H.; Walsh, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 1128−1130.