

143. Oxidative Coupling of 6,6-Dimethylpentafulvenyl Anion¹⁾

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Oxidative treatment of anion **11** (obtained by deprotonation of 6,6-dimethylpentafulvene **10**, *Scheme 3*) with CuCl_2 gives a very complex mixture of coupling products **13** (18%), **14** (16%), **15** (36%), **16** (5%), and **17** (6%) (*Scheme 4* and *Table 2*). These results show that the reactive intermediate obtained by oxidation of **11** (which is believed to be the fulvenyl radical **12**) has several reactive sites. According to the experiments, reactivity is decreasing in the series $\text{C}(7) > \text{C}(2)/\text{C}(3) > \text{C}(5) > \text{C}(1)/\text{C}(4)$ (*Table 2*), while simple frontier-orbital considerations would suggest the sequence $\text{C}(7) > \text{C}(5) > \text{C}(2)/\text{C}(3) > \text{C}(1)/\text{C}(4)$. The results suggest that SOMO-SOMO interaction of the approaching fulvenyl radicals **12** is the central effect governing regioselectivity and product distribution, while *Coulomb* and steric interactions are secondary effects (*Table 4*).

1. Introduction. – Oxidative couplings are important reactions in nature where enzymes catalyze the formation and the coupling of radicals. It is well known for quite a long time that oxidative couplings serve as a key-step in the biosynthesis of many classes of natural products [4–9]. Some of these reactions are considered to be induced by enzymes containing Cu^{II} [9] [10]. *Glaser* was the first to discover that hydrocarbons like phenylacetylenes with a considerable CH-acidity could be coupled to diacetylenes by bubbling air through a solution containing Cu^{I} besides the acetylene [11]. Since that time, transition-metal-induced oxidative couplings of CH-acidic hydrocarbons or (more important) of metalated organic anions have attracted a considerable interest as a convenient method of C–C bond formation [12].

Until very recently, much less was known about oxidative couplings of *Hückel* anions like cyclopentadienide or cyclononatetraenide, although *Doering* had realized in 1958 that cyclopentadienide may be coupled by iodine to give bi(cyclopentadienyl) [13]³⁾, while *Maréchal et al.* [14] had investigated the Cu^{II} -induced oxidative coupling of indenyl *Grignard* to bi(indenyl)⁴⁾. Furthermore, *Hafner et al.* observed that treatment of cyclononatetraenide with I_2 according to *Doering* gave a 30% yield of bi(cyclononatetraenyl) [16].

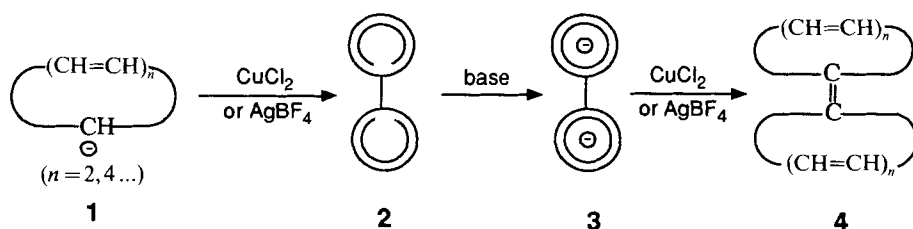
¹⁾ Coupling Reactions, Part 12; Part 11: [1], short communication: [2].

²⁾ Part of the dissertation [3].

³⁾ By twofold deprotonation of di(cyclopentadienyl) and bubbling O_2 through the solution of the hereby formed dianion, *Doering* was the first to prepare very dilute solutions of pentafulvalene [13].

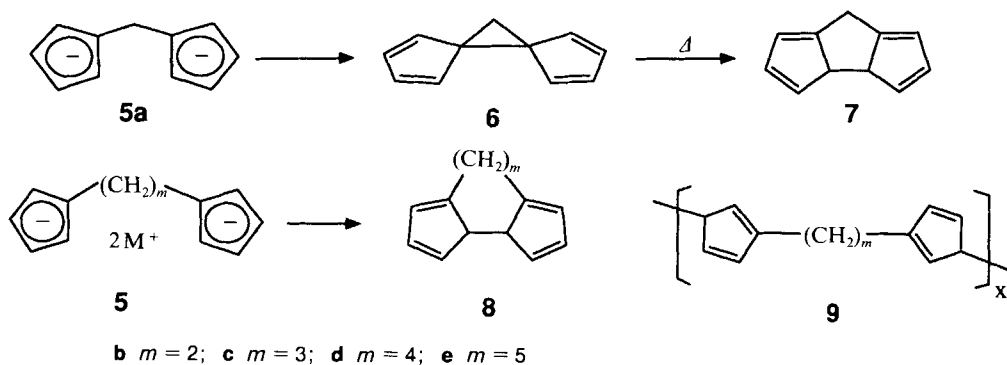
⁴⁾ Very recently, *Simmross* and *Müllen* [15] investigated the oxidative coupling of 2,2'-biindenyls.

