121. Oxidative Coupling of α,ω-Di(cyclopentadienyl)alkane-diides[1])

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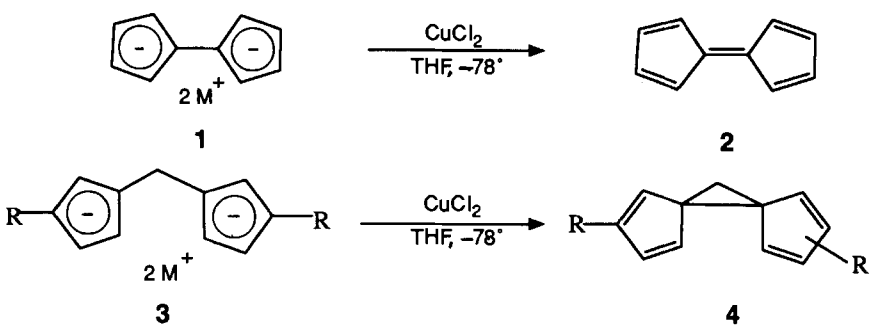
(17.V.94)

The Cu^{II}-induced oxidative coupling of α,ω-di(cyclopentadienyl)alkane-diides **6** ($n = 2$–5) has been shown to proceed mainly by an intermolecular pathway to give polymers **8**, while the yield of intramolecular coupling **6** → **7** strongly decreases with increasing number n of C-atoms of the alkyl chain (*Scheme 3*). For $n = 2$, intramolecular coupling may be considerably enhanced by replacing the H-atoms of the CH_2CH_2 bridge of **6a** ($n = 2$) by Me groups. In this case, intramolecular couplings **11** → **20** (*Scheme 7*) and **22** → **23** + **24** (*Scheme 8*) are accomplished with a total yield of 59% and 54%, respectively. All the intramolecular couplings investigated so far proceed stereoselectively to give the C_2-symmetrical cyclohexanes **7a**, **20** and **23** with a fixed chair conformation. These results are easily explained, if a conformational equilibrium **E** ⇄ **F** is operative in which large substituents R are assumed to enhance the *gauche*-conformation **F** which is the favored conformation for intramolecular couplings. Bridged dihydropentafulvalenes **20** and **23** are quantitatively rearranged to the thermodynamically favored bridged pentafulvenes **27** and **28** under base or acid catalysis, respectively (*Scheme 9*).

1. Introduction. – More than three decades ago, *Doering* observed that cyclopentadienide reacts in the presence of iodine to give bi(cyclopentadienyl) in an undisclosed yield; after twofold deprotonation (to give **1**) and bubbling air through the solution, he was the first to identify pentafulvalene (**2**) by its UV spectrum [5]. This observation remained nearly unnoticed for a long time, until *Hafner* and coworkers applied the same sequence to the synthesis of di- and tetra(*tert*-butyl)pentafulvalenes [6]. Later, we realized that bi(cyclopentadienyl) may be prepared nearly quantitatively by oxidative coupling of sodium cyclopentadienide in the presence of $CuCl_2$. After deprotonation (to give **1**) treatment of dilithiobi(cyclopentadienyl)diide (**1**) with $CuCl_2$ gives unstable pentafulva-

Scheme 1



[1]) Coupling Reactions, Part 13; Part 12: [1], Short Communication: [2].

[2]) Part of the dissertation [3].

[3]) Part of the diploma work [4].

lene (**2**) in a high yield [7] (*Scheme 1*). This experimental improvement resulted in the synthesis of several so far unknown parent fulvalenes [8].

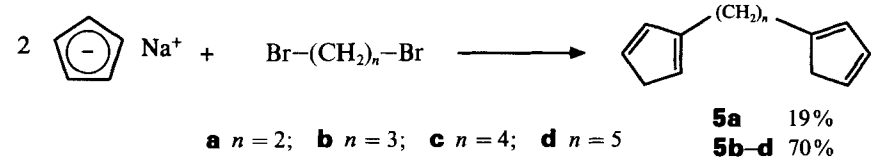
It would be interesting to look at the coupling behavior of homologous α,ω-di(cyclopentadienyl)alkane-diides in the presence of $CuCl_2$, which could give rise either to novel tricyclic compounds or to polymers. A few years ago, *Hafner* and *Thiele* investigated the Cu^{II}-induced reaction of disodiumdi(cyclopentadienyl)methanediide (**3**, R = H) [9] and convincingly demonstrated that intramolecular oxidative coupling **3** → **4** is an important pathway[4]). Even more interesting is the fact that compounds **4** (R = H as well as *t*-Bu), on heating in pentane, are stereoselectively rearranged to cyclopenta[*a*]pentalenes [9].

Obviously, in both cases **1** and **3**, intramolecular oxidative reaction is significant, although the preparative yields are considerably decreasing from 73% (**2** [7]) to 24% (**4** [9]). If one assumes that α,ω-di(cyclopentadienyl) diradicals are formed by oxidative treatment of dianions of type **1** and **3**[5]), then the chances for an intramolecular bond formation are ideal for **1**, and they are expected to substantially decrease with increasing length of the alkanediyl 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 questions concerning the competition between intramolecular/intermolecular coupling, the regioselectivity as well as the stereoselectivity of the coupling reactions is of interest as well. In this context, we investigated the Cu^{II}-induced coupling of a series of α,ω-di(cyclopentadienyl)alkane-diides with varying length of the alkyl chain.

2. Oxidative Coupling of Homologous α,ω-Di(cyclopentadienyl)alkyl-diides (6) (*n* = 2–5). – 2.1. *Synthesis and Structure of α,ω-Di(cyclopentadienyl)alkanes* (**5**). α,ω-Di(cyclopentadienyl)alkanes (**5**) are quite easily synthesized by reaction of an excess of sodium cyclopentadienide with the corresponding α,ω-dibromoalkanes at −30 to 0° [4] [10][6]). After low-temperature filtration over silica gel with pentane and evaporation of solvents nearly colorless oils **5b–d** are isolated with yields of *ca.* 70% (*Scheme 2*)[7]). In the

Scheme 2



[4]) Similarly, **3** (R = *t*-Bu) on treatment with $CuCl_2$ gives the diastereoisomeric mixture of **4** (R = *t*-Bu) in an undisclosed yield. The preparative yield of **4** (R = H) is 24%.

[5]) It is interesting to note that a marked color change is observed during reaction **1** → **2**. The starting brownish color of the slurry of anhydrous $CuCl_2$ in THF turns to intense green during reaction at −78°. The final color of the mixture is deep red, corresponding to **2**, while colorless $CuCl_2$ has been precipitated.

[6]) Solution of α,ω-di(cyclopentadienyl)alkanes of type **5** have been prepared earlier in solution [10]. Additionally, we isolated and characterized them spectroscopically [4]. Due to easy *Diels-Alder* polycycloadditions [11], they have to be stored at low temperature.

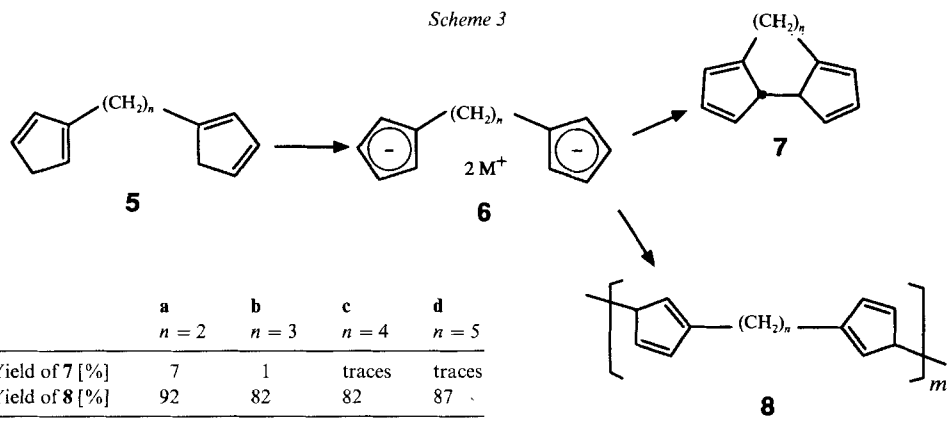
[7]) Besides traces of pentane, compounds **5a–d** are surprisingly pure according to 300-MHz ^{1}H-NMR and 75-MHz ^{13}C-NMR spectra.

case of **5a**, the yield drops to 19% due to the well-known intramolecular cyclization of the intermediary formed ω-(bromoethyl)cyclopentadienide to give spiro[2.4]heptadiene [12] [13]. To avoid polycycloadditions [11], all the products **5a–d** have to be stored at −70°, although they may be easily handled in solutions.

The structure of compounds **5a–d** follows from spectroscopic investigations which clearly show that, as expected due to easily occurring [1,5]-H shifts [14], the isomeric cyclopentadienes with the structure elements **A** and **B** are dominating so that in each case three isomers (with combination **AA**, **AB**, and **BB**) may be formed. This is demonstrated by the number of lines in the proton-decoupled ^{13}C-NMR spectra. It is easily seen that, with increasing length of the alkanediyl chain, both rings are more and more decoupled from each other so that for the ring-C-atoms of **5d** there is, with exception of the quarternary C-atoms, only one set of lines of type **A** as well as of type **B**.

2.2. *Oxidative Coupling.* Dianions of type **6** are easily formed by deprotonation of α,ω-di(cyclopentadienyl)alkanes with BuLi in THF at −30° (*Scheme 3*). To the resulting suspension[8]), 2 mol-equiv. of powdered $CuCl_2$ are added at −30°[9]). After stirring 1 h at −30°, the resulting reaction mixture is either filtered through deactivated silica gel in order to obtain intramolecular coupling products **7**, or slowly added to MeOH in order to precipitate polymers **8**. These polymers are further rinced with MeOH and dried at 10^{-2} Torr, while tricyclic compound **7a** is purified by chromatography and distillation in vacuum.

