97. Oxidative Coupling of 2-Alkyl-6,6-dimethylpentafulvenyl Anions[1])

by **Shaochun You**[2]) and **Markus Neuenschwander***

Institute of Organic Chemistry, University of Bern, Freiestrasse 3, CH-3012 Bern

(7.IV.93)

$CuCl_2$-Induced oxidative coupling of 2-(*tert*-butyl)-6,6-dimethylpentafulvenyl anion **9** predominantly takes place at C(7) and C(5) to give [7–7] and [7–5] coupling products **15** and **16** in 35 and 47% yields, respectively (*Scheme 3*) whose structures are elucidated from 1D- and 2D-NMR analysis. Compared with the product distribution observed for 6,6-dimethylpentafulvenyl anion **2** (*Scheme 1*), no coupling at C(2)/C(3) of **9** is observed. This means that, besides electronic effects, steric effects are also important in oxidative couplings of fulvenyl anions. The same couplings occur in the case of 2,3-bis(6,6-dimethylfulven-2-yl)-2,3-dimethylbutane dianion **10** as well, but, due to electronic as well as conformational effects (*Scheme 5*), intermolecular coupling (to give polymers **17**, *Scheme 4*) is strongly favored over intramolecular coupling. Mechanisms explaining base-catalyzed isomerization **15a** ⇄ **15b** ⇄ **15c** (*Scheme 6*) as well as isomerization **16a** ⇄ **16b** (*Scheme 7*) are proposed.

1. Introduction. – Transition-metal-induced oxidative couplings of metalated organic anions are of considerable interest, since they provide a convenient method of C–C bond formation. Reactions of that type could be generally interesting, they could especially be attractive with respect to the synthesis of theoretically important compounds as well as of natural products. So it is well known today that oxidative coupling of indenide [3], cyclopentadienide [4], and cyclononatetraenide [5] proceeds nearly quantitatively in the presence of Cu^{II} salts at low temperatures, thus providing a straightforward access to pentafulvalenes [4] and nonafulvalenes [5]. If the reaction is applied to α,ω-di(cyclopentadienyl)alkyldiides, then the 'coupling mode' as well as regioselectivity of the coupling reaction are strongly dependent on the number n of CH_2 groups between the cyclopentadienide units. While intramolecular coupling is still important for $n = 1$ [6], intermolecular coupling (to give reactive polymers with cyclopentadiene rings in the polymer chain) dominates for $n = 2$ [7].

Delocalized anion **2**, which is easily obtained by deprotonation of 6,6-dimethylpentafulvene (**1**), is a very attractive ambident anion for oxidative couplings, because **2** as well as the fulvenyl radical **3** (which is assumed to be formed after withdrawal of one electron from **2**[4])) have several reactive sites. Recently, we showed that $CuCl_2$-induced oxidative coupling of **2** results in a very complex mixture of products **4** (18%), **5** (16%), **6** (36%), **7**[3]) (5%), and **8**[3]) (6%; *Scheme 1*) [8]. If these dimers are formally split into the corresponding

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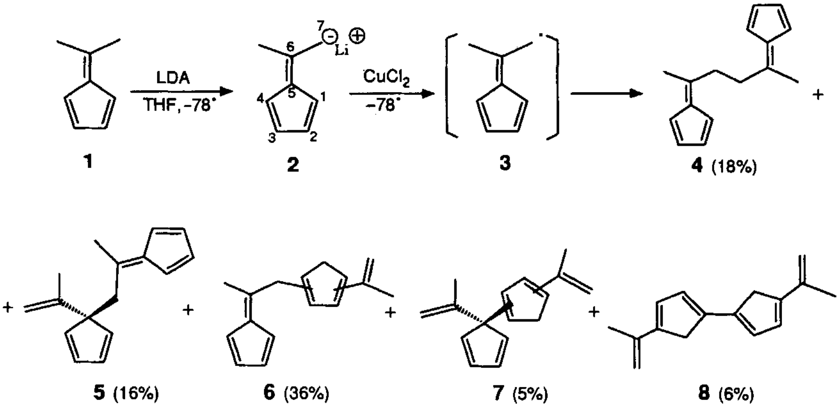
[1]) Coupling Reactions, Part 11; Part 10: [1].

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

[3]) Compounds **6** and **7** are obtained as mixtures of tautomeric cyclopentadienes, while crystalline tautomer **8** has been isolated.

[4]) The mechanism of the Cu^{II}-induced coupling reaction of **2** is still unknown. So it is not yet clear whether dimerization proceeds by recombination of free fulvenyl radicals **3** or by C–C bond formation out of a metalorganic complex of **2**.

Scheme 1. *Products Obtained by Oxidative Coupling of* **2**



fulvenyl radicals **3**, then the positions of **3**, which reacted together, may be easily determined, and a reactivity index of the positions of **3** (or **2** respectively[4])[5])) may be established [8]. The experimental results clearly show that reactivity is decreasing in the series C(7) > C(2)/C(3) > C(5) > C(1)/C(4), while simple frontier-orbital considerations of radical **3**[5]) would suggest the sequence C(7) > C(5) > C(2)/C(3) > C(1)/C(4). These findings hint to the conclusion that SOMO-SOMO interactions are very important in recombination reactions of radicals of type **3**, while the somewhat reduced reactivity of C(5) might be the result of steric and/or electronic effects (loss of conjugation).

To look at the influence of steric effects on oxidative couplings, we investigated the Cu^{II}-induced coupling of 1-(*tert*-butyl)-6,6-dimethylpentafulvenyl anion **9**. If steric effects would be important, then a replacement of anion **2** by anion **9** should result in a dramatic decrease of coupling at C(2) and C(3) of **9** (see products **6**, **7**, and **8** in *Scheme 1*). Furthermore, although large amounts of polymers had to be expected, we looked at the coupling behavior of dianion **10**.

2. Synthesis of Starting Materials. – Fulvene **12** is prepared in good yields (85%) by *Thiele* synthesis [9] from (*tert*-butyl)cyclopentadiene (**11**), which is easily available by nucleophilic attack of MeLi at the exocyclic C(6) of 6,6-dimethylfulvene (**1**) [10], a reaction which is well known for simple pentafulvene [11] (*Scheme 2*). The structure of **12** follows from its spectroscopic data: The UV spectrum (in hexane) is very similar to that of **1**, showing a strong absorption around 270 nm (ε = 23220) with blurred fine structure as well as a typically weak absorption at 350 nm (ε = 430). The most characteristic feature of the ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) is the *ABX* spectrum of H–C(3) at 6.54, H–C(4) at 6.52, and H–C(1) at 6.14 ppm with coupling constants $J(1,3) = 1.75$, $J(1,4) = 2.17$, and $J(3,4) = 5.34$. Furthermore, ^{13}C chemical shifts of C(1) at 111.7, of C(2) at 156.3, of C(3) at 130.5, and of C(4) at 121.3 ppm are very typical[6]). Deprotonation

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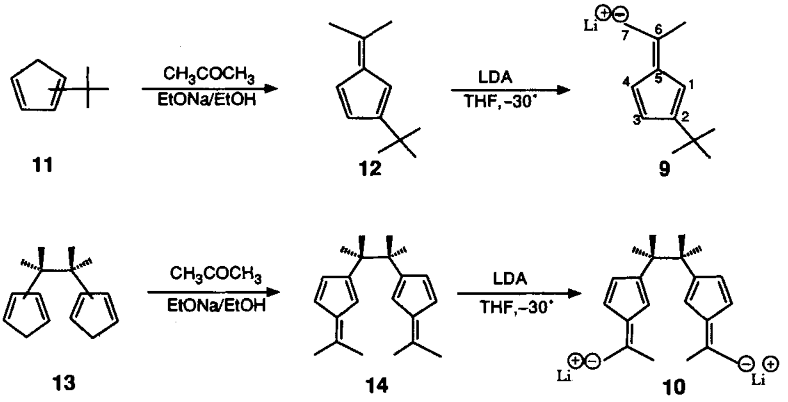
[5]) Note that the *Hückel* coefficients of the SOMO of radical **3** are identical to those of the HOMO of anion **2**.

