Oxidative Coupling of \( \alpha,\omega \)-Di(cyclopentadienyl)alkyl-diides**

Shaochun You [1], Matthias Gubler [2], and Markus Neuenschwander*

**Short Communication; Coupling Reactions, part 8.

Abstract. The CuI-induced oxidative coupling of \( \alpha,\omega \)-di(cyclopentadienyl)alkyl-diides \( 6 (n = 2 \text{ to } 5) \) as well as of 1,1,2,2-tetramethyl derivatives \( 10 \) and \( 13 \) of \( 6a (n = 2) \) has been investigated in view of pertinent questions concerning the ‘coupling mode’ (e.g. intramolecular versus intermolecular coupling), as well as regioselectivity and stereoselectivity of the coupling reaction. As far as the ‘coupling mode’ is concerned, intermolecular coupling \( 6 \rightarrow 8 \) strongly dominates over intramolecular coupling \( 6 \rightarrow 7 \) (Scheme 2) and the yields of intramolecular coupling products strongly decrease from 7\( \% \) \( (7a, n = 2) \) to 1\( \% \) \( (7b, n = 3) \) to traces \( (7c, 7d, n = 4, 5) \). It is interesting to note that intramolecular coupling may be considerably enhanced by replacing the H-atoms of the \( \text{CH}_2\text{CH}_2\) bridge of \( 6a (n = 2) \) by Me groups (see \( 10 \rightarrow 11 \) and \( 13 \rightarrow 14 + 15 \), Scheme 4). As far as regioselectivity is concerned, intramolecular coupling of 1,2-di(cyclopentadienyl)ethene-diides, \( 6a, 10, \) and \( 13 \), proceeds as a clean 2,2’-coupling of the cyclopentadiene rings within the limits of NMR identification. Furthermore, the couplings \( 6a \rightarrow 7a \) and \( 10 \rightarrow 11 \) (as well as \( 13 \rightarrow 14 + 15 \) proceed stereoselectively to give the \( C_2 \)-symmetrical cyclohexanes \( 7a \) and \( 11 \) with a fixed chair conformation.

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Oxidative Coupling of $\alpha,\omega$-Di(cyclopentadienyl)alkyl-diides

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Abstract. The CuII-induced oxidative coupling of $\alpha,\omega$-di(cyclopentadienyl)alkyl-diides 6 (n = 2 to 5) as well as of 1,1,2,2-tetramethyl derivatives 10 and 13 of 6a (n = 2) - has been investigated in view of pertinent questions concerning the 'coupling mode' (e.g. intramolecular vs. intermolecular coupling), as well as regioselectivity and stereoselectivity of the coupling reaction. As far as the coupling mode is concerned, intermolecular coupling 6 $\rightarrow$ 8 strongly dominates over intramolecular coupling 6 $\rightarrow$ 7 (Scheme 2) and the yields of intramolecular coupling products strongly decrease from 7% (7a, n = 2) to 1% (7b, n = 3) to traces (7c, 7d, n = 4, 5). It is interesting to note that intramolecular coupling may be considerably enhanced by replacing the H-atoms of the CH$_2$CH$_2$ bridge of 6a (n = 2) by Me groups (see 10 $\rightarrow$ 11 and 13 $\rightarrow$ 14 $\rightarrow$ 15, Scheme 4). As far as regioselectivity is concerned, intramolecular coupling of 1,2-di(cyclopentadienyl)ethene-diides, 6a, 10, and 13, proceeds as a clean 2,2'-coupling of the cyclopentadiene rings within the limits of NMR identifications. Furthermore, the couplings 6a $\rightarrow$ 7a and 10 $\rightarrow$ 11 (as well as 13 $\rightarrow$ 14 $\rightarrow$ 15) proceed stereoselectively to give the $C_2$-symmetrical cyclohexanes 7a and 11 with a fixed chair conformation.
troscopic investigations show that, as expected, tautomeric cyclopentadienes A and B are dominating, so that in each case five tautomers (with combinations AA, AB, and BB) may be formed. This is supported by the number of lines of the proton noise-decoupled ^13C-NMR spectra. It is easily seen that, with increasing length of the alkyl chain, both rings are completely decoupled from each other so that for the ring C-atoms (with exception of the quarternary ones), there is only one set of lines of type A as well as of type B.