Scheme 3



	a $n=2$	b $n=3$	c $n=4$	d $n=5$
Yield of **7** [%]	7	1	traces	traces
Yield of **8** [%]	92	82	82	87

The result of the $CuCl_2$-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** in dilute solutions, and they rapidly approach zero with increasing number (n) of CH_2 units. It is interesting to note that the yield of **7a** decreases from 7 to 5% if the reaction takes place at −100° instead of −30°.

2.3. *Structure of Intramolecular Coupling Products.* While coupling of di(cyclopentadienides) **6c** ($n = 4$) and **6d** ($n = 5$) gives only traces of intramolecular coupling products (of presumed structure **7c** and **7d**), isolation of small amounts of **7b** proved to be

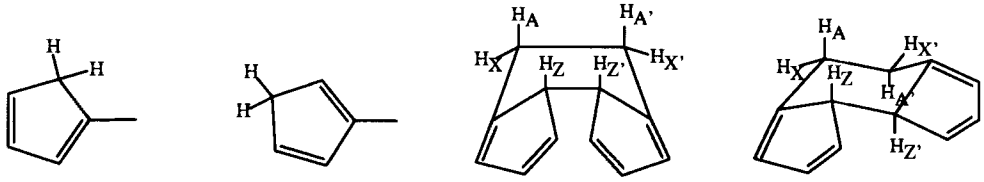
[8]) In most cases, the Li salts of the dianions **6** are precipitating.

[9]) During reaction, brownish $CuCl_2$ slowly dissolves, and color changes from brown to green are observed.

extremely difficult, because HPLC separation from 1,3-di(cyclopentadienyl)propane **5c** was impossible. ^{1}H- as well as ^{13}C-NMR data as well as $M^{+\cdot}$ and MS fragmentations are compatible with tricyclic structure **7b**, but do not definitely prove it.

Regioselectivity and stereoselectivity of intramolecular coupling **6** → **7** have been investigated in the case **6a** → **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 $M^{+\cdot}$ as well as the intensity of the isotope peaks are consistent with $C_{12}H_{12}$. Furthermore, the basic MS fragmentation corresponds to the formation of two C_6H_6 units[10]). In the UV spectrum the long-wavelength absorption at 249 nm is in accordance with the presence of cyclopentadiene rings.

In the ^{13}C-NMR spectrum of **7a**, the lines of one quarternary (150.1 ppm), three tertiary vinylic C-atoms (135.4, 132.3, 123.7 ppm), and of one tertiary alkyl-C-atom (56.3 ppm) are in agreement with two symmetrically oriented cyclopentadiene rings, while the original CH_2CH_2 bridge gives rise to one signal at 28.2 ppm. The conclusion from the spectroscopically confirmed structure **7a** ($n = 2$) is that the coupling mode is not a 1,1-coupling but a 2,2′-coupling of the di(cyclopentadienyl)diide **6a**. The central problem in determining the steric course of the coupling step is to distinguish between achiral **7aC** (having a mirror plane) and C_2-symmetrical **7aD** (see *Formula*).



A **B** **7aC** **7aD**

Expansions of the high-resolution ^{1}H-NMR spectrum (during irradiation of the broad signal of a vinylic H-atom at 6.163 ppm) are shown in *Fig. 1*. The most interesting feature is the complex pattern of the H-atoms of the CH_2CH_2 bridge, centered at 2.822 and 2.320 ppm, which is an $AA'XX'$-type spectrum being slightly disturbed by further small long-range couplings. An approximate analysis gives a geminal ^2J coupling ($J_{AX} = -12.5$ Hz), a large ^3J coupling ($J_{AA'} = 13.75$ Hz), and two small-to-medium ^3J couplings ($J_{XX'} = 2.15$ Hz and $J_{AX'} = 5.45$ Hz). These couplings convincingly established the C_2-symmetrical cyclohexane chair arrangement of **7aD**. Furthermore, the J_{AB} coupling of 5.41 Hz of the two olefinic protons at 6.502 and 6.484 ppm is consistent with the presence of a cyclopentadiene CH=CH bond.

2.4. *Structure of Polymers* **8**. Similarly to other polymers with cyclopentadiene units [15], powdered polymers **8** are very easily cross-linked by traces of oxygen[11]) so that an investigation of **8** in solution was impossible. Therefore, solid-state NMR experiments

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[10]) This is very reasonably for **7a** ($n = 2$) where fragmentation of both allylic C–C bonds can easily give two fulvenyl units. As expected, this type of fragmentation is not relevant for **7b** ($n = 3$).

[11]) The presence of oxygen was demonstrated by elemental analysis of polymers **8**. After deduction of oxygen, C,H percentages are reasonably (but not exactly) fitting to the expected structural elements **8**.

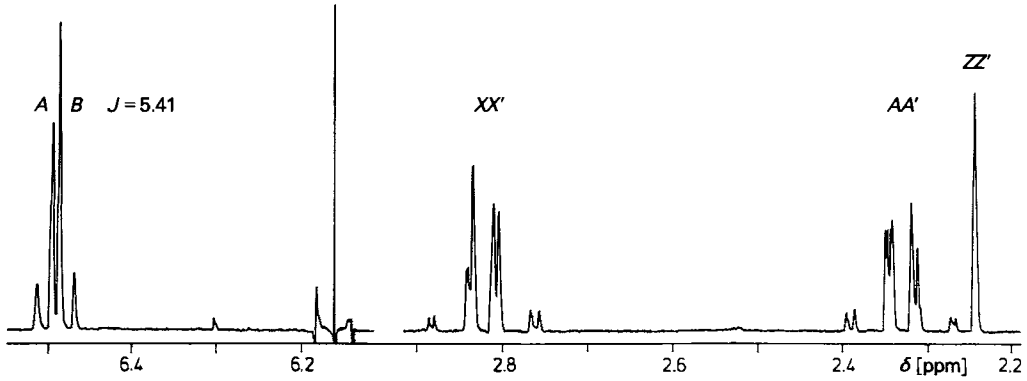


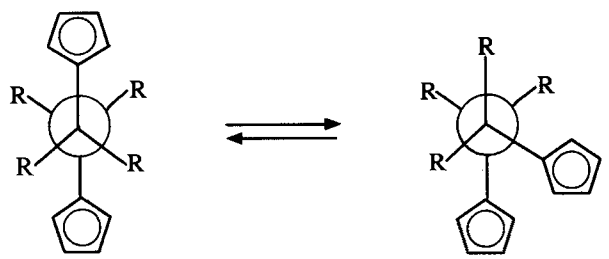
Fig. 1. *^{1}H-NMR Spectrum* (300 MHz, $CDCl_3$) *of* **7a** ($n = 2$) *with expansions of the vinylic and the alkyl range during irradiation at 6.16 ppm*

have been performed. Despite relatively broad lines, the ^{13}C-NMR results of polymers are completely compatible with the proposed structure[12]), and chemical shifts of signals are very similar to those of the corresponding monomeric α,ω-di(cyclopentadienyl)alkanes **5**.

2.5. *Conclusions.* The most important conclusion is that the oxidative coupling of α,ω-di(cyclopentadienyl)alkane-diides **6** predominantly proceeds by an intermolecular mode (even in dilute solutions) to give reactive polymers **8** in high yields. This is especially surprising for deprotonated α,ω-di(cyclopentadienyl)alkane **6a** where we expected a much higher extent of the intramolecular coupling **6a** → **7a** ($n = 2$). A reasonable tentative explanation is that, even in the case of **6a** ($n = 2$), the reacting species (possibly the diradical) is reacting out of the conformation with two *trans*-diaxial cyclopentadiene rings, while the transition metal obviously does not seem to enhance intramolecular coupling.

In this case, it would be interesting to replace the H-atoms of the CH_2CH_2 bridge of **6a** by larger substituents in order to increase the importance of the *gauche*-conformation **F** in the equilibrium **E** ⇌ **F**[13]) (*Scheme 4*) which is supposed to be the favorable conforma-

Scheme 4



E **F**

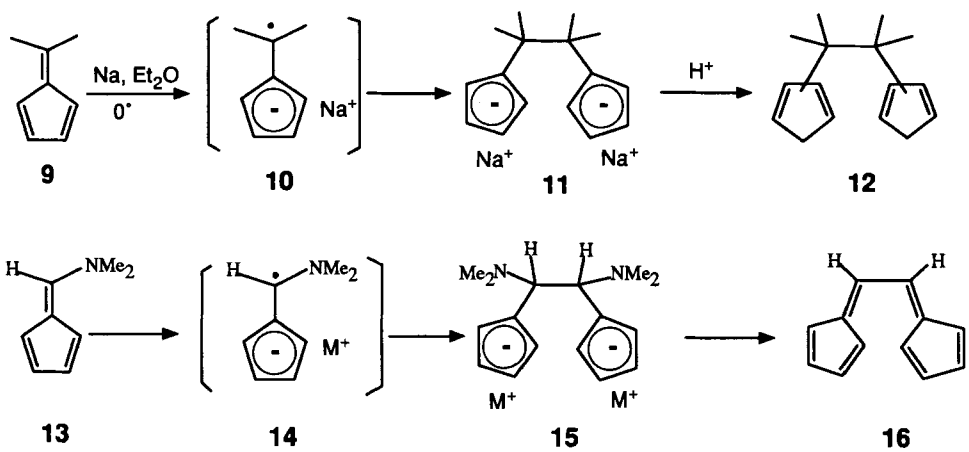
[12]) All the polymers **8a–d** are characterized by broad lines in the ranges of 145, 128–130, 41–42, 54–64, and 30–31 ppm. See the Table in [2].

[13]) This argument is supported by force-field calculations; see later.

tion in view of an intramolecular coupling of type **6a** → **7a**. Due to the fact that a formal replacement of the H-atoms of the CH_2CH_2 bridge of **5a** ($n = 2$) by Me groups is relatively easy, we decided to investigate the Cu^{II}-induced oxidative coupling of di-anions **12** and **21** in more detail.