[6]) For 6,6-dialkylpentafulvenes, C(1)/C(4) are absorbing at 120 ± 2 ppm [12]. Substitution of C(2) by a *t*-Bu group should induce a marked high-field shift of C(1) by *ca.* 12 ppm and a marked low-field shift of C(2) of *ca.* 26 ppm, but leave C(3) and C(4) nearly uninfluenced [13]. The experimental shifts match these expectations.

Scheme 2. *Synthesis of Anion* **9** *and Dianion* **10**



12 → **9** is realized by reacting fulvene **12** with 1.1 mol-equiv. of LDA at –30° in THF. This step is easily controlled by looking at the yellow color of **11** which disappears within minutes at –30° but only very slowly at –78°.

Similarly 2,3-bis(6,6-dimethylpentafulven-2-yl)-2,3-dimethylbutane (**14**) is obtained in very good yields by *Thiele* synthesis [9] from 2,3-di(cyclopentadienyl)-2,3-dimethylbutane (**13**) [14] which is available by reductive coupling of two molecules of 6,6-dimethylfulvene in the presence of Na according to *Rinehart et al.* [15]. Deprotonation **14** → **10** takes easily place by adding difulvene **14** to a slight excess of LDA in THF at –30°.

3. Oxidative Coupling of 2-(*tert*-Butyl)-6,6-dimethylpentafulvenyl Anion 9. – Similar to the oxidative coupling of anion **2** [8], the THF solution of anion **9** is dropwise added to the stirred brownish slurry of anhydrous $CuCl_2$ in THF at –30°. During reaction, $CuCl_2$ dissolves to finally give a dark-green solution[7]) which is filtered over deactivated silica gel at –30°. After elution, the orange-red solution is carefully concentrated (0°/0.3 mbar) to give an orange-red oil.

Both the TLC (silica gel, pentane/Et_2O 100:1) as well as the NMR spectra show that the crude reaction mixture is quite simple compared with the mixture resulting from the oxidative coupling of anion **2** [8]. The TLC only displays two separate spots (R_f 0.69 and 0.45), and the NMR spectra show that **15a** as well as **16a** and **16b** are the predominant products (*Scheme 3*). **15a** could be separated from the mixture of **16a** and **16b** by flash chromatography over Et_3N-deactivated silica gel (pentane/Et_2O 100:1), while separation of compounds **16a** and **16b** was impossible. It is interesting to note that isomerization **16a** ⇄ **16b** is obviously faster than that of **15a**, which equilibrates to the mixture **15a** ⇄ **15b** ⇄ **15c** under base catalysis or when store in the solid state at –70° over months[8]).

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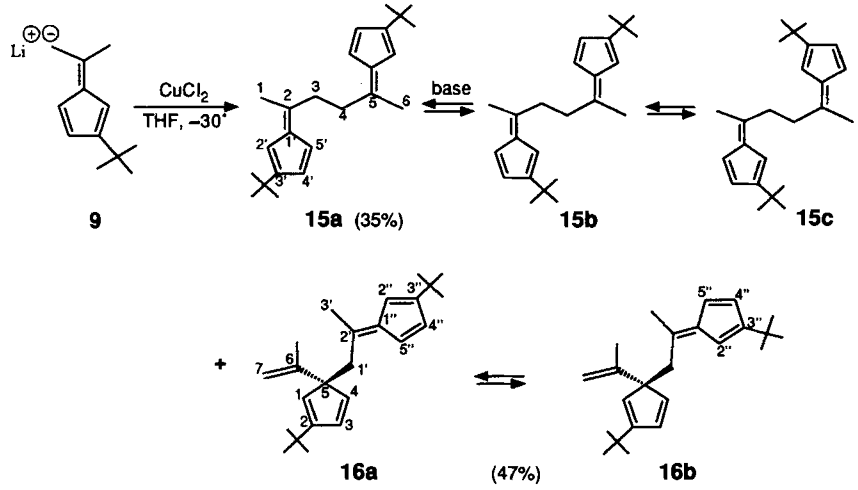
[7]) The reaction mixture looks like a transparent green solution but may contain small amounts of inorganic salts.

[8]) Reasonable mechanisms for the stereoselective formation of **15a** (and probably of **16a**) under kinetic control, for the base-catalyzed isomerization of **15a** and **16a** as well as for the much faster equilibration of **16a** ⇄ **16b** will be discussed later.

Scheme 3. *Products Obtained by Oxidative Coupling of Anion* **9**



3.1. *Structure Elucidation of Dimer* **15a**. First of all, the elemental analysis as well as the MS data support the molecular formula $C_{24}H_{34}$. IR as well as UV spectra are in agreement with the fulvene structural element, which is responsible for the intense UV absorption with maxima at 265 ($\varepsilon = 32100$) and 280 nm ($\varepsilon = 35630$) as well as the broad and weak absorption at 352 nm ($\varepsilon = 975$); according to the ε values, two fulvene units should be present per molecule.

The detailed structure results from the ^{1}H- and ^{13}C-NMR spectra: the most characteristic feature of the 400-MHz ^{1}H-NMR spectrum (*Fig. 1*, top) is the *ABX* spectrum of the ring protons centered at 6.55 (H–C(4')), 6.51 (H–C(5')), and 6.12 ppm (H–C(2')) with characteristic coupling constant $J(4',5') = 5.40$, $J(2',4') = 1.79$, and $J(2',5') = 2.18$ Hz. The signal of H–C(4') is additionally broadened by small long-range coupling with $CH_3(1)$, while all the alkyl groups are absorbing in the expected range. NOE experiments unambiguously establish the position of the two *t*-Bu groups relative to each other as well as the structure of **15a** (*Scheme 3* and *Fig. 1*, bottom). Irradiation of the *t*-Bu groups at 1.21 ppm induces, as expected, a positive NOE of H–C(2') and H–C(4') (*Fig. 1, a*). On the other hand, if the Me group at 2.22 ppm is irradiated, only H–C(2') shows a NOE (*Fig. 1, b*). Finally, if the CH_2 protons at 2.69 ppm are irradiated, a positive NOE is observed for H–C(5'). Furthermore, the ^{13}C-NMR spectrum of **15a** is in full agreement with the proposed structure. The chemical shifts of the fulvene C-atoms are very similar to those of **12** (*Table 1*), while introduction of two *t*-Bu groups in **4** (see **4** → **15a**) produces the expected effects on C-atoms of the fulvene sceleton (*Table 1*).

3.2. *Isomerization of* **15a** *to a Mixture* **15a/15b/15c**. As shown before, oxidative coupling of anion **9** with $CuCl_2$ gives, besides products **16a** and **16b**, isomerically pure difulvene **15a**, provided that low-temperature workup takes place immediately after reaction at −30°. If the basic reaction mixture (originally containing a slight excess of LDA) is stirred at room temperature for additional 2 h before workup, then a mixture of three isomers will be obtained. The same isomerization surprisingly takes place, if pure **15a** is stored in the refrigerator at −70° for several months.