The result of CuCl_2-induced coupling of di(cyclopentadienides) 6 is surprising in so far that the yields of intramolecular coupling products are very small even in the case of 7a (\(n = 2\)) and in dilute solutions, and they rapidly decay to zero with increasing \(n\).

Regioselectivity and stereoselectivity of intramolecular coupling 6 \(\rightarrow\) 7 have been investigated in the case 6a \(\rightarrow\) 7a (\(n = 2\)), where all the spectra clearly show that only one diastereoisomer with the molecular formula C_{12}H_{12} has been formed, being consistent with structure 7a: first of all the M^+ as well as the intensity of the isotope peaks are consistent with the molecular formula C_{12}H_{12}. It is interesting to see that the basic MS fragmentation is the formation of two units of C_6H_6 (which is very reasonable for structure 7a). In the UV spectrum, the long-wavelength absorption at 249 nm fits to the presence of cyclopentadiene rings. In the ^13C-NMR spectrum, the lines of one quarternary (150.1 ppm), three tertiary vinylic C-atoms (\(\delta 35.4\); \(\delta 32.3\); \(\delta 23.7\) ppm) and one tertiary alkyl-C-atom (\(\delta 6.3\) ppm) are in agreement with two symmetrically placed cyclopentadiene rings, while the original CH_2CH_2 bridge generates one signal at 27.1 ppm. The conclusion from the spectroscopically confirmed structure 7a (\(n = 2\)) is that

Obviously in both cases 1 and 3, intramolecular oxidative coupling is significant, although the preparative yields are considerably decreasing from 73% (2 [5]) to 24% (4 [8]). If one assumes that \(\alpha,\omega\)-di(cyclopentadienyl) diradicals are formed by oxidative treatment of dianions of type 1 and 3 [9] then the chances for an intramolecular bond formation are ideal for 1, and they are expected to dramatically decrease with increasing length of the alkyl chain between the rings. On the other hand, the chances of polymer formation by intermolecular coupling should increase in the same series; these polymers with cyclopentadiene units in the chain should be very reactive.

Besides the questions concerning the competition between intramolecular/intermolecular coupling, regioselectivity as well as stereoselectivity of coupling reactions are of interest as well. In this context, we investigated the Cu^II-induced coupling of a series of \(\alpha,\omega\)-di(cyclopentadienyl)alkyl-diides with varying length of the alkyl chain.
Similarly to other polymers with cyclopentadiene units [14], powdered polymers 8 are very easily cross-linked by traces of oxygen so that an investigation of polymer solutions was impossible [15]. Therefore, solid-state NMR experiments have been performed [16]. Despite relatively broad lines, the 13C-NMR results of the polymers 8 are completely compatible with the proposed structure, and chemical shifts of the observed signals are very similar to those of the corresponding monomeric α,ω-di(cyclopentadienyl)alkanes (Table).

### Table. 13C-NMR Results (δ in ppm) of α,ω-Di(cyclopentadienyl)alkanes 5 and Polymers 8

<table>
<thead>
<tr>
<th>No.</th>
<th>5a-5d</th>
<th>8a-8d</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a-5d</td>
<td>146.8-149.4 126.0-134.7 41.3-43.4 –</td>
<td>29.3-30.9</td>
</tr>
<tr>
<td>5b-5e</td>
<td>146.9-149.8 125.9-134.8 41.2-43.3 –</td>
<td>27.9-30.5</td>
</tr>
<tr>
<td>5f-5g</td>
<td>147.2-150.0 125.8-134.8 41.2-43.5 –</td>
<td>28.6-32.4</td>
</tr>
<tr>
<td>5h-5i</td>
<td>147.4-150.2 125.8-135.0 41.3-43.6 –</td>
<td>28.7-31.2</td>
</tr>
<tr>
<td>8a-8d</td>
<td>145° (128-130°) 41-42° (54-64°)</td>
<td>30-31°</td>
</tr>
</tbody>
</table>

* 100 MHz, CDCl3  
* Solid-state NMR (Bruker AMX) under MAS conditions.  
* Center of the broad peak.