In the course of early attempts towards nonafulvenes, we observed⁵⁾ that cyclonona-tetraenide is nearly quantitatively transformed to bi(cyclononatetraenyl) in the presence of AgBF_4 , and we realized later a straightforward synthetic concept⁵⁾ for pentafulvalene **4** ($n = 2$) [19], nonapentafulvalene [20], and nonafulvalene **4** ($n = 4$) [21] (Scheme 1).

Scheme 1. Synthetic Concept for Fulvalenes **4**

Oxidative coupling of *Hückel* anions **1** like cyclopentadienide ($n = 2$) or cyclonona-tetraenide ($n = 4$) takes easily and nearly quantitatively place in the presence of Cu^{II} salts like CuCl_2 ⁶⁾. Twofold deprotonation of the hereby formed dihydrofulvalene **2**, which is quite tedious in the case of bi(cyclononatetraenyl) [22], gives the corresponding dianion **3**, while another oxidative treatment⁶⁾ **3** \rightarrow **4** results in the formation of the central $\text{C}=\text{C}$ bond of fulvalenes **4**.

If reactions of type **1** \rightarrow **2** are applied to α,ω -di(cyclopentadienyl)alkanediiides, then the 'coupling mode'⁷⁾ as well as regioselectivity of the coupling reaction are strongly dependent on the number m of CH_2 units (Scheme 2). As *Hafner* and *Thiele* showed for $m = 1$ [23], intramolecular oxidative coupling **5a** \rightarrow **6** proceeds regioselectively and is

Scheme 2. Oxidative Coupling of α,ω -Di(cyclopentadienyl)alkanediiides with CuCl_2 

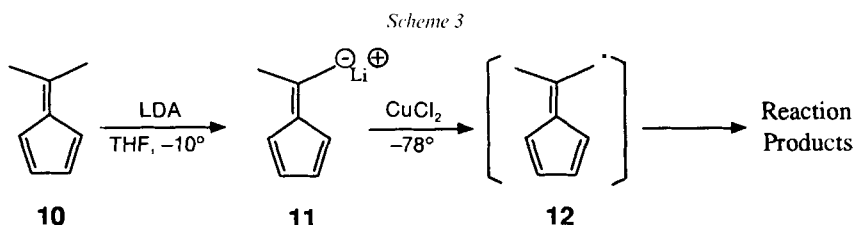
⁵⁾ This observation was first reported in [17], while the synthetic concept depicted in Scheme 1 was realized years later [18].

⁶⁾ Various oxidants may be used [17] [18]. Usually CuCl_2 gives better yields with cyclopentadienides, while AgBF_4 gives better yields with cyclononatetraenides.

⁷⁾ Intramolecular *vs.* intermolecular coupling (to give polymers).

synthetically attractive in view of the thermally induced rearrangement of the dispirocyclopropanes **6** to cyclopenta[*a*]pentalenes **7**. On the other hand, intermolecular coupling **5** → **9** to give polymers strongly dominates over intramolecular coupling **5** → **8**⁸⁾ for $m > 2$ [24], and the yields of **8** strongly decrease from 7% (**8b**, $m = 2$) to 1% (**8c**, $m = 3$) to traces (**8d**, **8e**, $m = 4,5$).

Deprotonated 6,6-dimethylpentafulvene (**11**) is a very attractive ambident anion for oxidative couplings, because the delocalized anion **11** as well as the fulvenyl radical **12** (which is assumed to be formed after withdrawal of one electron from **11**⁹⁾) have several reactive sites (*Scheme 3*). So, regioselectivity of the Cu^{II}-induced coupling of **11** is very interesting, which may formally take place at C(1)–C(5) and C(7). If reactivity of all these C-atoms would be the same, then a large number of reaction products would have to be expected, which is still increased by the fact that tautomeric mixtures of cyclopentadienes may be formed [26].