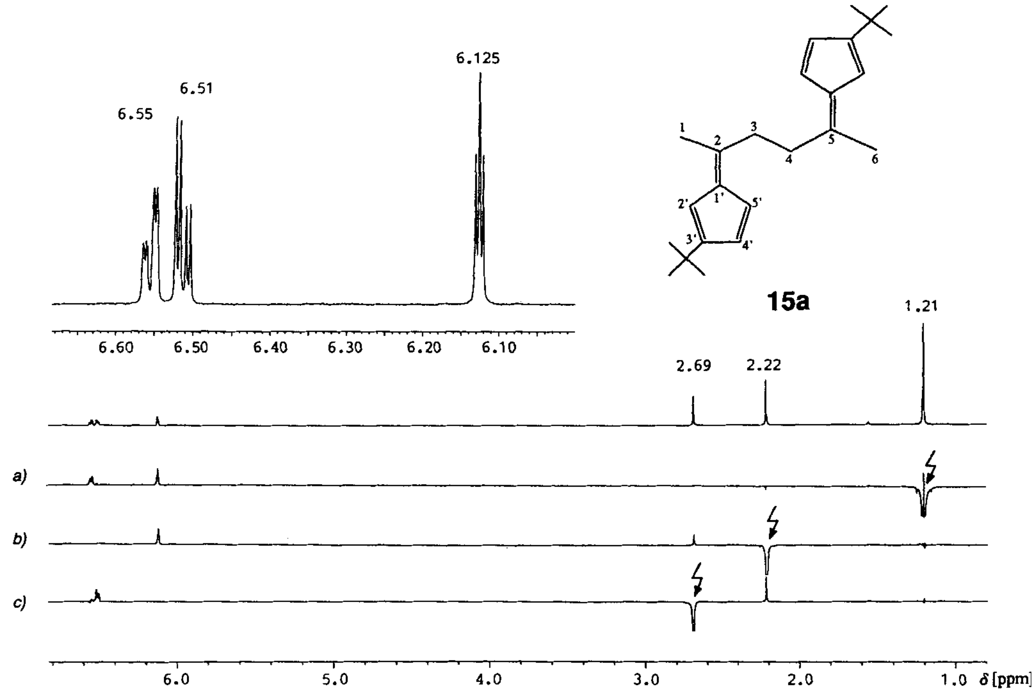
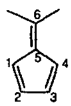
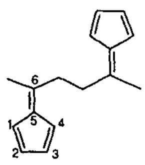
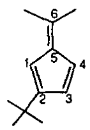
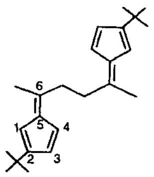


Fig. 1. *^1H-NMR Spectrum* (400 MHz, $CDCl_3$) *of* **15a** *with expansion of the vinyl range* (top) *and NOE experiments* (bottom)

Table 1. *Selected ^{13}C-Chemical Shifts* ($CDCl_3$, rel. to TMS) *of Fulvenes* **1** *and* **12**[a]) *and of Difulvenes* **4**[a]) *and* **15a**[b])[c])

Compound	 **1**	 **4**	 **12**	 **15a**
C(1)	120.4	120.79/120.04[d])	111.74	112.0
C(2)	130.4	131.25	156.53	157.25
C(3)	130.4	131.25	130.46	131.13
C(4)	120.4	120.79/120.04[d])	121.29	120.97
C(5)	142.7	143.04	141.94	142.46
C(6)	148.7	151.51	146.68	146.95

[a]) For C(1)–C(5), calculations of δ values according to [13] starting with **1** give a good fit with the experimental results.

[b]) For C(1)–C(5), calculations of δ values according to [13] starting with **12** give a good fit with the experimental results.

[c]) For comparison of compounds **1**, **4**, **12**, **15a**, the usual numbering of the fulvene skeleton has been adopted.

[d]) Assignment ambiguous.

All the spectroscopic data of the isomeric mixture are very similar to those of pure **15a**. The MS shows the same M^+ and an identical fragmentation pattern with very similar relative intensities. In the ^{1}H-NMR spectrum, all absorptions are in the same areas as those of **15a**, but the splitting pattern of the *ABX* spectrum of the vinylic protons appears blurred compared with **15a** (see *Fig. 1*), and the signals around 2.7, 2.2, and 1.2 ppm consist of several lines. The same is true for all the signals of the ^{13}C-NMR spectrum: all the signals are in the same areas as those of **15a**, the maximum number of lines being four, four lines being visible in the case of C(3)/C(4) around 36.5 ppm and C(1)/C(6) around 20.6 ppm (*Fig. 2*). Isomerization has the strongest effect on the *t*-Bu groups ($\Delta\delta$ of CH_3: 3.1 ppm) followed by C(5′) (0.6 ppm) and C(2′) (0.55 ppm). Finally it is interesting to note that the most intensive lines of the clusters around 36.5 and 20.6 ppm belong to isomer **15a**. In both clusters (*Fig. 2*), there are two new lines of similar intensity as well as a very weak additional line.

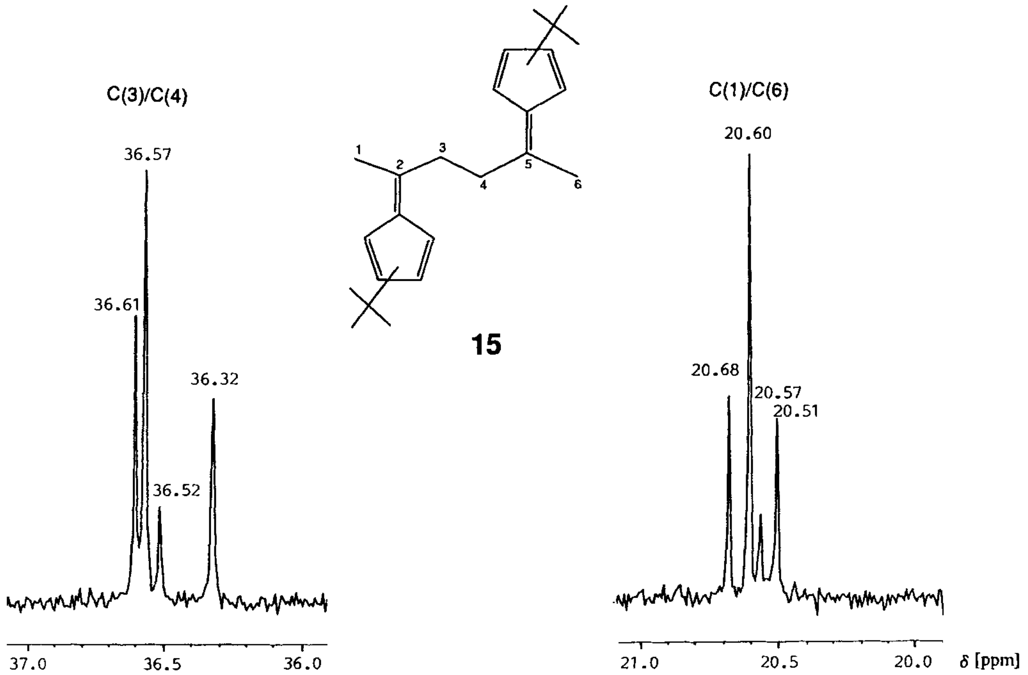


Fig. 2. *Part of the alkyl range of the ^{13}C-NMR spectrum of the isomeric mixture* **15** (75 MHz, $CDCl_3$)

These results show that base-catalyzed isomerization consists in a formal change of *t*-Bu groups between ring-C-atoms C(3′) and C(4′)[8]). By comparison the most intensive ^{13}C-NMR lines belong to isomer **15a**. The two lines of medium intensity (*Fig. 2*) are assigned to isomer **15b** with two different pentafulvenyl units, while the weak lines are assigned to isomer **15c**.

3.3. *Structure of the Isomeric Mixture* **16a/16b**. Analytical evidence shows that isomers of **16** have the same molecular weight as **15a**. Formation of both compounds may be easily explained by formally connecting two radicals (formed from **9** by withdrawal of one electron) at C(7) and C(5), respectively. The only difference between **16a** and **16b** is the position of the *t*-Bu groups in the fulvene unit of **16**.