Expansions of the high-resolution 1H-NMR spectrum of 7a are shown in Fig. 1. The most interesting features are the complex pattern of the H-atoms of the CH2CH2 bridge as well as of the vinylic H-atoms of the cyclopentadiene rings [13]. Decoupling of H-3(H-C(5)) at 1.60 ppm gives an AB-type spectrum of the remaining vinylic protons of the cyclopentadiene rings with a typical JAB = 5.41 Hz (Fig. 1). Furthermore, the AA'XX'-type spectrum centered at 2.82 and 2.33 ppm, although still slightly disturbed by further small long-range coupling, allows an approximate analysis. The system is characterized by a geminal 2J-coupling (JAA = -12.5 Hz), a large 3J-coupling (JAB = 13.75 Hz), and two small to medium 2J-couplings (JAA' = 2.15 Hz and JAX' = 5.45 Hz). These couplings convincingly prove the C2-symmetrical cyclohexane chair arrangement of 7aD.

Scheme 4

```
\begin{align*}
9 & \xrightarrow{2 \text{ BuLi} \text{ THF} \text{-30°C}} 10 \\
12 & \xrightarrow{2 \text{ MeLi} \text{ THF} \text{ 0°C}} 13 \\
14 & \xrightarrow{\text{CuCl}_2} 15
\end{align*}
```
which is supposed to be the favourable conformation in view of an intramolecular coupling of type 6a → 7a. Due to the fact that a formal replacement of the H-atoms of the CH₃CH₂CH₂ bridge of 5a (n = 2) by Me groups is relatively easy, we decided to investigate the Cuᴵᴵ induced oxidative coupling of di-anions 10 and 13 in more detail (Scheme 4).

2,3-Dimethyl-2,3-di(cyclopentadienyl)butane (9) is quite easily available by reductive coupling of two molecules of 6,6-dimethylpentafulvene in the presence of Na [18]. Recently, we used this coupling in another context for the Thiele-synthesis of 2,3-dimethyl-2,3-di[(6,6-dimethyl)pentafulvenyl]butane (12), which is isolated in a high yield of 90-95% [19]. Deprotonation 9 → 10 is realized by addition of 2 mol-equiv. of BuLi to the THF solution of 9 at −30°C. If the solution of the di-anion 10 is slowly added to a slurry of abs. CuCl₂ in THF, then 7,7,8,8-tetramethyltricyclo[7.3.0.0²⁶]dodeca-3,5,9,11-tetraene (11) is formed in a 59% yield [20]. Similarly, di-anion 13 may be elegantly prepared by nucleophilic attack of MeLi at the exocyclic C-atoms of the fulvene units of difufulene 12, a reaction which is well known for simple pentafulvenes [21]. Adding the solution of the resulting di-anion 13 to a slurry of abs. CuCl₂ in abs. THF gives a mixture of 4, 11-(14) and 3,11-di(tert-butyl) derivatives 15 with 34 and 20% yields [20]. Out of this mixture, C₂-symmetrical compound 14 has been isolated.

The structure of the isolated triyclic compounds 11 and 14 follows from the spectroscopic data which show close similarities to those of 7a (n = 2). In both cases, the basic MS peak corresponds to M⁺/2, and in the UV, the cyclopentadiene rings absorb at 248 nm. In the ¹³C-NMR spectrum, the chemical shifts of 14 and 11 show the expected trends compared with 7a. In the ¹H-NMR spectrum of 11, the chemical shifts as well as the splitting pattern of the protons support the proposed structure (besides the configuration): Irradiation of H-C(1)/H-C(2) at 2.4 ppm makes the clean ABX system of the vinylic protons visible and allows an unambiguous assignment of these protons.