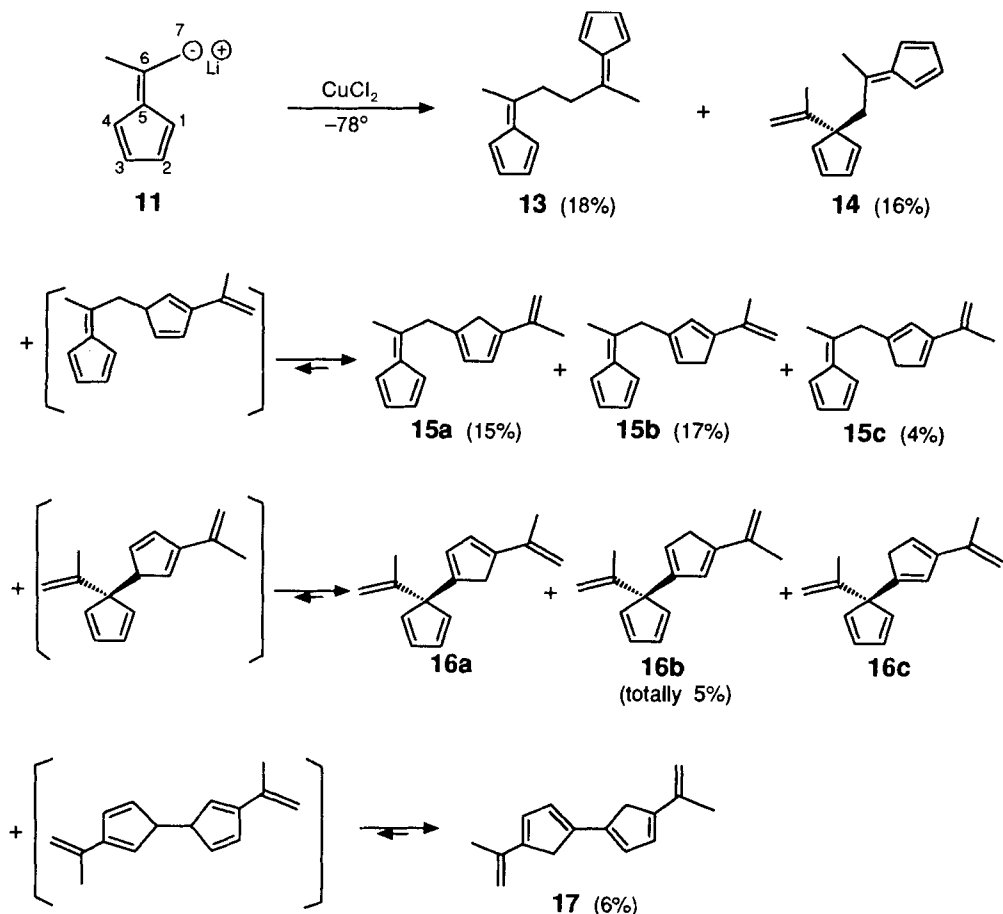
2. Results. – Anion **11** is easily prepared by reacting 6,6-dimethylfulvene (**10**) at -10° with 1.1 equiv. of LDA in THF [27]. Subsequently, the solution of **11** is added dropwise to the stirred brownish slurry of anhydrous CuCl₂ in THF at -78° (*Scheme 4*)¹⁰⁾. During reaction, CuCl₂ dissolves to finally give a dark green-brown solution which is filtered over deactivated silica gel at -30° . After elution, the red solution is carefully concentrated ($0^\circ/0.2$ mbar) to give a 92% yield of the crude mixture of dimers¹¹⁾.