3. Oxidative Coupling of 2,3-Dimethyl-2,3-di(cyclopentadienyl)butanediide (11). – 3.1. *Synthesis of 2,3-Dimethyl-2,3-di(cyclopentadienyl)butane* (**12**). Compound **12** is available in yields up to 50%[14]) by reductive coupling of two molecules of 6,6-dimethylpentafulvene (**9**) in the presence of Na metal according to *Rinehart et al.* [16]. The reaction is assumed to proceed over fulvenyl radical anion **10** which, after coupling **10** → **11** and protonation, gives the di(cyclopentadiene) **12** (*Scheme 5*). In a recent paper [17], *Oda* and coworkers reported on the reductive coupling of 6-(dimethylamino)pentafulvene (**13**) in the presence of Li-naphthalenide for which a similar sequence **13** → **14** → **15** may be anticipated. Due to the leaving groups of dianion **15**, elimination of Me_2N^- smoothly gives 6,6′-bifulvenyl **16**. This result motivated us to investigate the reductive coupling **9** → → **12** in the presence of Li- or Na-naphthalenide as well, with the disappointing result that the yields of **12** were only in the range of 15–25% [3].

Scheme 5

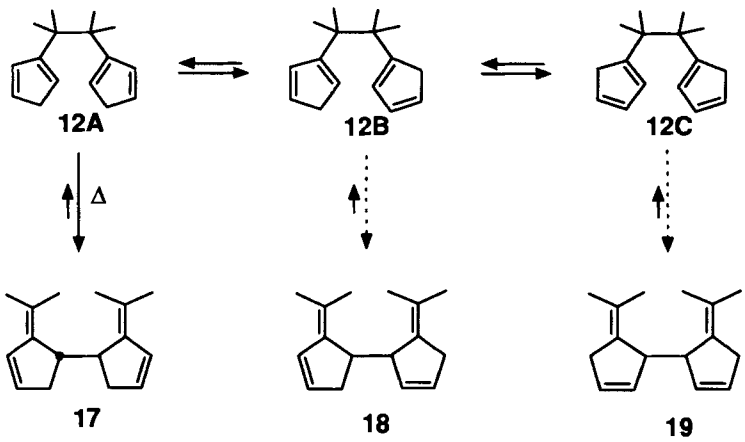


3.2. Cope *Rearrangement of* **12**[15]). The mixture of tautomers **12** is quite instable even in dilute solutions at room temperature and nearly quantitatively isomerizes to 1,1′-bi(2-isopropylidenecyclopent-3-enyl) **17** (*Scheme 6*). This result is easily explained by a [3,3] sigmatropic shift starting with **12A**. On the basis of an ^{1}H-NMR analysis at 300 MHz, no other isomer is formed. The structure of **17** is unambiguously assigned by spectroscopic methods [13] which exclude isomers **18** and **19**. In the UV spectrum, a characteristic

[14]) This is true for scales up to 8 mmols [13]. Smaller yields are obtained in runs on larger scales even if lower reaction temperatures (−30°) are applied.

[15]) We observed this rearrangement during ^{13}C-NMR overnight experiments of **12** at room temperature [13]. Earlier, *Oku et al.* [18] reported that reductive coupling of **9** with Na directly gives **17** and not the primary coupling product. This is in contrast to our results (*Scheme 5*).

Scheme 6



absorption of the substituted butadiene units is observed at 244 nm (ε = 18000) which is not expected for **19**. According to the NMR spectra, **17** contains two identical structural units displaying signals of two quarternary (142.75 and 121.89 ppm) and two tertiary (134.75 and 131.04 ppm) vinylic C-atoms as well as of an alkyl-CH(42.50) CH_2 (34.47) and two CH_3 groups (21.59 and 21.49 ppm) in the ^{13}C-NMR spectrum. In the ^{1}H-NMR spectrum, there are resonances of two mutually coupling vinylic H-atoms at 6.35 and 5.90 ppm (J = 5.67 Hz) and, besides the signals of CH_3 groups at 1.82 and 1.78 ppm, the signals of an *ABX* system at 3.19 (*X*), 2.38 (*B*) and 2.15 ppm (*A*). Irradiation at 3.19 ppm leaves an *AB* system of the diastereotopic CH_2 protons with J_{AB} = 18.75 Hz.

This result indicates that, despite the well-known equilibrium between the three predominant tautomers of **12** (*Scheme 6*) which are visible in the ^{13}C-NMR spectrum [13], it is exclusively **12A** which rearranges to **17** with a half-lifetime of 2.2 h in $CDCl_3$ at 50°. Obviously, there are electronic and/or steric factors that lower the energy of the transition state of the reaction **12A** → **17** more than that of the processes **12B** → **18** and **12C** → **19**, which are not known in detail[16]).

3.3. *Oxidative Coupling of* **11**. 2,3-Dimethyl-2,3-di(cyclopentadienyl)butane **12** is quantitatively deprotonated (to give **11**) by adding of 2.2 mol-equiv. of BuLi at −30°. If the THF solution of dianion **11** is slowly added to a slurry of abs. $CuCl_2$ in THF, then 7,7,8,8-tetramethyltricyclo[7.3.0.$0^{2,6}$]dodeca-3,5,9,11-tetraene (**20**) is formed in a 59% yield (*Scheme 7*)[17]). Oxidative coupling of **11** may be realized by adding anhydrous $CuCl_2$ to the cooled (−30°) solution of dianion **11** as well, but then the analytical yield of **20** drops to 42%.

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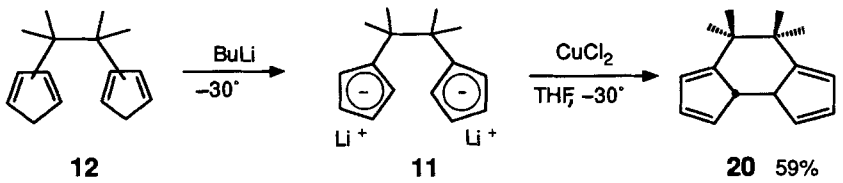
[16]) Electronically, it has to be mentioned that during the transformation **12a** → **17** both additional C=C bonds keep their conjugation with the '*Cope* system', which is not the case for processes **12B** → **18** and **12C** → **19** (for this argument, see [19] and literature cited there). There are possible steric reasons as well, since for the sequences **12B** → **18** and **12C** → **19** the protons of one (**12B**) and both (**12C**) ring CH_2 groups are in a nearly ecliptic arrangement with the CH_3 groups in the transition state.

[17]) Yield determined by ^{1}H-NMR using $MeNO_2$ as a standard. Compound **20** is quite instable and polymerizes easily even at low temperature.

Scheme 7

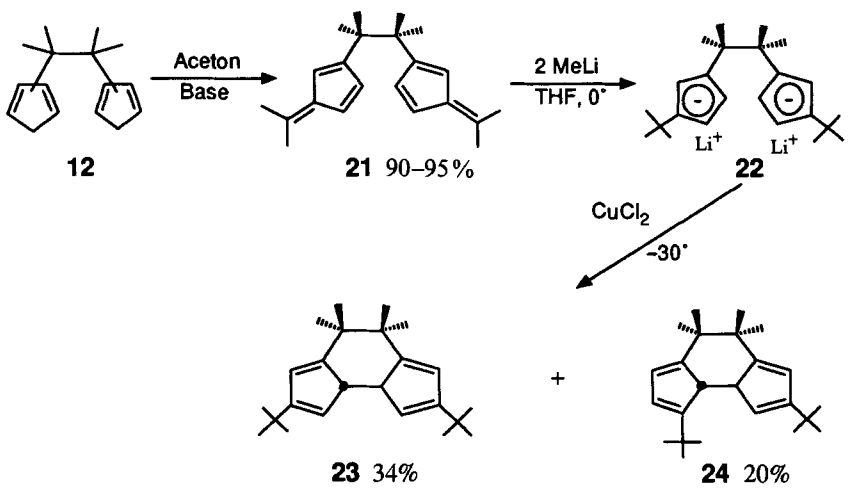


The structure of the isolated tricyclic compound **20** follows from the spectroscopic data which show a close similarity to those of **7a** ($n = 2$): as for **7a** ($n = 2$), the basic MS peak of **20** correspond to $M^{+}/2$. This is reasonable for structure **20**, since both allylic bonds are relatively weak. In the UV spectrum, the long-wavelength absorption at 248 nm ($\varepsilon = 5750$) supports the presence of cyclopentadiene rings. In the NMR spectra, the number of lines as well as the splitting pattern (^{1}H-NMR) are typical for **20**: so, irradiation of the ring-CH groups at 2.42 ppm leads to a clean *ABX* spectrum of the vinylic H-atoms at 6.51, 6.48, and 6.11 ppm with typical coupling $J_{AB} = 5.26$, $J_{AX} = 1.50$, and $J_{BX} = 1.69$ Hz.

Intramolecular 2,2′-coupling of dianion **11** may give two sterically different coupling products of type **7aC** or **7aB** while according to spectroscopic data only one isomer **20** is formed. While extensive NOE experiments are in favor of the chair arrangement as in **7aD**, they cannot completely rule out the boat arrangement as in **7aC**. The final decision in favor of the C_2-symmetrical chair arrangement of **20** follows from ^{1}H-NMR experiments with chiral lanthanide shift reagents: adding 2 mol-equiv. of [Eu(hfc)$_3$] and 2 mol-equiv. of [Ag(fod)] to 1 mol-equiv. of **20** in $CDCl_3$ results in a doubling of the NMR signals at 6.1, 2.4, and 0.9 ppm.

4. Oxidative Coupling of 2,3-Dimethyl-2,3-bis[3-(*tert*-butyl)cyclopentadienyl]butanediide 22. – Furthermore, it is interesting to investigate whether introducing *t*-Bu units at the cyclopentadienide rings of **11** would change the coupling behavior of dianion of type **22** (*Scheme 8*). It may be anticipated that the conformational equilibrium **E** ⇄ **F**

Scheme 8



could be changed in favor of **E** after introducing two relatively spaceous substituents at the five-membered rings. On the other side, polymerizations **6** → **8** (see *Scheme 3*) should be sterically strongly hindered.