The structure of **16a** and **16b** mainly follows from ^{1}H- and ^{13}C-NMR investigations including ^{1}H,^{1}H- as well as ^{1}H,^{13}C-COSY spectra as well as NOE experiments. In the ^{1}H-NMR spectrum (*Fig. 3*), two sets of very similar signals (with an identical splitting pattern) of all the protons are visible in an approximate ratio of 2:1. For each isomer, the ^{1}H-NMR spectrum (*Fig. 3*) reveals the presence of two different *t*-Bu groups at 1.18 and 1.04 ppm. According to COSY experiments, the Me group absorbing at 1.77 ppm as well as the two vinylic protons absorbing at 4.95/4.93 and 4.79/4.77 ppm are parts of an isopropenyl unit, which is placed at C(5) of a 2-(*tert*-butyl)cyclopentadiene ring. The *ABX* systems[9]) of the cyclopentadiene protons H–C(1), H–C(3), and H–C(4) are ob-

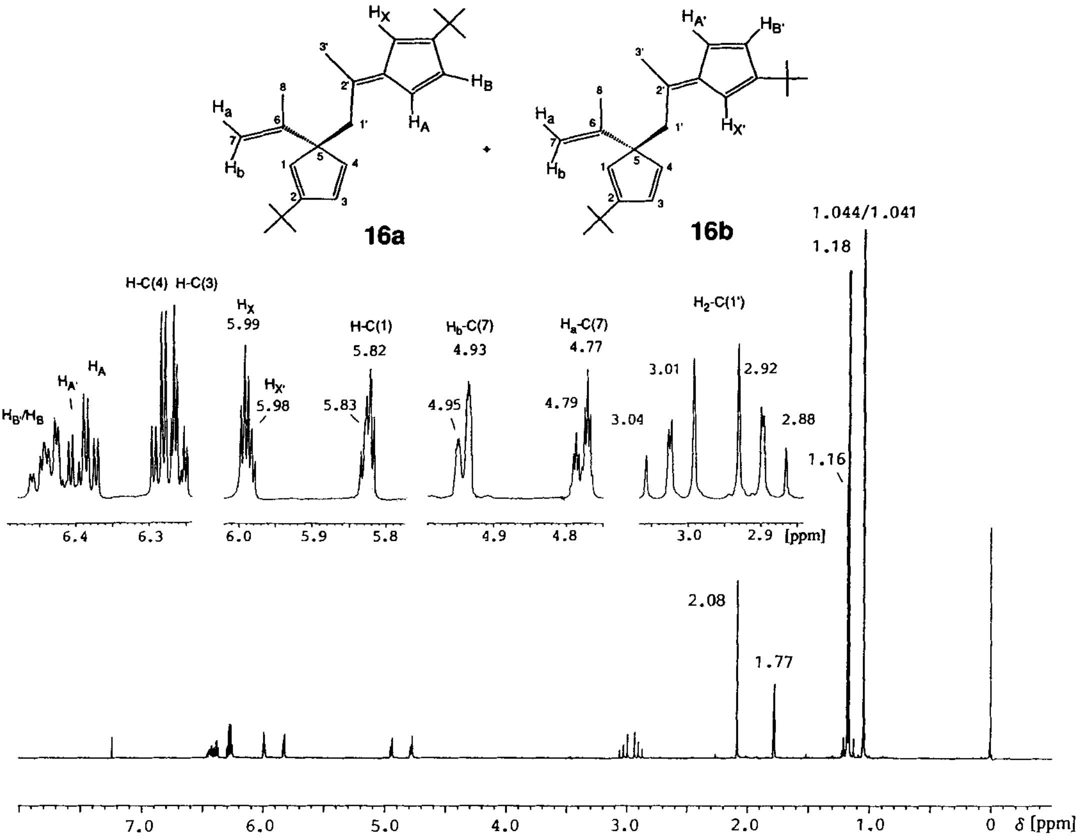


Fig. 3. *^{1}H-NMR Spectrum* (400 MHz, CDCl$_3$) *of the mixture* **16a/16b**, *with expansions of the signals between 6.5 and 2.8 ppm*

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[9]) For each isomer **16a** and **16b**, the *ABX* systems of protons H–C(1) (5.830/5.822 ppm), H–C(3) (6.263/6.258 ppm), and H–C(4) (6.288/6.288 ppm) are so completely overlapping that, at first sight, only one *ABX* system is visible. Coupling constants are typical for cyclopentadienes and the same for **16a** and **16b**: $J(1,3) = 1.71$, $J(1,4) = 2.27$, $J(3,4) = 5.40$ Hz (*cf.* [16]). This similarity supports the conclusion that the isopropenylcyclopentadiene unit is identical for **16a** and **16b**.

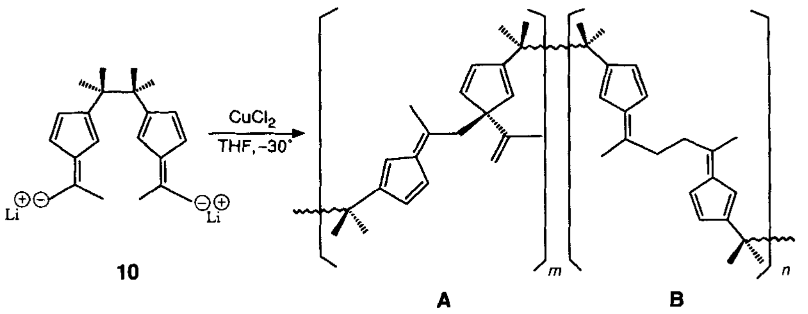
served at 5.82, 6.26, and 6.29 ppm. The second structure element of both isomers **16a**/**16b** is a 2-[3-(*tert*-butyl)cyclopenta-2,4-dien-1-ylidene]propyl unit whose C(1′) is linked with C(5) of the cyclopentadiene[10]): due to the center of chirality at C(5), CH_2 protons at C(1′) are not equivalent so that two *AB* systems with $J = -12.6$ for **16a** and with $J = -12.4$ Hz for **16b** appear at 3.04 and 2.88 ppm (**16b**) and at 3.01 and 2.92 ppm (**16a**). The connectivity between CH_2(1′) and CH_3(3′) (2.08 ppm) as well as between CH_3(3′) and the complex and overlapping *ABX* systems of the fulvene ring protons (range of 6.37–6.47 ppm and 5.99 ppm) is demonstrated by cross-peaks in the COSY spectrum.

Due to the fact that the *ABX* systems of the fulvene ring protons are less overlapping than the nearly identical *ABX* systems of the cyclopentadiene protons[9]), it is reasonably to assume that **16a** and **16b** differ by the positions of the *t*-Bu group in the *fulvene unit*, while the isopropenyl-cyclopentadiene units are identical. This is elegantly proved by NOE experiments which simultaneously show that **16a** is the predominant isomer: by irradiating CH_3(3′) of the fulvene unit (the signals of both isomers are overlapping at 2.08 ppm), the following protons of the *ABX* (**16a**) and *A′B′X′* systems (**16b**) show a strong positive NOE[11]): H_x of the major isomer as well as $H_{A'}$ of the minor isomer. This result is only compatible, if H_x of the predominant isomer **16a** is placed in close proximity to the exocyclic Me group of the fulvene unit.

These structural conclusions are confirmed by the ^{13}C-NMR spectrum of the isomeric mixture **16a**/**16b** whose proton-bearing C-atoms are assigned by ^{1}H,^{13}C shift correlation. The observed chemical shifts of **16a**/**16b** correlate well with model compound **5** (*Scheme 1*) if the $\Delta\delta$ increments due to the additional *t*-Bu groups are taken into account [13].