Spectroscopic investigations show that the mixture of coupling products is extremely complex. So, the ¹H-NMR spectrum (*Fig. 1*) displays several signals in the range of vinylic cyclopentadiene ring protons (*ca.* 6.7–5.9 ppm), of terminal vinylic protons (*ca.* 5.2–4.7 ppm) of cyclopentadiene CH₂ or CH (*ca.* 3.6–3.1 ppm), of CH₂–C=C (*ca.* 3.1–2.8 ppm), and of CH₃–C=C units (*ca.* 2.3–1.7 ppm). Separation of the main components from the reaction mixture turned out to be extremely difficult due to the fact that most products are thermally unstable hydrocarbons of the same molecular weight, while

⁸⁾ NMR Investigations show that intramolecular coupling **5b** → **8b** ($m = 2$) proceeds regioselectively as a clean 2,2'-coupling of the cyclopentadienide rings. If the H-atoms of the CH₂CH₂ bridge of **5b** are replaced by Me groups, then intramolecular 2,2'-coupling is favored again (60% yield) and proceeds regioselectively.

⁹⁾ It has to be pointed out that the mechanism of the Cu^{II}-induced coupling is still unknown. So, it is not yet clear whether dimerization proceeds by recombination of free fulvenyl radicals **12** or by C–C bond formation out of a metalorganic complex. According to very typical color changes observed during coupling reactions, free radicals are assumed to be present in solution. Cyclopentadienyl radicals have been detected by ESR spectroscopy [25].

¹⁰⁾ Oxidative coupling may be realized by adding anh. CuCl₂ to the cooled (-78°) solution of anion **11** as well. While product distribution is similar to that given in *Scheme 4* and *Table 2*, the total yield (determined by ¹H-NMR) drops to 68%.

Scheme 4. Reaction Products Obtained by Oxidative Coupling of Anion **11** with CuCl_2 in $\text{THF}^{11)}$ 

complexity of the mixture is increased by easily occurring tautomerizations of compounds with cyclopentadiene units¹²⁾. Nevertheless, pure samples of **13**, **14**, **15a**¹³⁾, **16**¹³⁾, and **17** have been obtained by low-temperature crystallization (**17**), flash-chromatography (**13**, **14**, and **16**)¹³⁾, and HPLC or MPLC (**15a**, see *Exper. Part*).

Despite the complexity of the reaction mixture, the relative amount of compounds **13**–**17** could be determined by adding a small amount of CH_3NO_2 as a reference to the evaporated crude reaction mixture. After dilution with CDCl_3 , $^1\text{H-NMR}$ integrals of all the CH_2 signals between 2.70 and 3.60 ppm were recorded at 300 MHz and compared with the integrals of the reference at 4.27 ppm. These analytical yields are given in *Scheme*

¹¹⁾ Analytical yields in % determined by $^1\text{H-NMR}$.

¹²⁾ Tautomerizations of products **15**–**17** with cyclopentadiene units may occur at low temperature by base catalysis or, in many cases, at ambient temperature by concerted 1,5-H shifts [26].

¹³⁾ While HPLC allowed to separate **15a** from **15b**, the mixture of tautomers **16** could not be separated.