Dianion **22** is easily available in a high yield by *Thiele* condensation of **5** with acetone in the presence of base (**12** →**21** [13]) followed by nucleophilic addition of MeLi at the exocyclic C-atoms of the fulvene units of **21**. This type of reaction is well-known for simple pentafulvenes ([20], for surveys, see [21]). Similarly to **11**, the solution of the resulting dianion **22** is added to a slurry of anhydrous $CuCl_2$ in abs. THF to give a mixture of tricyclic compounds **23** and **24** in a total yield of 55%. Both compounds are thermally rather unstable and sensitive to oxygen as well, they furthermore can isomerize to the corresponding fulvenes at room temperature in $CDCl_3$ (see later).

The structure of **23** and **24** follows from the spectroscopic data which show close similarities to **20**: *e.g.* the MS and UV spectra of **23** are very similar to those of **20**, and the basic MS process is, in both cases, the formation of $M^+/2$, which is a result of the fragmentation of both allylic bonds. In the ^{1}H- and ^{13}C-NMR spectra, all the alkyl resonances of the cyclohexane ring of **23** are virtually identical to those of **20**, while the trends observed for the vinylic resonances are in agreement with the substitution pattern. Furthermore, only one isomer **23** has been formed which consists of two symmetrical subunits; and since all the ^{1}H- and ^{13}C-chemical shifts of the cyclohexane ring are nearly identical to those of **20**, compound **23** must have C_2 symmetry.

These results show that the coupling behavior of dianion **22** does not dramatically change compared with dianion **11**. A reasonable explanation is that, although *t*-Bu groups should again favor **22E** in the conformational equilibrium **22E** ⇄ **22F**, polymerization is hindered due to the strong steric shielding of the cyclopentadienide units of **22**.

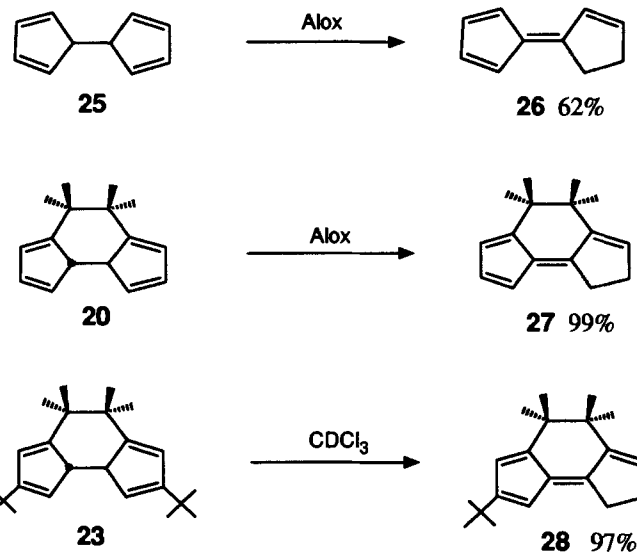
5. Isomerization of Coupling Products 20 and 23. – It is well known that vinylcyclopentadienes undergo quite easily isomerization in the presence of base to give the thermodynamically more stable pentafulvenes [22]. A very impressive rearrangement of that type has been observed for 5,5′-bi(cyclopentadienyl) (= 9,10-dihydropentafulvalene; **25**), during chromatography over basic Alox [7]; it probably proceeds over a series of consecutive deprotonation/protonation reactions. The same isomerization may be initiated by traces of acid as well [23] [24][18]); however, the yields of fulvene **26** are considerably lower due to the fact that acids may initiate polymerizations (*Scheme 9*).

Our experiments show that the same types of isomerizations are observed in the case of bridged 9,10-dihydropentafulvalenes **20** and **23**, and they proceed in both cases nearly quantitatively. The only surprising observation is that, while the process **20** → **27** easily takes place during chromatography over basic Al_2O_3 as usual, the reaction **23**→**28** does not take place under these conditions. To catalyze this isomerization, **23** has to be stored at room temperature for two days in $CDCl_3$ to give **28** in a very high yield. It is reasonable to assume that base catalysis is sterically hindered by the bulky substituents of **23** while acid catalysis is still possible; on the other hand polymerization of **28** is slowed down as well due to steric reasons.

The structure of both compounds is deduced from spectroscopic data. Both **27** and **28** have a 6-vinylpentafulvene structure element which is responsible for the typical UV

[18]) Compound **26** has been first prepared by acid-catalyzed treatment of 'dicyclopentadienol'. In the course of that rearrangement, **25** is supposed to be formed as an intermediate [24].

Scheme 9



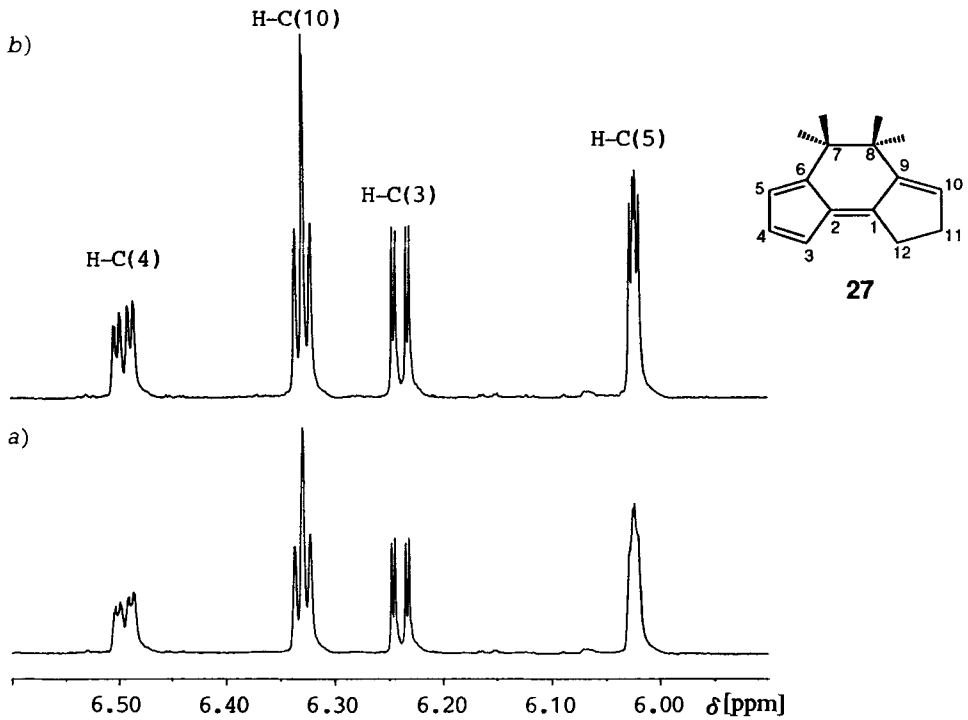


Fig. 2. *Part of the ^{1}H-NMR spectrum of bridged pentafulvene* **27** (300 MHz, $CDCl_3$). *a*) References spectrum; *b*) spectrum during decoupling of CH_2(12) at 2.97 ppm.

absorptions around 406 nm ($\varepsilon \approx 1200$ for **27**). MS Fragmentations are similar to those of **20** and **23**, respectively (which supports equilibria **20**⇄**27** and **23**⇄**28**), and chemical shifts (^{1}H- and ^{13}C-NMR) as well as splitting patterns (^{1}H-NMR) are typical for **27** and **28**, respectively. In the ^{1}H-NMR spectrum of **27**, most *multiplets* of vinylic H-atoms are considerably broadened by long-range couplings with CH_2(12) (*Fig. 2*, below). If these two H-atoms are decoupled, then the *AMX* pattern of H–C(3), H–C(4)[19]), and H–C(5) is clearly visible, and the observed J values of $J(3,4) = 5.12$, $J(4,5) = 2.25$, and $J(3,5) = 1.23$ Hz are typical for pentafulvenes [25] and demonstrate the considerable alternation of bond lengths in the fulvene unit of **27** [26]. Furthermore, H–C(10) couples with CH_2(11) and is therefore split into a triplet ($J = 2.97$ Hz).

Corresponding to the different substitution patterns of **28**, ^3J coupling between vinylic H-atoms are missing in the ^{1}H-NMR spectrum, the ^4J coupling between H–C(3) and H–C(5) being 1.84 Hz[20]). Due to the *t*-Bu group at C(11), the alkyl H-atoms of **28** form an *ABXY* splitting pattern together with H–C(10), coupling constants being very typical for the proposed structure [3].

6. Discussion. – In this contribution, the preparative and structural aspects of the Cu^{II}-induced oxidative coupling of α,ω-di(cyclopentadienyl)alkane-diides **6** ($n = 2$–5) as well as of 1,1,2,2-tetramethyl derivatives **11** and **22** have been investigated. All these reactions proceed in a high yield (if polymers are included), possibly *via* cyclopentadienyl radicals[21]); however, it has to be pointed out that the mechanism of Cu^{II}-induced coupling reactions is still unknown.

As far as the '*coupling mode*' is concerned, it is interesting to note that oxidative coupling of dianions **6** even in dilute solution predominantly proceeds by an intermolecular mode to give reactive polymers **8a** ($n = 2$), **8b** ($n = 3$), **8c** ($n = 4$), and **8d** ($n = 5$) in high yields (see *Scheme 3*). This is especially surprising for deprotonated α,ω-di(cyclopentadienyl)alkane-diide **6a** ($n = 2$), where, at first sight, we expected a much higher extent of the intramolecular coupling **6a** → **7a**. On the other hand, if a conformational equilibrium **E** ⇄ **F** is operative, it is reasonable to assume that, for R = H, conformation **E** with *trans*-diaxial cyclopentadiene rings is energetically favored over conformation **F** with a *gauche*-arrangement of the cyclopentadiene ring. This is easily confirmed by an approximation of the potential energies of both conformers **E** and **F** by MM2 force-field calculations[22]). Furthermore, it is important to note that the transition metal does not seem to enhance intramolecular coupling by complexation of the cyclopentadienyl rings in the *gauche*-conformation **F**. As soon as H-atoms of the CH_2CH_2 bridge are replaced by larger substituents, the importance of the *gauche*-conformation **F** in the equilibrium should increase. This is supported by approximate force-field calculations[22]). In fact, our experiments show that the total yields of intramolecular coupling products are considerably increasing for coupling **11** → **20** and **22** → **23** + **24**.