4. Oxidative Coupling of 2,3-Bis(6,6-dimethylfulven-2-yl)-2,3-dimethylbutane Dianion 10. – If the THF solution of dianion **10** is slowly added to the stirred brownish slurry of anhydrous $CuCl_2$ in THF at −30°, a dark-green solution[7]) is obtained which, after filtration of inorganic salts, gives a sticky orange-red oil of oligomers **17** with a 90% yield (*Scheme 4*). The oligomeric mixture is extremely sensitive towards traces of oxygen which induces cross-linking of the molecules. GPC investigations (THF, ultrastyragel) reveal a very broad molecular-weight distribution with a weight-average M_w of 55300 and a number-average M_n of 2210 giving a M_w/M_n ratio of 25.

Scheme 4. *Oxidative Coupling of Dianion* **10**



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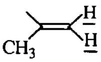
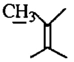
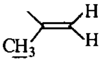
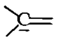
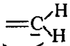
[10]) For C-atom numbering, see *Scheme 3*.

[11]) Additionally, H–C(4) and H–C(1) of the cyclopentadiene show a medium NOE.

NMR-Spectroscopic investigation of the oligomeric mixture **17** conclusively shows that **A** and **B** are the predominant structural elements being present in nearly equivalent amounts. Due to the relatively small M_n, linewidths are comparably small in the ^{13}C- as well as in the ^{1}H-NMR spectrum so that the typical units of **A** and **B** may be identified. Furthermore, structure elucidation is supported by comparison with model compounds **15** and **16** (*Table 2*): in the ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **17**, all the typical absorptions of **15** and **16** are present. The same is true for the ^{13}C-NMR spectrum (100 MHz, $CDCl_3$), with the restriction that the *t*-Bu groups of **A** and **B** show the expected high-field shift [13] compared with the *t*-Bu groups of **15** and **16**, while small shift differences of some C-atoms of **17** are probably induced by the arrangement of **A** and **B** in the polymer chain.

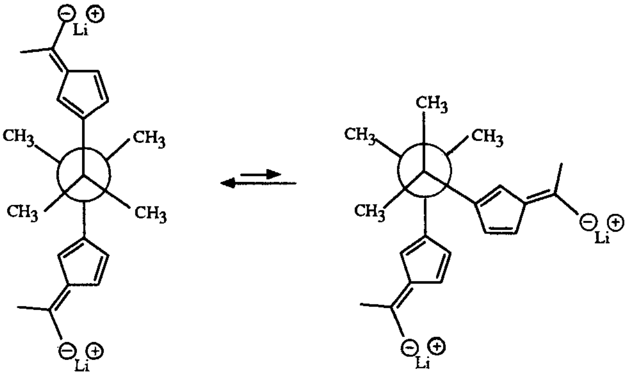
Our results show that in the case of dianion **10** the predominant 'coupling mode' is an intermolecular coupling giving reactive polymers **17** in a high yield which are built up from the expected structural elements **A** and **B** (*Scheme 4*). We believe that the predomi-

Table 2. *^{1}H- and ^{13}C-NMR Absorptions* (δ relative to TMS) *of Polymer* **17** *Compared with Compounds* **16a/16b** *and* **15a**

Unit	**16a/16b**	**15a**	Polymer **17**
Ring- (=C−H)	~ 6.44	6.55	6.5–6.2a)
	~ 6.38	6.51	
	6.29	6.12	6.2–6.0a)
	6.26		
	5.99		
	5.82		5.9
	4.95/4.93	–	5.0
	4.79/4.77		4.8
−CH₂−	3.1–2.8b)	2.69	3.1–2.8a)
			2.7
	2.08	2.22	2.2
			2.1
			2.05
	1.77	–	1.8
$C(CH_3)_3$	1.18/1.16/1.04	1.21	1.2a)
	156.3–143.7c)	157.2/146.9/142.5	159.1–141.8c)
Ring- (=C−H)	142.7/142.6		140–137
	132.3–129.9d)	131.1	134.0–132.1e)
	122.1/121.6	121.0	119.5–118.4e)
	112.6/111.9	112.0	117.1–116.1e)
	110.7/110.6	–	112.6–110.5e)
	64.13/64.10	–	64.0
−CH₂−	40.98/40.93	36.6	41.5–40.7e)
			37.1/36.6
Alkyl-CH₃	29.7/29.15	29.7	24.5a)
=C−CH₃	23.1/20.9	20.7	23.2–22.7e)
			21.5–19.7e)

a) Envelope. b) Two *AB* systems. c) Range of signals. d) 5 Signals. e) Several signals.

Scheme 5



nant polymer formation (instead of an intramolecular coupling) is on one side due to the sterically favorable '*anti*'-arrangement (favored by the bulky fulvenyl units) over the sterically unfavorable *gauche*-arrangement which could induce intramolecular coupling (*Scheme 5*). On the other hand, there are electronic reasons for a preferred intermolecular coupling as well, since HMO calculations show that the HOMO of anions of type **2** (or the SOMO of radicals of type **3**, see *Scheme 1*) are characterized by large *Hückel* coefficients of C(7) and C(5) and comparably small *Hückel* coefficients of the other ring C-atoms.

5. Discussion. – We previously showed [8] that $CuCl_2$-induced oxidative coupling of dimethylfulvenyl anion **2** (which is supposed to proceed over radical **2**[4]) gives a very complex mixture of products which reflects the relative reactivities of the sites of anion **2** (or radical **3**) decreasing in the series C(7) > C(2)/C(3) > C(5) > C(1)/C(4). This result reasonably fits to qualitative expectations based on frontier-orbital interactions of radical **2**, if pronounced stereoelectronic effects on C(5) are considered. Additional bulky substituents introduced at C(2)/C(3) of anion **2** are expected to strongly reduce oxidative couplings at C(2)/C(3) of anion **9** and dianion **10**. The experimental result shows that this is exactly happening: oxidative coupling of anion **9** takes exclusively place at C(7) and C(5) to give the [7–7] and [7–5] coupling products[12]) **15** and **16** with experimental yields of 35 and 47%, respectively, while products resulting from couplings at C(2)/C(3) (see **6**, **7**, and **8** resulting from anion **2**) are not observed.

Spectroscopic investigations surprisingly show that coupling of anion **9** results, under kinetically controlled conditions at low temperature, in the formation of only one [7–7] coupling product **15a**, which later on isomerizes under base catalysis to the isomeric mixture **15a**/**15b**/**15c**. The exclusive formation of **15a** under kinetically controlled conditions is reasonable, if low-temperature deprotonation of fulvene **12** is considerably faster for the sterically less shielded Me group of **12** giving anion **9** (*Scheme 3*)[13]). A straight-

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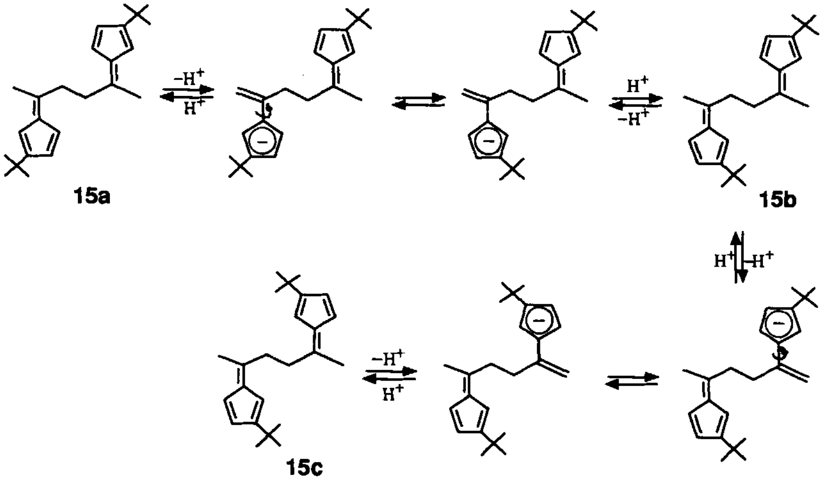
[12]) [7–5] means coupling of two anions **9** at C(5) and C(7), giving products **16**, while [7–7] coupling gives products **15**.