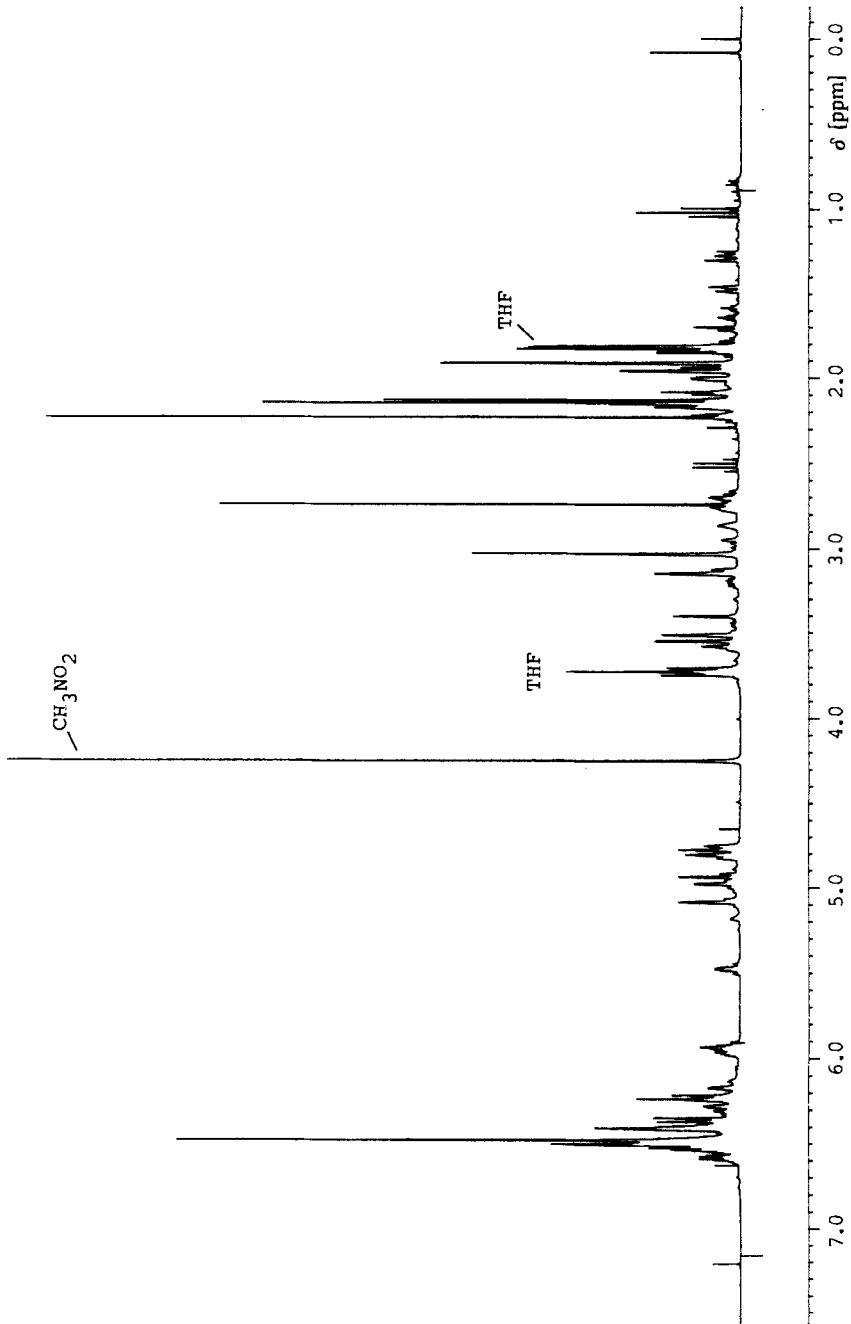


Fig. 1. $^1\text{H-NMR}$ Spectrum (300 MHz, CDCl_3) of the crude reaction mixture together with some THF and the reference signal of MeNO_2

4 and Table 2 (see later), the total analytical yield of **13–17** amounting to 81%. According to these results, tautomeric mixture **15** (36%) is predominantly formed, followed by **13** (18%) and **14** (16%). On the other hand, tautomers **16** (5%) as well as **17** (6%) are less important. The qualitative conclusion is that oxidative coupling mainly takes place at C(7) of anion **11** (or of fulvenyl radical **12⁹**).

3. Structure of Compounds 13–17. – Due to the fact that all compounds are structurally similar hydrocarbons with the molecular formula $C_{16}H_{18}$, they are characterized by nearly the same MS-fragmentation pattern and similar IR spectra. On the other hand, pentafulvene structural units are easily identified by their typically weak and broad UV absorption around 360 nm which is extending to the visible range. Therefore, spectroscopic structure elucidation is mainly based on 1H - and ^{13}C -NMR results. All the assignments summarized in Table 1 are supported by 1D and 2D pulse sequences including DEPT, H,H- as well as H,C-COSY experiments, by selective H,H-decoupling and NOE experiments.

Similar to various simple 6,6-dialkylpentafulvenes [28][29], **13** is characterized by four nearly equivalent pentafulvene ring protons and two pairs of ring C-atoms in the typical range [30] at 131.26/131.25 and 120.79/120.04 ppm¹⁴). Accordingly, the fulvene unit of **14** is recognized by the two pairs of tertiary ring C-atoms absorbing at 130.70/130.38 and 120.98/120.81 ppm, respectively¹⁴). In the NMR spectra of **14**, the isopropenyl unit is identified by the narrow *multiplets* of terminal vinylic protons at 4.95 and 4.79 ppm as well as the narrow *doublet of doublets* of the Me group at 1.83 ppm. Both the isopropenyl group and the fulvene unit of **14** are connected to C(5) of the cyclopentadiene ring whose protons display a nicely resolved *AA'XX'* spectrum with typical coupling constants. Therefore, C(5) of the cyclopentadiene ring of **14** absorbs at high frequency (65.10 ppm).