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[19]) H–C(4) has an additional small long-range coupling ($J = 0.4$ Hz), which is probably due to a ^7J coupling with H–C(10).

[20]) For the numbering of **28**, see formula of **27** in *Fig. 2*.

[21]) Cyclopentadienyl radicals have been detected in another context by ESR spectroscopy [27].

[22]) *Allinger*'s MMPMI [28], Formate QCPE 395, Version 1980 has been used, and cyclopentadienide rings have been approximated by aromatic rings. Even with this approximation, where charge repulsion has been neglected, the energy difference between **E** and **F** is 1.1 kcal/mol for R = H and only 0.4 kcal/mol in favor of **E** for R = Me.

According to our results, we believe that the conformational equilibrium **E** ⇄ **F** is a very important factor determining the '*coupling mode*' of oxidative couplings of 1,2-di-(cyclopentadienyl)ethanediides **6a**, **11**, and **22**. While conformation **E** is suitable for intermolecular coupling (to give polymers, see **6** → **8**), the *gauche*-conformation **F** is very prone to intramolecular coupling[23]). In this case, a 2,2′-coupling has to be expected giving rise to six-membered rings, and this is exactly what happens in all the intramolecular couplings of dianions **6a**, **11**, and **22**. On the other hand, a 1,1′-coupling (to give cyclobutanes) would need an ecliptic arrangement of the cyclopentadiene rings which is energetically unfavorable.

This means that the observed *regioselectivity* is easily explained, if conformation **F** is important for intramolecular couplings, and, last but not least, intramolecular 2,2′-couplings out of conformation **F** are expected to give C_2-symmetrical coupling products **7a**, **20**, and **23**, so that the importance of **F** in all the investigated coupling processes is compatible with the observed *stereoselectivities* as well.

The authors thank the *Swiss National Science Foundation* (projects No. 20-26167.89 and 20-31.217.91) for financial support. They thank PD. Dr. *P. Bigler* for various 1D- and 2D-NMR experiments and Dr. *P. Bönzli* for helpful discussions.

Experimental Part

General. All the procedures were applied in abs. solvents under N_2 or Ar. Prior to the introduction of the reagents, the reaction vessel was thoroughly flame-dried while being flushed with a stream of N_2 or Ar. For reagents, solvents, and equipments used, see [3]. Spectra were recorded on the following instruments: UV: *Perkin-Elmer 554*; IR: *Perkin-Elmer 399 B* and *782*; NMR: *Bruker AM-400* and *AC-300*, *Varian EM-360*; MS: *Varian MAT/CH 7A*; HR-MS: *Varian-MAT 311*. Microanalyses were carried out by Drs. *H.* and *K. Eder*, Institute of Pharmaceutical Chemistry, Service of Microchemistry, Quai Ernest-Ansermet 30, CH-1211 Genève.

1. Synthesis of α,ω-Di(cyclopentadienyl)alkanes 5a–d[6]). – 1.1. *General Procedure.* A 100-ml two-necked flask fitted with a magnetic stirrer, septum, and N_2 bubbler is charged with the soln. of Na-cyclopentadienide (NaCPD) in THF and cooled to the appropriate temp. Then, the dibromo-alkane is dropwise added under stirring. Stirring is continued for 1 h at the same temp. and 1 h at a higher temp. For precipitating NaBr, pentane is added to the redbrown mixture which afterwards is quickly transferred into a cooled chromatography column containing 30 g of silica gel (*Chem. Fabrik Uetikon, C 560*) and quickly eluted (if necessary by applying a weak N_2 pressure) by means of pentane. The nearly colorless soln. is carefully evaporated (low-temp. rotating evaporator) at −20°/0.05–0.1 Torr to give a nearly colorless oil which is stored at −70°.

1.2. *1,2-Di(cyclopentadienyl)ethane* (**5a**, $n = 2$). To 76 ml of 1.6M NaCPD in THF (106 mmol) are slowly added 4.7 ml (50 mmol) of 1,2-dibromoethane at −30°. Stirring is continued for 1 h at −30°, then 1 h at 0°, and 30 ml of pentane are added at 0°. After filtration (−20°) and evaporation: 2.3 g of a pale-yellow oil containing a considerable amount of spiro[2.4]hepta-4,6-diene. This by-product is removed by high-vacuum evaporation over 3 h at 0°/10^{-3} Torr to give 1.56 g (19%) of a pale-yellow oil of **5a**. ^{1}H-NMR (300 MHz, $CDCl_3$)[24]) = 6.43 (*m*); 6.25 (*m*); 6.18 (*m*); 6.04 (*m*); 2.95 (*m*); 2.88 (*m*); 2.65 (*m*); 2.60 (*m*). ^{13}C-NMR (75 MHz, $CDCl_3$): 149.49 (*s*); 149.40 (*s*); 146.87 (*s*); 146.81 (*s*); 134.72 (*d*); 134.62 (*d*); 133.72 (*d*); 133.66 (*d*); 132.43 (*d*); 130.59 (*d*); 126.53 (*d*); 126.45 (*d*); 126.04 (*d*); 125.99 (*d*); 43.35 (*t*); 43.27 (*t*); 41.26 (*t*); 30.87 (*t*); 30.06 (*t*); 30.04 (*t*); 29.26 (*t*).

1.3. *1,3-Di(cyclopentadienyl)propane* (**5b**, $n = 3$). To 7.7 ml of 1.63M NaCPD in THF (12.5 mmol) are slowly added 0.51 ml (5 mmol) of 1,3-dibromopropane at 0°. Stirring is continued for 1 h at 0°, then 7 ml of pentane are added. After filtration (−20°) and evaporation: 630 mg (72%) of **5b**. ^{1}H-NMR (300 MHz, $CDCl_3$)[24]): 6.43 (*m*); 6.25 (*m*); 6.17 (*m*); 6.03 (*m*); 2.97 (*m*); 2.89 (*m*); 2.43 (*m*); 1.8 (*m*). ^{13}C-NMR (75 MHz, $CDCl_3$): 149.77 (*s*); 149.68 (*s*); 147.02 (*s*); 146.95 (*s*); 141.33 (*s*); 134.77 (*d*); 134.73 (*d*); 133.71 (*d*); 133.66 (*d*); 132.45 (*d*); 130.50 (*d*); 130.47

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[23]) Additionally, the four CH_3 groups of the ethane unit of dianions **11** and **22** act like a 'hydrophobic umbrella' in conformation **F**, thus hindering the approach of cyclopentadienide units of other dianions.

[24]) Mixture of 3 tautomers; that is why integral ratios are omitted.

(*d*); 128.84 (*d*); 126.43 (*d*); 126.40 (*d*); 125.97 (*d*); 125.95 (*d*); 43.26 (*t*); 41.25 (*t*); 30.60 (*t*); 30.43 (*t*); 29.68 (*t*); 29.61 (*t*); 29.56 (*t*); 28.81 (*t*); 27.95 (*t*).

1.4. *1,4-Di(cyclopentadienyl)butane* (**5c**, $n = 4$): To 70 ml of 1.4M NaCPD in THF (98 mmol) are slowly added 5.9 ml (50 mmol) of 1,4-dibromobutane at −20°. Stirring is continued for 1 h at −20°, then for 1 h at 0°, after what 30 ml of pentane are added at 0°. After filtration (−20°) and evaporation 6.6 g (71%) of **5c**. ^{1}H-NMR (300 MHz, $CDCl_3$)[24]): 6.42 (*m*); 6.25 (*m*); 6.15 (*m*); 6.00 (*m*); 2.94 (*m*); 2.87 (*m*); 2.39 (*m*); 1.53 (*m*). ^{13}C-NMR (75 MHz, $CDCl_3$): 149.97 (*s*); 149.90 (*s*); 147.20 (*s*); 147.14 (*s*); 143.85 (*s*); 134.79 (*d*); 134.76 (*d*); 133.63 (*d*); 133.59 (*d*); 132.45 (*d*); 130.39 (*d*); 127.86 (*d*); 126.30 (*d*); 126.27 (*d*); 125.84 (*d*); 125.80 (*d*); 43.48 (*t*); 43.23 (*t*); 41.20 (*t*); 32.37 (*t*); 30.57 (*t*); 29.71 (*t*); 29.55 (*t*); 29.49 (*t*); 28.83 (*t*); 28.67 (*t*); 28.63 (*t*); 25.98 (*t*); 25.62 (*t*); 23.36 (*t*).

1.5. *1,5-Di(cyclopentadienyl)pentane* (**5d**, $n = 5$): To 60 ml of 1.4M NaCPD in THF (84 mmol) are slowly added 5.44 ml (40 mmol) of 1,5-dibromopentane. Stirring is continued for 1 h at −20°, then for 1 h at 0°, and 30 ml of pentane are added at 0°. After filtration (−20°) and evaporation: 5.9 g (73%) of **5d**. ^{1}H-NMR (300 MHz, $CDCl_3$)[24]): 6.42 (*m*); 6.24 (*m*); 6.13 (*m*); 5.98 (*m*); 2.93 (*m*); 2.86 (*m*); 2.37 (*m*); 1.57 (*m*); 1.37 (*m*). ^{13}C-NMR (75 MHz, $CDCl_3$): 150.23 (*s*); 150.19 (*s*); 147.43 (*s*); 147.40 (*s*); 134.92 (*d*); 134.90 (*d*); 133.67 (*d*); 133.33 (*d*); 132.55 (*d*); 130.46 (*d*); 126.29 (*d*); 126.27 (*d*); 126.12 (*d*); 125.82 (*d*); 43.57 (*t*); 43.34 (*t*); 41.30 (*t*); 30.78 (*t*); 30.04 (*t*); 29.92 (*t*); 29.73 (*t*); 29.45 (*t*); 29.39 (*t*); 29.36 (*t*); 29.22 (*t*); 29.05 (*t*); 28.85 (*t*); 28.83 (*t*); 28.72 (*t*).