There are more problems in distinguishing the boat arrangement C from the C₂-symmetrical chair arrangement D (see formula) although the chemical shifts of the Me groups seem to be quite typical for axial (0.90 ppm) and equatorial (1.24 ppm) Me groups of cyclohexanes of type D. Unfortunately, extensive NOE experiments [22] proved to be not very conclusive, so that the boat conformation may not be completely ruled out. The C₂-symmetrical chair arrangement may be unambiguously proved by adding chiral shift reagents resulting in a splitting of most of the NMR signals of Fig. 2 [23].

These results convincingly show that the intramolecular coupling mode 6a → 7a may be considerably enhanced by replacing the H-atoms of the CH₃CH₂CH₂ bridge of di-anion 6a (n = 2) by Me groups (see 10 → 11) possibly by favouring gauche-conformations F which should be ideal for the envisaged intramolecular process. All the intramolecular couplings 6a → 7a, 10 → 11, and 13 → 14 are regioselective and involve a 2,2'-coupling of the cyclopentadiene units. Within the limits of high-field NMR identification, these couplings proceed stereoselectively to give the C₂-symmetrical compounds 7a (n = 2), 11, and 14 in which the cyclohexane ring is arranged in a fixed chair conformation.

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[9] It is interesting to note that a marked colour change is observed during the reaction 1 → 2: the starting brownish colour of the slurry of anh. CuCl₂ in THF turns to an intense green during reaction at −78°C. The final colour of the mixture is deep red, corresponding to 2, while colourless CuCl has been precipitated.
[10] Preparative yields. Yields of polymers B after purification by precipitation in MeOH, filtration under Ar, rinsing with MeOH, and drying at 10⁻² Torr/RT. for 3–5 h.
[11] Aαβ(Dicyclopropenyl)ene of type 5 have been first prepared in solution by A. Lüttringhaus, W. Kulick, Makromol. Chem. 1961, 46, 569. Additionally, we isolated compounds 4a-d and 8a-d in ca. 70% yields and characterized them spectroscopically. Due to easy Diels-Alder polycondensation [12], they have to be stored at low temperature.
[13] Both, the AA'XX' system of the H-atoms of the CH₂=CH₂ bridge as well as the ABX-type spectrum of the vinylic H-atoms are complicated by additional small couplings (Fig. 1, above).
[15] The presence of oxygen was demonstrated by elemental analysis of polymers 8. After deduction of oxygen, C/H percentages, reasonably (but not exactly) fitting to the expected structural elements B have been obtained.

We are grateful to Bruker Spectrospin AG, Ful- landen, Switzerland for solid-state NMR experiments under 'magic angle spinning' (MAS) conditions.

According to MMII force-field calculations (QCPE, version 1980), the energy differences between E and F are 1.1 kcal/mol in favour of E for protons (R = H) and only 0.4 kcal/mol in favour of E for Me groups (R = Me). This clearly shows that in the conformational equilibrium E → F is more important for R = Me than for R = H.


M. Fischer, M. Neuenwander, unpublished results.

[16] The final colour of the mixture chromes 10 and 11 gives the diastereomemic mixture of 8 (R = H) and 11, respectively. Due to easy Diels-Alder polycondensation [12], they have to be stored at low temperature.

Fig. 2. ¹H-NMR Spectrum (300 MHz, CDCl₃) of 11 with expansions of the vinylic range after decoupling at 2.4 ppm (above)

**Fig. 2.** ¹H-NMR Spectrum (300 MHz, CDCl₃) of 11 with expansions of the vinylic range after decoupling at 2.4 ppm (above)