NMR Investigations show that the isolated tautomer **15a** consists of a fulvene as well as of a 1-isopropenylcyclopenta-1,3-dienyl unit, both structural elements being easily identified: first of all, the 1H - and ^{13}C -NMR data of the fulvene unit are nearly identical with those of **13** (see Table 1). On the other hand, the presence of a second CH_2 group (producing signals at 3.57 and 38.25 ppm) shows that the substitution pattern of the cyclopentadiene ring of **15a** is different from that of **14**. This is additionally shown by the *multiplets* of two vinylic cyclopentadiene protons absorbing at 6.30 and 6.20 ppm. Due to the fact that the coupling constant between these two protons is only 2.3 Hz, 1,2-substitution patterns of the cyclopentadiene ring may be excluded, so that tautomeric structures **15a/15b/15c** are possible. The following arguments are in favor of structure **15a** of the isolated tautomer: first of all, as expected for **15a**, the shift difference of the two tertiary vinylic cyclopentadiene C-atoms ($\Delta\delta = 1.3$ ppm) is very small. Then the exocyclic as well as the ring- CH_2 groups do not display a homoallylic 3J -coupling (which would be expected and is found for **15b**, see later).

While **15a** has been separated from other tautomers and isomers, a second tautomer **15b** was only obtained as a mixture containing **15b** and **14**¹⁵). Fortunately, NMR investi-

¹⁴) Furthermore, the resonances of the two quarternary C-atoms at 151.51 and 143.04 ppm (**13**) as well as at 150.74 and 144.03 ppm (**14**) perfectly match the estimated values according to [31], starting with the basic set of 6,6-dimethylpentafulvene [30].

¹⁵) Traces of third tautomer **15c** have been isolated.

Table 1. ¹H- (300 or 400 MHz) and ¹³C- Chemical Shifts (75 or 100 MHz) of Isolated Compounds **13**, **14**, **15a**, **16^a**, and **17** (δ, CDCl₃)

Structure elements	¹ H-NMR						¹³ C-NMR					
	13	14	15a	16a + 16b + 16c^a	17		13	14	15a	16a + 16b + 16c^a	17	
CH ₃ ^{b)}	2.25	2.17	2.17	-	-		20.96	23.10	20.82	-	-	
CH ₂ ^{b)}	2.75	3.04	3.57	-	-		36.74	40.84	42.22	-	-	
R ¹	6.48	6.45	6.60	-	-							
R ²	6.40	6.50					151.51 ^{c)}	150.74 ^{c)}	150.56 ^{c)}			
							143.04 ^{d)}	144.03 ^{e)}	144.45 ^{e)}			
							131.26	130.70	131.20			
							131.25	130.38	131.05			
							120.79	120.98	121.02			
							120.04	120.81	120.46			
	4.95	4.99	4.99	5.19 (w); 5.08 (s); 5.01 (m);	5.10					148.3-144.8; 139.3 ^{d)} ;	146.37 ^{e)} ;	
	4.79	4.77	4.77	4.97 (w); 4.92 (s); 4.90 (m);	4.84					112.05; 111.81;	110.47;	
	1.83	1.93	1.93	4.89 (w); 4.82 (s); 4.81 (s);	1.97					111.21; 110.48;	20.30	
				4.78 (m); 4.77 (m); 4.77 (w);						109.91;		
				1.97 (w); 1.95 (s); 1.93 (m);						22.36; 20.95;		
				1.73 (m); 1.73 (w); 1.71 (s) ^{f)}						20.59; 20.52;		
										20.49; 20.25		
										148.3-144.8; 139.3 ^{d)} ;	142.48 ^{e)} ;	
										129.87; 128.22;	139.22 ^{e)} ;	
										128.17; 126.33;	129.80;	
										126.05; 125.01;	127.67;	
										42.95; 41.61; 39.97	39.66	
										142.47; 142.40;		
										141.79; 130.05;		
										129.45;		
										68.07; 67.33		

^{a)} Mixture of three tautomers in relative amounts of **26 (16a)**: **60 (16b)**: **14% (16c)**. Some signals are overlapping and, therefore, invisible. ¹H-NMR Intensities are given as follows: s = strong (**16b**); m = medium (**16a**); w = weak (**16c**).