2. Synthesis and Oxidative Coupling of α,ω-Di(cyclopentadienyl)alkane-diides 6. – 2.1. *Tricyclo[7.3.0.0^{2,6}]dodeca-3,5,9,11-tetraene* (**7a**). In a round-bottomed, two-necked 50-ml flask equipped with magnetic stirrer, septum, and N_2 bubbler, 1.1 g (7 mmol) of **5a** are dissolved in 20 ml of anh. THF. After cooling at −30°, 10 ml of 1.55M BuLi (15.4 mmol) in hexane are slowly added during 15 min. During addition, colorless dianion **6a** precipitates. After stirring for 30 min at r.t., the flask is again cooled down to −30°. Then, 2.07 g (15.4 mmol) of anh. $CuCl_2$ are added in one portion under intensive stirring. After addition, stirring at −30° is continued for 1 h. Then, at *ca.* half of the solvent is removed by rotatory evaporation at −30°. The residual mixture is quickly transferred into a cooled (−50°) chromatography column containing 25 g of NEt_3-deactivated silica gel[25]) and filtered by eluting with pentane under slight N_2 pressure. Then pentane soln. is evaporated at −30°/10 Torr to give *ca.* 500 mg of a crude product, which is again filtered over 30 g of NEt_3-deactivated silica gel[25]) for FC (*J. T. Baker*, No. 70241, size 30–60 μm). After evaporation of solvents at −30°/10 Torr: 300 mg of crude colorless oil. Final FC over 40 g of NEt_3-deactivated silica gel[25]) gives, after evaporation of the first fraction, 21 mg of a colorless oil of **7a**. Yield determined by ^{1}H-NMR after first filtration, with $MeNO_2$ as a reference: 7%. UV (hexane): 249. IR (CCl_4/CS_2): 3095*w*, 3065*m*, 3025*w*, 2950*s*, 2930*m–s*, 2905*m*, 2840*m*, 1610*w*, 1530*w*, 1435*m*, 1354*w*, 1329*w*, 1260*m*, 1180*w*, 1100*m*, 1020*m*, 987*m*, 860*m–s*, 730*s*, 700*m*. ^{1}H-NMR: *Fig. 1*. ^{13}C-NMR ($CDCl_3$): 150.09 (*s*); 135.39 (*d*); 132.32 (*d*); 123.72 (*d*); 56.33 (*d*); 28.18 (*t*). MS: 157 (10), 156 (74, $M^{+\cdot}$), 155 (54), 154 (14), 153 (30), 152 (20), 151 (6), 150 (2), 142 (4), 141 (44), 139 (2), 130 (2), 129 (14), 128 (30), 127 (10), 126 (2), 116 (6), 115 (50), 102 (3), 96 (2), 94 (8), 79 (2), 78 (100), 76 (18), 75 (11), 74 (4), 65 (4), 64 (2), 63 (8), 52 (10), 51 (10), 50 (4), 39 (8).

2.2. *General Procedure for Polymers* **8a–d**. In a round-bottomed two-necked flask equipped with magnetic stirrer, septum, and N_2 bubbler, **5** is dissolved in THF, the soln. is cooled down to −30° under magnetic stirring, and 2 mol-equiv. of BuLi (in hexane) are slowly added. During addition, colorless dianion **6** precipitates. After stirring for 30 min at r.t,, the flask is again cooled down to −30°. Then, 1.8 to 1.9 mol-equiv. of anh. $CuCl_2$ are added in one portion at −30° under intensive stirring. After addition, stirring is continued for 1 h at −30°. To precipitate the polymers **8**, the reaction mixture is portionwise transferred into a syringe and dropwise added to 100 ml of MeOH under stirring[26]). The nearly colorless precipitate is carefully filtered under Ar[27]), rinsed (3×) with totally 70 ml of MeOH, and dried at 20°/10^{-3} Torr over 3–5 h.

2.3. *Poly[1,2-di(cyclopentadienyl)ethane]* (**8a**, $n = 2$). 600 mg (3.5 mmol) of **5a** are dissolved in 40 ml of abs. THF, then 5 ml (8 mmol) of 1.6M BuLi in hexane as well as 970 mg (7.2 mmol) of anh. $CuCl_2$ are added. After drying: 550 mg (92%) of **8a**[28]). Anal. calc. for $(C_{12}H_{12})_n$: C 92.25, H 7.75; found[27]): C 91.43, H 8.57.

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[25]) NEt_3-deactivated silica gel is prepared by treating a slurry of silica gel in pentane with NEt_3 (5 wt-% corresponding to silica gel). The slurry is rotated in a rotatory evaporator for 2 h without vacuum, then most of the excessive NEt_3 is removed by washing the slurry with pentane/Et_2O 3.1: Finally, remaining solvents are removed by drying the silica gel under rotating at 100°/50 Torr.

[26]) Figure of the equipment used for precipitating polymers **8** and filtering: [29], p. 1113.

[27]) Note that polymers **8** are extremely O_2-sensitive. Despite precautions, O_2 could not be completely avoided during workup. Therefore, found C,H values are given after deduction of oxygen. O_2 induces cross-linking of polymers which become insoluble.

[28]) Table of solid-state ^{13}C-NMR data: [2].

2.4. *Poly[1,3-di(cyclopentadienyl)propane]* (**8b**, $n = 3$). 600 mg (3.8 mmol) of **5b** are dissolved in 40 ml of abs. THF, then 4.4 ml (6.9 mmol) of 1.6M BuLi in hexane as well as 852 mg (6.3 mmol) of anh. $CuCl_2$ are added. After drying: 537 mg (82%) of **8b**[28]). Anal. cal. for $(C_{13}H_{14})_n$: C 92.77, H 7.23; found[27]): C 90.82, H 9.18.

2.5. *Poly[1,4-di(cyclopentadienyl)butane]* (**8c**, $n = 4$). 656 mg (3.6 mmol) of **5c** are dissolved in 40 ml of abs. THF, then 4.5 ml (7.2 mmol) of 1.6M BuLi in hexane as well as 871 mg (6.48 mmol) of anh. $CuCl_2$ are added. After drying: 537 mg (82%) of **8c**[28]). Anal. calc. for $(C_{14}H_{16})_n$: C 93.26, H 6.84; found[27]): C 90.74, H 9.26.

2.6. *Poly[1,5-di(cyclopentadienyl)pentane]* (**8d**, $n = 5$). 686 mg (3 mmol) of **5d** are dissolved in 40 ml of abs. THF, then 3.7 ml (6 mmol) of 1.6M BuLi in hexane as well as 720 mg (5.3 mmol) of anh. $CuCl_2$ are added. After drying: 600 mg (87%) of **8d**[28]). Anal. calc. for $(C_{15}H_{18})_n$: C 93.46, H 6.53; found[27]): C 93.30, H 6.70.

3. Synthesis and Oxidative Coupling of 2,3-Dimethyl-2,3-di(cyclopentadienyl)butanediide (11). – 3.1. *2,3-Dimethyl-2,3-di(cyclopentadienyl)butane* (**12**). A round-bottomed, four-necked 400-ml flask is equipped with a magnetic stirring bar, 50-ml dropping funnel, thermometer, and N_2 bubbler, flame-dried while being flushed with Ar and then charged with 10 ml (2.4M, 240 mmol) of Na-sand as well as with 150 ml of abs. Et_2O. The suspension is cooled to −30°, then 12.7 g (120 mmol) of freshy dist. *6,6-dimethylfulvene* (**9**), dissolved in 25 ml of abs. Et_2O, are dropwise added within 140 min under stirring. After addition is complete, stirring is continued for 18 h at −30°. The org. phase is poured into a 250-ml separatory funnel, the remaining Na-sand is washed (2×) with abs. Et_2O (2 × 50 ml). To the combined Et_2O phases, 100 ml of ice-water are added. After shaking, the org. phase is separated. The H_2O phase is extracted (2×) with Et_2O (2 × 100 ml). The Et_2O phases are combined, washed with 50 ml of ice water, dried ($MgSO_4$), and filtered. Removal of the solvent at r.t./12 Torr gives 6.46 g of crude **12** as yellow crystals. Twofold recrystallization from 10 ml of pentane at −70° gives 3.50 g (27%) of slightly yellow crystals. M.p. 76–77°[29]). UV (hexane): 245 (7045). IR ($CHCl_3/CS_2$): 3110*w*, 3060*w*, 2980*m*, 2960*m*, 2919*w–m*, 2870*w–m*, 2390*w*, 2350*w*, 1512*w*, 1503*w*, 1470*w*, 1372*w–m*, 1360*w–m*, 1350*w*, 1145*w–m*, 1110*w–m*, 980*w–m*, 995*w*, 938*w–m*, 900*m–s*, 755*w–m*, 680*w–m*, 650*m*, 640*m*. ^{1}H-NMR (80 MHz, $CDCl_2$): 632 (*m*), 6.23 (*m*), 5.90 (*m*) (totally 6 H); 2.88 (*m*), 2.73 (*m*) (totally 4 H); 1.15 (*s*, 12 H). ^{13}C-NMR (25 MHz, $CDCl_3$): 155.98 (*s*); 153.63 (*s*); 153.21 (*s*); 135.27 (*d*); 134.91 (*d*); 131.52 (*d*); 131.04 (*d*); 130.77 (*d*); 130.66 (*d*); 127.79 (*d*); 126.81 (*d*); 43.61 (*t*); 41.50 (*s*); 40.96 (*s*); 40.59 (*t*); 25.15 (*q*); 25.11 (*q*); 25.06 (*q*); 24.42 (*q*); 24.37 (*q*); 24.30 (*q*); 24.24 (*q*). MS: 214 (10, $M^{+\cdot}$), 109 (4), 108 (56), 107 (100), 106 (39), 93 (11), 92 (10), 91 (56), 79 (12), 77 (5), 65 (6), 43 (4). HR-MS: 214.1722 ($C_{16}H_{22}$, $M^{+\cdot}$; calc. 214.1713).