[13]) We assume that anion **9** is rapidly consumed after formation. Otherwise, similar to *Scheme 6*, isomerization would be relatively fast due to the reduced bond order of the exocyclic C=C bond of **9**, which results from contributions of mesomeric isopropenyl-cyclopentadienide.

Scheme 6. *Base-Catalyzed Equilibration* **15a** ⇄ **15b** ⇄ **15c**

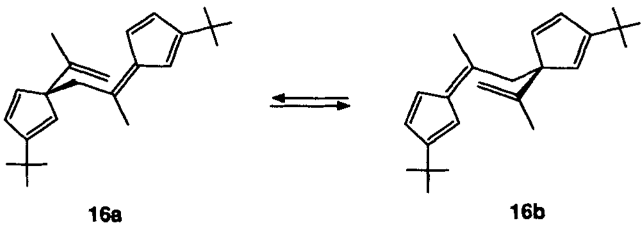


forward mechanism for base-catalyzed isomerization of difulvene **15a** is proposed in *Scheme 6* and includes deprotonation of a Me or CH_2 group of **15a** giving an isopropenyl-cyclopentadienide unit in which rotation around the exocyclic C–C bond is comparably easy[14]).

Since compounds **16** contain the same fulvene unit as **15a**, base-catalyzed isomerization **16a** ⇄ **16b** should be possible under the same conditions as for **15a** according to the mechanism outlined in *Scheme 6*. The only surprising fact is that isomerization **16a** ⇄ **16b** is obviously much faster than for **15a**[15]). A reasonable explanation is given by the fact that **16a**, which is believed to be primarily formed, may easily isomerize to **16b** by a concerted *Cope* rearrangement without base-catalysis (*Scheme 7*).

Our investigations show that $CuCl_2$-induced oxidative coupling of anion **9** predominantly takes place at C(7) and C(5) to give [7–7] and [7–5] coupling products **15** and **16**,

Scheme 7. Cope *Rearrangement* **16a**⇄**16b**



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[14]) Deprotonation of 6,6-dimethylpentafulvene (**1**) $pK_a \approx 22.7$ [17]) is easy in the presence of strong bases (see [18] [8] and the results of this paper). Note that isopropenyl-cyclopentadienides are mesomeric to the appropriate fulvenyl anions.

[15]) Note that low-temperature coupling of anion **9** at –30° gives isomerically pure **15a** under kinetic control, but always an isomeric mixture **16a**/**16b**.

respectively. Because of steric interactions of bulky substituents, no coupling at C(2)/C(3) is observed, while couplings at C(1)/C(4) are unfavorable by electronic reasons. This means that, besides electronic effects, steric effects are important in oxidative coupling of fulvenyl anions as well. The same types of couplings are occurring in the case of dianion **10**, but due to electronic as well as conformational effects (*Scheme 5*) intermolecular coupling (to give polymers **17**) is strongly favored over intramolecular coupling. Reasonable mechanisms explaining base-catalyzed isomerization **15a** $\rightleftarrows$ **15b** $\rightleftarrows$ **15c** (*Scheme 6*) as well as isomerization **16a** $\rightleftarrows$ **16b** (*Scheme 7*) are proposed.

The authors thank the *Swiss National Foundation* (project No. 20-31217.91) for financial support as well as Mr. *B. Kilchör*, *Ciba-Geigy*, Marly, for GPC investigations.

Experimental Part

General. All the reactions were run under Ar. Prior to the addition of the reagents, the reaction vessel was thoroughly flame-dried while being flushed with Ar. Anh. $CuCl_2$ was obtained by drying commerical $CuCl_2$ (*purum*, *Fluka 61173*) at 100°/0.2 mbar in a rotatory evaporator. 6,6-Dimethylpentafulvene was kindly donated by *Ciba-Geigy*, Marly, recrystallized two times from pentane at −50° and distilled in a low-temp. rotatory evaporator at r.t./0.2 mbar. Deactivated silica gel was prepared by treating a slurry of silica gel in pentane with Et_3N (5 weight-% with respect to silica gel) and rotating it in a rotatory evaporator for 2 h, then removing unreacted Et_3N by washing with pentane/Et_2O 3:1, followed by drying in a rotatory evaporator at 100°/50 Torr. Spectra were recorded on the following instruments: UV: *Perkin-Elmer 554*. IR: *Perkin-Elmer 399B*. NMR: *Varian XL-100*, *Bruker AC-300*, *Bruker AM-400*. MS: *Varian MAT CH 7A*. HR-MS: *Varian MAT-311*. Elemental analyses were performed by Dr. *H.* and *K. Eder*, Institute of Pharmaceutical Chemistry, Service of Microchemistry, Geneva.

Synthesis. – *(*tert*-Butyl)cyclopentadiene* (**11**) [10]. A 100-ml two-necked flask fitted with magnetic stirrer, septum, and Ar bubbler was flame dried and flushed with Ar. The flask was charged with 16.5 ml (25 mmol) of MeLi (1.4M in Et_2O) and cooled to 0° in an ice-bath. Freshly distilled *6,6-Dimethylfulvene* (**1**; 2.11 g, 20 mmol), dissolved in 24 ml of abs. Et_2O, was dropwise added by means of a syringe within 30 min under Ar (during the addition, colorless lithium (*tert*-butyl)cyclopentadienide was precipitating). After addition was complete, stirring was continued for an additional h at r.t. The mixture was quenched by adding 10 ml of cold 1N HCl. The org. phase was seperated and the aq. phase extracted two times (2 × 10 ml) with Et_2O. The Et_2O phases were combined, washed with ice-water and dried ($MgSO_4$). Removal of the solvent at −30°/1 Torr gave 2.14 g (87.7%) of a slightly yellow oil of **11**, which was used without further purification.

*2-(*tert*-Butyl)-6,6-dimethylfulvene* (**12**). A 500-ml flask fitted with magnetic stirrer was charged with 2.14 g (17.5 mmol) of (*tert*-butyl)cyclopentadiene and 50 ml of abs. EtOH. EtONa (100 ml, 2.4M in EtOH) was added dropwise within 30 min under Ar at r.t. The resulting red soln. was stirred for another h at r.t. Then, 20 ml of acetone were added in one portion, and the mixture was stirred overnight. Another 100 ml of EtONa (2.4M in EtOH) as well as 20 ml of acetone were added in the same way as above and stirring was continued overnight again. After removing most of the solvent at r.t./12 Torr, 50 ml of Et_2O as well as 75 ml of ice-water were added. The org. phase was seperated and the aq. phase extracted with Et_2O (2 × 40 ml). The Et_2O phases were combined, washed with ice-water, and dried ($MgSO_4$). After evaporation of solvents at r.t./12 Torr, the residue was purified by flash chromatography with pentane over 30 g of deactivated silica gel to give 2.41 g (85%) of **12** as an orange oil. R_f (pentane/Et_2O 100:1) 0.73. UV (hexane): 256 (sh, 17803), 263 (23227), 270 (23226), 279 (sh, 14951), 350 (431). IR (neat): 3102*w*, 3070*w*, 2998*w*, 2960*s*, 2930*m–s*, 2905*m–s*, 2865*m*, 1648*s*, 1618*w*, 1578*w*, 1523*w*, 1518*w*, 1500*w*, 1473*w–m*, 1458*m*, 1438*m*, 1390*w*, 1362*m*, 1352*m*, 1308*w*, 1268*m*, 1240*w*, 1200*w*, 1168*w*, 1150*w*, 1086*w*, 1072*w–m*, 1021*w*, 939*w–m*, 907*w*, 869*w–m*, 815*s*, 715*w*, 678*w*, 623*m*. ^1H-NMR (400 MHz, $CDCl_3$): 6.53 (*m*, 2 H); 6.14 (*t*, 1 H); 2.16 (*s*, 3 H); 2.15 (*s*, 3 H); 1.20 (*s*, 9 H). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 156.53 (*s*); 146.68 (*s*); 141.94 (*s*); 130.46 (*d*); 121.29 (*d*); 111.74 (*d*); 32.26 (*s*); 29.87 (*q*); 22.83, 22.73 (2*q*). MS: 163 (4), 162 (37, M^+), 148 (12), 147 (100), 133 (3), 132 (3), 129 (2), 120 (3), 119 (23), 117 (6), 116 (3), 115 (5), 107 (11), 105 (20), 103 (2), 93 (2), 91 (16), 79 (4), 77 (5), 67 (2), 65 (3), 57 (2), 55 (7), 41 (8). HR-MS: 162.1413 ($C_{12}H_{18}$, calc. 162.1409).