^{b)} Adjacent to fulvene units.

^{c)} Tentative assignments of quaternary C-atoms.

^{d)} Ranges of quaternary C-atoms, which have not been assigned.

^{e)} A₄X₄ System with coupling constants J(1.2) = J(3.4) = 5.34; J(1.4) = 2.03; J(1.3) = J(2.4) = 1.33; J(2.3) = 2.17 Hz.

^{f)} Overlapping AA'XX' systems with coupling constants similar to those of **14** (see Footnote e).

gations were not severely hampered due to the fact that, with exception of a vinylic cyclopentadiene proton, all the ^1H and ^{13}C resonances of **15b** were clearly visible. All the NMR-spectroscopic data are very similar to those of **15a** (see *Table 1*), with exception of the multiplicity of the vinylic cyclopentadiene ring protons and the considerably larger shift difference of at *ca.* 3 ppm between the corresponding C-atoms. The final structure proof for **15b** results from the homoallylic coupling between the ring CH_2 and the exocyclic CH_2 group which is proved by H,H-COSY experiments.

Despite the fact that tautomers **16a/16b/16c** could not be separated, the structure of **16** as well as the assignment of tautomers follows from NMR investigations. In the vinylic part of the ^1H -NMR spectrum (*Fig. 2*), typical chemical shifts and splitting patterns of all the important structural elements are visible: the range between 6.55 and 6.35 ppm contains the partly overlapping $AA'XX'$ systems of the 5,5-substituted cyclopentadiene units, the sector between 6.35 and 5.95 ppm is typical for 1,4- and 1,3-disubstituted cyclopentadienes, while terminal vinylic protons of isopropenyl units are absorbing between 5.2 and 4.75 ppm. Additionally, cyclopentadiene CH_2 groups are absorbing around 3.1 ppm, while Me signals of both types of isopropenyl units are found around 1.95 and 1.70 ppm. Due to the fact that signals of all tautomers are visible in the Me range at 1.95 ppm as well as in the $=\text{CH}_2$ range around 5 ppm (*Fig. 2*), the relative amount of **16a/16b/16c** may be estimated from integrals to be 26:60:14%. Assignment of tautomers follows from irradiating the cyclopentadiene CH_2 groups whose signals are overlapping at 3.14 ppm¹⁶⁾ which results in a change of the splitting pattern of the vinylic cyclopentadiene protons between 5.95 and 6.35 ppm (*Fig. 2*): both signals of the tautomer of medium intensity are simplified to an AB system with a typical $J = 2.21$ Hz which establishes the structure **16a**. On the other hand, the signals of the major isomer at 6.31 and 5.98 ppm appear as a narrow *multiplet* (due to additional long-range couplings) and as a *doublet* with $J = 1.40$ Hz which is typical for **15b**¹⁶⁾.

Isomer **17**, which has been isolated by low-temperature crystallization, produces very clean ^1H - as well as ^{13}C -NMR spectra which reveal the existence of only one tautomer in solution. Due to the symmetry of the molecule, there are only six signals of protons and eight ^{13}C resonances present which belong to two structure elements, namely two (equivalent) isopropenyl as well as two (equivalent) cyclopentadiene units (*Table 1*), whose protons and C-atoms are easily connected according to 2D experiments. All the H,H couplings are small and may be approximately determined by selective decoupling experiments [3]. So, irradiation of the cyclopentadiene CH_2 unit simplifies the *multiplets* of the vinylic cyclopentadiene protons at 6.43 and 6.41 ppm to an approximate AB system with $J_{AB} \approx 2.3$ Hz¹⁷⁾ which, as for **16a** (see above), strongly supports the presence of 1,4-disubstituted cyclopentadiene units.

NOE Experiments (*Fig. 3*) definitely prove the predominant (essentially coplanar) conformation of **17** and unambiguously confirm the assignment of protons $\text{H}-\text{C}(2)/\text{H}-\text{C}(3)$ and $\text{H}_a-\text{C}(7)/\text{H}_b-\text{C}(7)$ which had been made according to chemical-shift argu-

¹⁶⁾ The CH_2 groups of the minor tautomer **16c** absorbs at 3.06 ppm and is not decoupled. After irradiating at 3.06 ppm, both vinylic cyclopentadiene protons are expected to show long-range couplings with the isopropenyl group.