3.2. Cope-*Rearrangement of* **12**[15])[30]). *1,1'-Bi(2-isopropylidenecyclopent-3-enyl)* (**17**). A 25-ml, two-necked flask fitted with a condensor, magnetic stirring bar, and septum is charged with 10 ml of $CHCl_3$ as well as with 0.507 g (2.37 mmol) of **12**. The flask is placed in an oil-bath at 50°. After stirring at 50° for 26 h, the solvent is removed at r.t./10 Torr and the crude product is purified by FC over 100 g of silica gel with pentane to give 0.427 g (84%) of **17**. M.p. 31–32°. UV (hexane): 244 (18000). IR (neat): 3046*w–m*, 2960*m–s*, 2918*m–s*, 2860*m*, 2840*m*, 1437*m*, 1369*m*, 1290*w*, 1174*w–m*, 1142*w–m*, 1121*w–m*, 1090*w–m*, 970*w*, 930*w*, 870*w–m*, 739*m–s*, 650*w–m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.35 (*dt*, $J = 5.67, 2.21$, 2 H); 5.90 (*dt*, $J = 5.67, 2.58$, 2 H); 3.19 (*d*, $J = 6.98$, 2 H); 2.38 (*ddm*, $J = 18.75, 6.98$, 2 H); 2.15 (*d*, $J = 18.75$, 2 H); 1.82 (*s*, 6 H); 1.78 (*s*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$); 142.75 (*s*); 134.75 (*d*); 132.04 (*d*), 121.89 (*s*); 42.50 (*d*); 34.47 (*t*); 21.59 (*q*); 21.49 (*q*). MS: 214 (5, $M^{+\cdot}$), 108 (26), 107 (71), 106 (67), 105 (20), 93 (24), 92 (9), 91 (100), 79 (20), 78 (4), 77 (16), 66 (4), 65 (19), 63 (4), 53 (4), 51 (7), 41 (14), 39 (13), 32 (5). Anal. calc. for $C_{16}H_{22}$ (214.336); C 89.65, H 10.35; found: C 89.37, H 10.30.

3.3. *Synthesis and Oxidative Coupling of* **11**: *7,7,8,8-Tetramethyltricyclo[7.3.0.0^{2,6}]dodeca-3,5,9,11-tetraene* (**20**). A 50-ml two-necked flask fitted with a magnetic stirrer, septum, and Ar bubbler is flame-dried and flushed with Ar. The flask is charged with 0.214 g (1 mmol) of **12** as well as with 10 ml of abs. THF and cooled to −30° under Ar. Then, 1.4 ml (2.2 mmol) of BuLi (1.6M in hexane) are dropwise added within 30 min. The mixture is stirred for additional 30 min at −30° and warmed up to r.t. to give a soln. of **11**.

A second flame-dried 50-ml flask fitted with a magnetic stirrer, septum, and Ar bubbler is charged with 0.30 g (2.2 mmol) of anh. $CuCl_2$ as well as with 15 ml of abs. THF and cooled at −30°. To the yellow-brown suspension, the freshly prepared soln. of **11** is added dropwise within 30 min at −30° by means of a syringe. After addition, stirring is continued for 15 min at −30° to give a dark-brown soln. Inorg. salts are filtered off by transferring the resulting mixture with a syringe under Ar into a cooled (−30°) column containing 25 g of Et_3N-deactivated silica

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[29]) Further recrystallization gives almost colorless crystals with m.p. 79–80°. The ^{1}H-NMR spectrum shows that one tautomer is predominant. The yield has not been optimized. Optimized yields are *ca.* 50% [13].

[30]) In a parallel reaction (in 10 ml of $CDCl_3$), portions of 0.4 ml are transferred into NMR tubes at intervals of 0.5, 1, 2, 3, 5, 10, and 26 h, and ^{1}H-NMR spectra (300 MHz) are recorded immediately. This allows to determine the half-lifetime $\tau_{1/2} = 2.2$ h from the signal appearing at 3.19 ppm.

gel[25]), elution is realized (under slight N_2 pressure) with pentane. The orange fraction is collected at −30° and concentrated at −30°/0.2 mbar to give an orange oil. An exactly weighed amount of CH_3NO_2 is added to the mixture which is diluted with 5 ml of $CDCl_3$ for recording the ^{1}H-NMR spectrum: 58.8% yield according to the integral of the bridghehead protons at 2.42 ppm relative to the integral of the reference at 4.27 ppm[31]). A pure sample of **20**[30]) was obtained by FC over Et_3N-deactivated[25]) silica gel with pentane: Et_2O 100:1 (R_f 0.69) at r.t. followed by filtration over Et_3N-deactivated silica gel with pentane: Et_2O 100:1 at −30°. UV (hexane): 248 (5750). IR (neat): 3120*w*, 3085*w*, 3065*w–m*, 3030*w*, 2970*m–s*, 2935*m*, 2915*m*, 2875*m*, 1600*w*, 1525*w–m*, 1468*w–m*, 1148*w*, 1390*w*, 1372*m*, 1367*m*, 1353*w*, 1310*w*, 1256*w*, 1239*w*, 1200*w–m*, 1189*w*, 1145*w–m*, 1115*w*, 987*w*, 960*w*, 915*w*, 872*w–m*, 850*m*, 820*w*, 730*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.51 (br. *dd*, 2 H); 6.48 (*dd*, 2 H); 6.11 (*m*, 2 H); 2.42 (br. *s*, 2 H); 1.24 (*s*, 3 H); 0.90 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.11 (*s*); 135.42 (*d*); 131.78 (*d*); 122.58 (*d*); 53.45 (*d*); 40.85 (*s*); 27.17 (*q*); 20.10 (*q*). MS: 213 (7), 212 (42, M^+), 197 (12), 182 (10), 167 (8), 166 (6), 165 (9), 153 (4), 152 (5), 128 (3), 107 (14), 106 (100), 105 (9), 103 (2), 92 (4), 91 (45), 89 (2), 79 (6), 77 (4), 65 (4), 41 (2). HR-MS: 212.1569 ($C_{16}H_{20}$, M^+ calc.: 212.1565).

4. Synthesis and Oxidative Coupling of 2,3-Dimethyl-2,3-bis[3-(*tert*-butyl)cyclopentadienyl]butanediide (22). – 4.1. *Synthesis of 2,3-Dimethyl-2,3-bis(6,6-dimethylpentafulven-2-yl)butane* (**21**)[32]). A 100-ml three-necked round-bottomed flask is charged with 1.28 g (6 mmol) of **12** as well as with 40 ml of abs. EtOH. Under Ar, 20 ml of EtONa (2.4M) are added dropwise within 30 min at r.t. The resulting red soln. is stirred for an additional h at r.t. Then, 5 ml of acetone are added and stirred overnight. Another 20 ml of EtONa (2.4M) as well as 5 ml of acetone are added and stirring is continued overnight. The resulting mixture is transferred into a 100-ml round flask and most of the solvent evaporated at 0°/0.2 mbar. Then, 20 ml of CH_2Cl_2 are added. To this mixture, 20 ml of 3% ice-cooled aq. HCl are carefully dropped. The org. phase is separated and the aq. phase extracted with 20 ml of CH_2Cl_2. The combined org. phases are washed with ice-cooled H_2O and dried ($MgSO_4$). After removal of the solvent, the residue is recrystallized from 50 ml of Et_2O at −70° give 1.63 g (92.4%) yellow crystals of **21**. M.p. 137–138°. UV (hexane): 355 (910), 276 (42600). IR (neat): 3100*w*, 2980*m–s*, 2908*m*, 2875*w–m*, 1641*s*, 1563*w*, 1437*m*, 1373*m–s*, 1350*m–s*, 1301*w–m*, 1128*w–m*, 1088*w*, 1067*w–m*, 940*w–m*, 864*w–m*, 818*s*, 716*w*, 629*w–m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 640 (*d*, 4 H); 6.18 (*t*, 2 H); 2.15 (*s*, 12 H); 1.20 (*s*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 153.26 (*s*); 145.87 (*s*); 141.76 (*s*); 133.50 (*d*); 118.65 (*d*); 116.46 (*d*); 41.33 (*s*); 24.69 (*q*); 22.71 (*q*); 22.66 (*q*). MS: 294 (6, M^+), 148 (70), 147 (100), 146 (12), 145 (6), 133 (15), 132 (12), 131 (18), 130 (3), 129 (8), 128 (6), 120 (6), 119 (65), 118 (3), 117 (31), 116 (12), 115 (25), 107 (17), 106 (10), 105 (77), 104 (3), 103 (9), 102 (3), 93 (7), 96 (8), 96 (69), 89 (7), 79 (20), 78 (7), 77 (27), 74 (5), 69 (43), 67 (3), 65 (18), 63 (12), 62 (5), 61 (3), 59 (9), 57 (3), 55 (26), 53 (7), 51 (13), 50 (9), 49 (3), 45 (8), 44 (3), 43 (8), 42 (4), 41 (31), 40 (3), 39 (21), 38 (4), 37 (5), 32 (21), 31 (9). Anal. calc. for $C_{22}H_{30}$ (249.46): C 89.73, H 10.27; found: C 89.50, H 10.46.

4.2. *Synthesis and Oxidative Coupling of* **22**: *7,7,8,8-Tetramethyl-4,11-di(*tert*-butyl)tricyclo[7.3.0.0^{2,6}]dodeca-3,5,9,11-tetraene* (**23**) *and 7,7,8,8-Tetramethyl-3,11-di(*tert*-butyl)tricyclo[7.3.0.0^{2,6}]dodeca-3,5,9,11-tetraene* (**24**). A 50-ml two-necked flask fitted with a magnetic stirrer, septum, and Ar bubbler is flame-dried flushed with Ar, charged with 1.5 ml (2.4 mmol) of MeLi (1.6M in Et_2O) as well as with 10 ml of abs. THF and cooled to 0°. 0.294 g of **21** dissolved in 5 ml of abs. THF, are added within 15 min at 0°. After addition, stirring is continued for 30 min at r.t. to give a soln. of **22** in THF.