*Synthesis and Oxidative Coupling of 2-(*tert*-Butyl)-6,6-dimethylfulvenyl Anion* (**9**). A 50-ml 2-necked flask fitted with a magnetic stirred, septum, and Ar bubbler was flame-dried and flushed with Ar. The flask was charged with 0.334 g (3.3 mmol) of anh. (i-Pr)$_2$NH as well as with 5 ml of abs. THF. *t*-BuLi (2.4 ml, 3.3 mmol; 1.4M in pentane) was added dropwise within 10 min at −10° by means of a syringe. After stirring the mixture for 30 min at r.t., the resulting LDA soln. was cooled to −30°, and 0.49 g (3.0 mmol) of **12**, dissolved in 5 ml of abs. THF, were added dropwise by means of a syringe within 15 min. After addition was complete, stirring was continued for 15 min at r.t. The ^{1}H-NMR spectrum of the almost colorless soln. showed that **12** had been consumed while anion **9** had been formed.

A second flame-dried 50-ml two-necked flask fitted with a magnetic stirrer, septum, and Ar bubbler was charged with 0.44 g (3.3 mmol) of anh. CuCl$_2$ as well as 15 ml of abs. THF and cooled at −30°. To the yellow-brown suspension the freshly prepared soln. of **9** (see above) was added dropwise within 30 min at −30° by means of a syringe. After addition was complete, stirring was continued for 15 min at −30° to give a dark-green soln. Inorg. salts were filtered off by transferring the resulting mixture with a syringe under Ar into a cooled (−30°) column containing 30 g of Et$_3$N-deactivated silica gel; elution was realized (under slight N$_2$-pressure) by means of pentane. *Ca.* 60 ml of a red fraction were collected at −30° and concentrated at 0°/0.3 mbar to give 0.48 g of a yellow oil. Further purification over 100 g of Et$_3$N-deactivated silica gel with pentane/Et$_2$O 100:1 gave 0.17 g (35%) of *2,5-bis[3-(*tert*-butyl)cyclopenta-2,4-dien-1-ylidene]hexane* (**15a**; R_f 0.45) and 0.24 g (47%) of *2-(*tert*-butyl)-5-{2-[3-(*tert*-butyl)cyclopenta-2,4-dien-1-ylidene]propyl}-5-isopropenylcyclopenta-1,3-diene* (**16**; R_f 0.69).

If the reaction mixture is stirred at r.t. for additional 2 h after addition of **9** to the CuCl$_2$ suspension in THF, a mixture of three isomers of **15** was obtained.

Isomer **15a**: UV (hexane): 257 (sh, 25320), 265 (32102), 280 (35629), 352 (979). IR (KBr): 3104*w*, 3095*w*, 3070*w*, 2960*s*, 2935*m*, 2902*m*, 2865*m*, 1640*s*, 1617*w*, 1579*w*, 1492*w*, 1474*w*, 1460*m*, 1434*w*, 1365*m*, 1353*m*, 1272*w–m*, 1265*w*, 1238*w*, 1201*w*, 1189*w*, 1112*w–m*, 1078*w–m*, 1020*w*, 940*w–m*, 909*w*, 878*m*, 821*s*, 720*w*, 628*m–s*, 528*w*. ^{1}H-NMR (400 MHz, CDCl$_3$): 6.555 (*dd*, 2 H); 6.513 (*dd*, 2 H); 6.125 (*t*, 2 H); 2.69 (*s*, 4 H); 2.22 (*s*, 6 H); 1.21 (*s*, 18 H). ^{13}C-NMR (100 MHz, CDCl$_3$): 157.25 (*s*); 146.95 (*s*); 142.47 (*s*); 131.13 (*d*); 120.97 (*d*); 112.00 (*d*); 36.61 (*t*); 32.26 (*s*); 29.73 (*q*); 20.67 (*q*). MS: 323 (10), 322 (33, M^+), 308 (8), 307 (29), 295 (4), 294 (17), 280 (5), 279 (19), 266 (9), 265 (30), 252 (5), 251 (25), 238 (5), 237 (7), 235 (3), 223 (13), 210 (5), 209 (28), 201 (14), 195 (18), 185 (10), 182 (7), 181 (13), 179 (5), 171 (5), 167 (5), 165 (4), 161 (7), 159 (8), 157 (6), 146 (18), 145 (32), 144 (12), 143 (11), 133 (15), 131 (31), 129 (13), 121 (40), 119 (27), 117 (11), 115 (11), 107 (11), 106 (10), 105 (42), 103 (6), 93 (10), 91 (37), 79 (17), 77 (11), 69 (4), 67 (3), 65 (3), 57 (100), 55 (16), 53 (6), 41 (33), 28 (24), 18 (10). Anal. calc. for $C_{24}H_{34}$: C 89.38, H 10.62; found: C 89.45, H 10.45.

Mixture **15a/15b/15c**. ^{1}H-NMR (300 MHz, CDCl$_3$): 6.62–6.57 (*m*, 2 H); 6.57–6.52 (*m*, 2 H); 6.18–6.13 (*m*, 2 H); 2.746 (*s*); 2.378 (*s*); 2.729 (*s*, 4 H); 2.255 (*s*); 2.236 (*s*, 6 H); 1.242 (*s*); 1.235 (*s*, 18 H). ^{13}C-NMR (300 MHz, CDCl$_3$): 157.16 (*s*); 157.13 (*s*); 157.01 (*s*); 148.84 (*s*); 148.75 (*s*); 142.52 (*s*); 142.48 (*s*); 131.13 (*d*); 131.08 (*d*); 131.05 (*d*); 121.55 (*d*); 120.94 (*d*); 111.96 (*d*); 111.44 (*d*); 111.41 (*d*); 36.61 (*t*); 36.57 (*t*); 36.52 (*t*); 36.32 (*t*); 32.24 (*s*); 32.20 (*s*); 29.71 (*q*); 20.68 (*q*); 20.61 (*q*); 20.57 (*q*); 20.51 (*q*).

Mixture **16a/16b**. UV (hexane): 272 (17431); 352 (sh, 421). **IR** (neat): 3104*w*, 3090*w*, 3070*w*, 2962*s*, 2935*m*, 2905*m*, 2870*m*, 1636*m–s*, 1615*w*, 1570*w*, 1500*w*, 1475*w–m*, 1460*m*, 1450*w–m*, 1391*w*, 1372*w–m*, 1365*m–s*, 1355*m*, 1275*w*, 1243*w*, 1200*w*, 1155*w*, 1140*w*, 1075*w*, 1021*w*, 942*w*, 905*w–m*, 890*m*, 865*w*, 818*s*, 741*w*, 720*w*, 668*w*, 650*w–m*, 622*m*.