A second flame-dried 50-ml flask fitted with a magnetic stirrer, septum, and Ar bubbler is charged with 0.30 g (2.2 mmol) of anh. $CuCl_2$ as well as with 10 ml of abs. THF and cooled at −30°. To the yellow-brown suspension, the freshly prepared soln. of **22** is dropwise added within 1 h at −30° by means of a syringe. After addition, stirring is continued for 30 min at −30° to give a dark-brown soln. Inorg. salts were filtered off by transferring the resulting mixture with a syringe under Ar into a cooled (−30°) column containing 25 g of Et_3N-deactivated silica gel[25]). After elution (under slight N_2 pressure) by means of pentane, the orange fraction (*ca.* 50 ml) is collected at −30° and concentrated at −30°/0.2 mbar to give an orange oil. The anal. yields of **23** (34.3%) and **24** (20%) are determined by the NMR procedure mentioned in *Sect. 3.3* using CH_3NO_2 as an internal standard. Pure **23**[31]) as well as a mixture of **23** and **24** are obtained by HPLC of MPLC over Et_3N-deactivated silica gel[25]) with pentane (R_f 0.76 and 0.73, pentane: Et_2O 200:1).

Data of **23**: UV (hexane): 248 (5800). IR (neat): 3062*w–m*, 2960*s*, 2950*m–s*, 2905*m–s*, 2870*m–s*, 1620*w–m*, 1558*w*, 1478*m*, 1465*m*, 1390*w–m*, 1371*m*, 1362*m–s*, 1260*m*, 1200*w–m*, 1140*w–m*, 1031*w*, 991*w*, 934*w*, 923*w*, 879*w*, 850*m–s*, 832*m*, 790*m–s*, 698*m*, 650*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.10 (*d*, 2 H); 6.00 (*m*, 2 H); 2.36 (*s*, 2 H); 1.21

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[31]) Since **20**, **23**, and **24** polymerize very easily at low-temperature (possibly induced by traces of oxygen), the prep. yield was not determined.

[32]) First synthesis: [13].

(*s*, 6 H); 1.17 (*s*, 18 H); 0.88 (*s*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$); 159.01 (*s*); 155.99 (*s*); 124.77 (*d*); 122.69 (*d*): 53.29 (*d*); 40.82 (*s*); 32.13 (*s*); 29.65 (*q*); 27.05 (*q*); 20.07 (*q*). MS: 325 (24), 324 (72, M^+), 310 (10), 309 (47), 294 (8), 267 (12), 253 (9), 238 (4), 237 (7), 223 (6), 211 (6), 209 (6), 207 (6), 197 (7), 195 (5), 183 (4), 181 (5), 169 (5), 165 (5), 163 (46), 162 (100), 148 (38), 147 (97), 133 (6), 132 (6), 131 (9), 119 (25), 117 (9), 107 (11), 105 (18), 91 (26), 79 (4), 57 (8), 55 (10), 41 (10). HR-MS: 324.2816 ($C_{24}H_{36}$, M^+, calc. 324.2817).

Data of **24**[33]): UV (hexane): 248 (5800). IR (neat): 3062*w–m*, 2960*s*, 2938*m–s*, 2902*m–s*, 2870*m–s*, 1620*w–m*, 1558*w*, 1470*w–m*, 1465*m*, 1390*w–m*, 1371*m*, 1362*m–s*, 1270*w*, 1258*w–m*, 1240*w*, 1200*w–m*, 1178*w*, 1140*w–m*, 923*w*, 849*m*, 830*m*, 790*m*, 698*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.315 (*t*, 1 H); 6.158 (*dd*, 1 H); 6.124 (*t*, 1 H); 5.972 (*dd*, 1 H); 2.671 (*dt*, 1 H); 2.593 (*dt*, 1 H); 1.289 (*s*, 9 H); 1.214 (*s*, 3 H); 1.197 (*s*, 9 H); 1.195 (*s*, 3 H); 0.904 (*s*, 3 H); 0.859 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.31 (*s*); 159.45 (*s*); 156.62 (*s*); 155.65 (*s*); 126.39 (*d*); 124.78 (*d*); 123.02 (*d*); 121.75 (*d*); 53.38 (*d*); 52.39 (*d*); 40.74 (*s*); 40.56 (*s*); 33.61 (*s*); 32.17 (*s*); 30.92 (*q*); 29.96 (*q*); 26.75 (*q*); 26.72 (*q*); 20.32 (*q*); 20.21 (*q*). MS: 325 (24), 324 (78, M^+), 310 (32), 309 (76), 294 (16), 279 (9), 268 (16), 267 (26), 253 (36), 238 (10), 237 (10), 223 (12), 211 (20), 209 (8), 207 (9), 197 (14), 196 (9), 195 (9), 183 (6), 182 (5), 181 (11), 169 (10), 163 (59), 162 (100), 148 (57), 147 (93), 133 (8), 132 (6), 131 (10), 119 (25), 117 (12), 107 (12), 105 (36), 91 (17), 79 (6), 57 (16), 41 (12), 18 (19). HR-MS: 324.2817 ($C_{24}H_{36}$, M^+, calc. 324.2817).

5. Isomerization of Coupling Products 20 and 23. – 5.1. *7,7,8,8-Tetramethyltricyclo[7,3,0,0^{2,6}]dodeca-1,3,5,9-tetraene* (**27**). A coolable chromatography column is packed with 50 g of basic Alox (activity I) and cooled to 10° with a cooling machine: 160 mg (0.75 mmol) of **20** are added at the top of the column and slowly eluted (*ca.* 1 drop/s) with pentane: Et_2O (5:1). *Ca.* 25 ml of a red soln. are collected and concentrated to give 158 mg (99% yield) of red crystals of **27**. Both TLC and ^{1}H-NMR show that **27** is the only product. No further purification is necessary. M.p. 39–40°. UV (hexane): 315 (29376), 322 (29554), 335 (sh, 20059), 406 (1270). IR: (neat): 3090*w*, 3065*w*, 2965*s*, 2930*w–m*, 2915*m*, 2875*m*, 2845*w–m*, 1643*s*, 1592*w*, 1559*w*, 1475*m*, 1468*m*, 1445*w–m*, 1390*w*, 1372*m*, 1368*m*, 1359*m*, 1342*w*, 1310*w*, 1246*w–m*, 1141*w–m*, 1072*w–m*, 1010*m*, 979*w*, 919*w*, 875*w*, 848*w*, 832*w–m*, 821*w*, 755*w–m*, 746*w–m*, 700*w–m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.485 (*dd*, 1 H); 6.32 (*t*, 1 H); 6.23 (*dd*, 1 H); 6.01 (br. *t*, 1 H); 2.97 (*m*, 2 H); 2.665 (*m*, 2 H); 1.13 (*s*, 6 H); 1.10 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 155.06 (*s*); 154.88 (*s*); 145.25 (*s*); 138.93 (*d*), 132.38 (*s*); 131.77 (*d*); 119.04 (*d*); 115.85 (*d*); 40.45 (*s*); 39.10 (*s*); 31.89 (*t*); 28.65 (*t*); 24.61 (*q*); 23.50 (*q*). MS: 213 (7), 212 (50, M^+), 198 (11), 197 (72), 183 (7), 182 (36), 181 (6), 169 (8), 168 (4), 167 (27), 166 (12), 165 (20), 153 (5), 152 (16), 151 (12), 141 (4), 128 (6), 115 (7), 107 (14), 106 (100), 105 (7), 91 (41), 79 (3), 77 (6), 65 (3). HR-MS: 212.1565 ($C_{16}H_{20}$, M^+, calc. 212.1560).

5.2. *7,7,8,8-Tetramethyl-4,11-di(*tert*-butyl)tricyclo[7.3.0.0^{2,6}]dodeca-1,3,5,9-tetraene* (**28**)[34]). 18.2 mg of **23** are stored in a NMR tube in $CDCl_3$ at r.t. for 2 d. While color turns to red, **23** isomerizes almost quantitatively to **28**. After removal of the solvent, the crude product is purified by FC over 35 g of Et_3N-deactivated silica gel[25]) (R_f 0.28, pentane/Et_2O 200:1) to give 17.7 mg (97% yield) of **28** as a red sticky oil. UV (hexane): 315 (sh, 28173), 323 (29746), 336 (sh, 20051, 406/710). IR (neat): 3060*w*, 2962*s*, 2910*m–s*, 2875*m–s*, 1645*m–s*, 1630*w*, 1590*w*, 1580*w–m*, 1508*w*, 1473*m–s*, 1465*m–s*, 1390*m*, 1373*m*, 1366*m–s*, 1330*w*, 1310*w–m*, 1256*w–m*, 1242*m*, 1208, 1142*w–m*, 1100*w–m*, 1020*w*, 1008*w–m*, 940*w*, 918*w*, 881*w*, 854*w*, 840*w*, 830*w–m*, 816*w*, 794*w*, 788*w*, 660*w–m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.16 (*d*, 1 H); 6.00 (br. *m*, 1 H); 5.82 (*dd*, 1 H); 2.87 (*dd*, 1 H); 2.75 (*m*, 1 H); 2.66 (*d*, 1 H); 1.22 (*s*, 9 H); 1.11 (*s*, 3 H); 1.09 (*s*, 6 H); 1.04 (*s*, 3 H); 0.89 (*s*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 158.78 (*s*); 155.38 (*s*); 151.17 (*s*); 146.02 (*s*); 138.73 (*d*); 132.22 (*d*); 119.11 (*d*); 107.06 (*d*); 55.73 (*d*); 40.77 (*s*); 39.09 (*s*); 33.61 (*s*); 32.58 (*s*); 30.98 (*t*); 29.90 (*q*); 27.39 (*q*); 25.37 (*q*); 24.25 (*q*); 23.18 (*q*). MS: 325 (4), 324 (19, M^+), 310 (4), 309 (17), 294 (2), 268 (4), 267 (4), 253 (8), 238 (4), 237 (4), 211 (4), 181 (2), 163 (14), 162 (100), 148 (12), 147 (90), 131 (4), 119 (11), 105 (16), 91 (8), 79 (4), 57 (12), 55 (7), 41 (10), 28 (13), 18 (93), 17 (58). HR-MS: 324.2814 ($C_{24}H_{36}$, M^+, calc. 324.2817).

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[33]) Taken from a mixture **23**/**24**.

[34]) Surprisingly no **28** is formed, if the conditions described in *5.1* are applied on **23**.

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