Isomer **16a**: ^{1}H-NMR (400 MHz, CDCl$_3$): 6.433 (*dd*, 1 H); 6.379 (*dd*, 1 H); 6.288 (*dd*, 1 H); 6.258 (*dd*, 1 H); 5.993 (*t*, 1 H); 5.822 (*t*, 1 H); 4.934 (*m*, 1 H); 4.771 (*m*, 1 H); 3.01 (*d*, 1 H); 2.92 (*d*, 1 H); 2.08 (*s*, 3 H); 1.77 (*m*, 3 H); 1.16 (*s*, 9 H); 1.04 (*s*, 9 H).

Isomer **16b**: ^{1}H-NMR (400 MHz, CDCl$_3$): 6.450 (*dd*, 1 H); 6.401 (*dd*, 1 H); 6.288 (*dd*, 1 H); 6.263 (*dd*, 1 H); 5.983 (*t*, 1 H); 5.830 (*t*, 1 H); 4.950 (*m*, 1 H); 4.790 (*m*, 1 H); 3.04 (*d*, 1 H); 2.88 (*d*, 1 H); 2.08 (*s*, 3 H); 1.78 (*m*, 3 H); 1.18 (*s*, 9 H); 1.04 (*s*, 9 H). ^{13}C-NMR (100 MHz, CDCl$_3$): 156.33 (*s*); 155.75 (*s*); 153.79 (*s*); 147.38 (*s*); 147.06 (*s*); 146.18 (*s*); 143.74 (*s*); 142.70 (*d*); 142.60 (*d*); 132.33 (*d*); 130.43 (*d*); 130.39 (*d*); 130.35 (*d*); 129.87 (*d*); 122.11 (*d*); 121.55 (*d*); 112.58 (*d*); 111.93 (*t*); 110.70 (*t*); 110.59 (*t*); 64.13 (*s*); 64.10 (*s*); 40.98 (*t*); 40.93 (*t*); 32.18 (*s*); 32.12 (*s*); 31.84 (*s*); 29.75 (*q*); 29.72 (*q*); 29.16 (*q*); 29.14 (*q*); 23.12 (*q*); 23.08 (*q*); 20.89 (*q*); 20.86 (*q*). MS: 323 (9), 322 (34, M^+), 308 (6), 307 (23), 294 (7), 280 (3), 279 (12), 266 (17), 265 (70), 252 (6), 251 (23), 250 (4), 237 (8), 235 (5), 223 (18), 210 (17), 209 (78), 208 (7), 207 (7), 201 (8), 200 (7), 195 (30), 194 (12), 193 (7), 185 (21), 181 (21), 179 (11), 167 (12), 165 (7), 161 (13), 159 (10), 157 (6), 146 (21), 145 (24), 144 (24), 143 (11), 133 (33), 131 (44), 130 (9), 129 (18), 128 (9), 121 (57), 119 (46), 117 (15), 116 (12), 115 (16), 107 (12), 106 (11), 105 (63), 103 (8), 93 (12), 91 (54), 79 (20), 77 (15), 69 (8), 67 (7), 65 (5), 57 (100), 55 (19), 41 (36), 28 (9), 18 (2). Anal. calc. for $C_{24}H_{34}$: C 89.38, H 10.62; found: C 89.19, H 10.60.

Synthesis and Oxidative Coupling of 2,3-Bis(6,6-dimethylfulven-2-yl)-2,3-dimethylbutane Dianion (**10**). To a cooled (−30°) THF soln. of LDA (2.4 mmol; prepared as above), 0.294 g (1.0 mmol) of *2,3-bis(6,6-dimethylfulven-2-yl)-2,3-dimethylbutane* (**14**) [14], dissolved in 6 ml of abs. THF, were dropwise added by means of a syringe within

10 min while stirring. After the addition was complete, stirring was continued for additional 15 min. The ^{1}H-NMR spectrum of the almost colorless soln. showed that the starting material had been consumed, while dianion **10** had been formed.

A second flame-dried 50-ml two-necked flask fitted with a magnetic stirrer, septum, and Ar bubbler was charged with 0.26 g (2 mmol) of anh. $CuCl_2$ as well as with 10 ml of abs. THF and cooled to $-30°$. To the yellow-brown suspension the freshly prepared soln. of **10** (see above) was added dropwise within 30 min at $-30°$ by means of a syringe. After addition was complete, stirring was continued for 15 min at the same temp. to give an almost homogeneous and dark-green soln. Inorg. salts were filtered off by transferring the resulting mixture with a syringe under Ar into a cooled ($-30°$) column containing 30 g of Et_3N-deactivated silica gel, and elution was realized (under slight N_2 pressure) by means of pentane. *Ca.* 60 ml of an orange fraction was collected at $-30°$ and concentrated at 0°/0.3 mbar to give 0.263 g (90.1%) of a slightly yellow sticky oil. Results of the GPC analysis (THF, ultra-styragel): $M_n = 2210$; $M_w = 55300$. ^{1}H- and ^{13}C-NMR data: *Table 2.*

REFERENCES

[1] P. Engel, C. Läng, M. Mühlebach, M. Neuenschwander, *Chimia* **1992,** *46,* 380.

[2] S. You, Dissertation, University of Bern, 1992.

[3] E. Maréchal, J.-J. Basselier, P. Sigwalt, *Bull. Soc. Chim. Fr.* **1964,** 1740.

[4] W. Rutsch, A. Escher, M. Neuenschwander, *Chimia* **1983,** *37,* 160; A. Escher, W. Rutsch, M. Neuenschwander, *Helv. Chim. Acta* **1986,** *69,* 1644.

[5] A. Escher, M. Neuenschwander, *Chimia* **1987,** *41,* 60; A. Escher, M. Neuenschwander, P. Engel, *Helv. Chim. Acta* **1987,** *70,* 1623.

[6] K. Hafner, G. F. Thiele, *J. Am. Chem. Soc.* **1985,** *107,* 5526.

[7] S. You, M. Gubler, M. Neuenschwander, *Chimia* **1991,** *45,* 387.

[8] S. You, M. Neuenschwander, *Chimia* **1992,** *46,* 377.

[9] J. Thiele, *Chem. Ber.* **1990,** *33,* 666; J. Thiele, H. Balhorn, *Liebigs Ann. Chem.* **1906,** *348,* 1.

[10] K. Hafner, *Liebigs Ann. Chem.* **1957,** *606,* 79; C. H. Schmidt, *Chem. Ber.* **1958,** *91,* 28.

[11] K. P. Zeller, 'Pentafulvenes', in 'Houben-Weyl, Methoden der organischen Chemie', Vol. 5/2c, 1985, p. 504: M. Neuenschwander, 'Fulvenes', in 'The Chemistry of Double-bonded Functional Groups', Ed. S. Patai, John Wiley, London, 1989, p. 1131–1268.

[12] R. Hollenstein, W. von Philpsborn, R. Vögeli, M. Neuenschwander, *Helv. Chim. Acta* **1973,** *56,* 847.

[13] D. E. Dorman, M. Jautelat, J. D. Roberts, *J. Org. Chem.* **1971,** *36,* 2757.

[14] M. Fischer, Dissertation, University of Bern, 1987.

[15] K. L. Rinehart, A. K. Frederichs, P. A. Kittle, L. F. Westman, D. H. Gustafson, R. L. Pruett, J. E. McMahan, *J. Am. Chem. Soc.* **1960,** *82,* 4111.

[16] U. Niggli, M. Neuenschwander, *Helv. Chim. Acta* **1990,** *73,* 2199.

[17] D. B. Knight, J. A. Harrelson, *J. Chem. Soc., Chem. Commun.* **1987,** 116.

[18] J. Hine, D. B. Knight, *J. Org. Chem.* **1970,** *35,* 3946; D. B. Knight, R. L. Hartless, D. A. Jarvis, *ibid.* **1972,** *37,* 688.