¹⁷⁾ Strictly speaking, due to small long-range couplings between the protons of the two equivalent cyclopentadiene rings, the four vinylic ring protons are of the type $AA'BB'$.

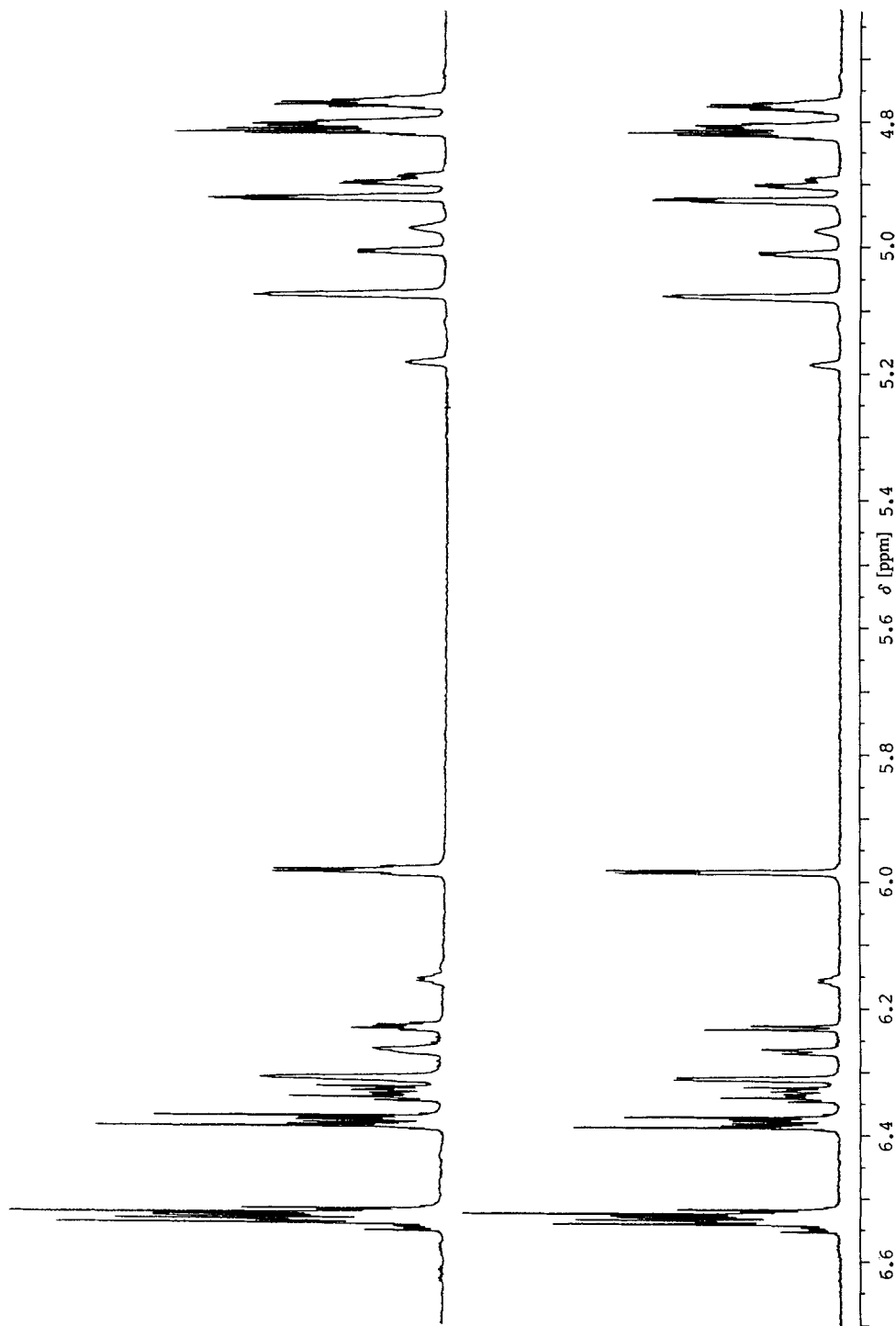


Fig. 2. Vinylic part of the $^1\text{H-NMR}$ spectrum of tautomeric mixture **16** (above). Below: spectrum after irradiating the signals of ring- CH_2 groups of **16a** and **16b** (overlapping at 3.14 ppm)

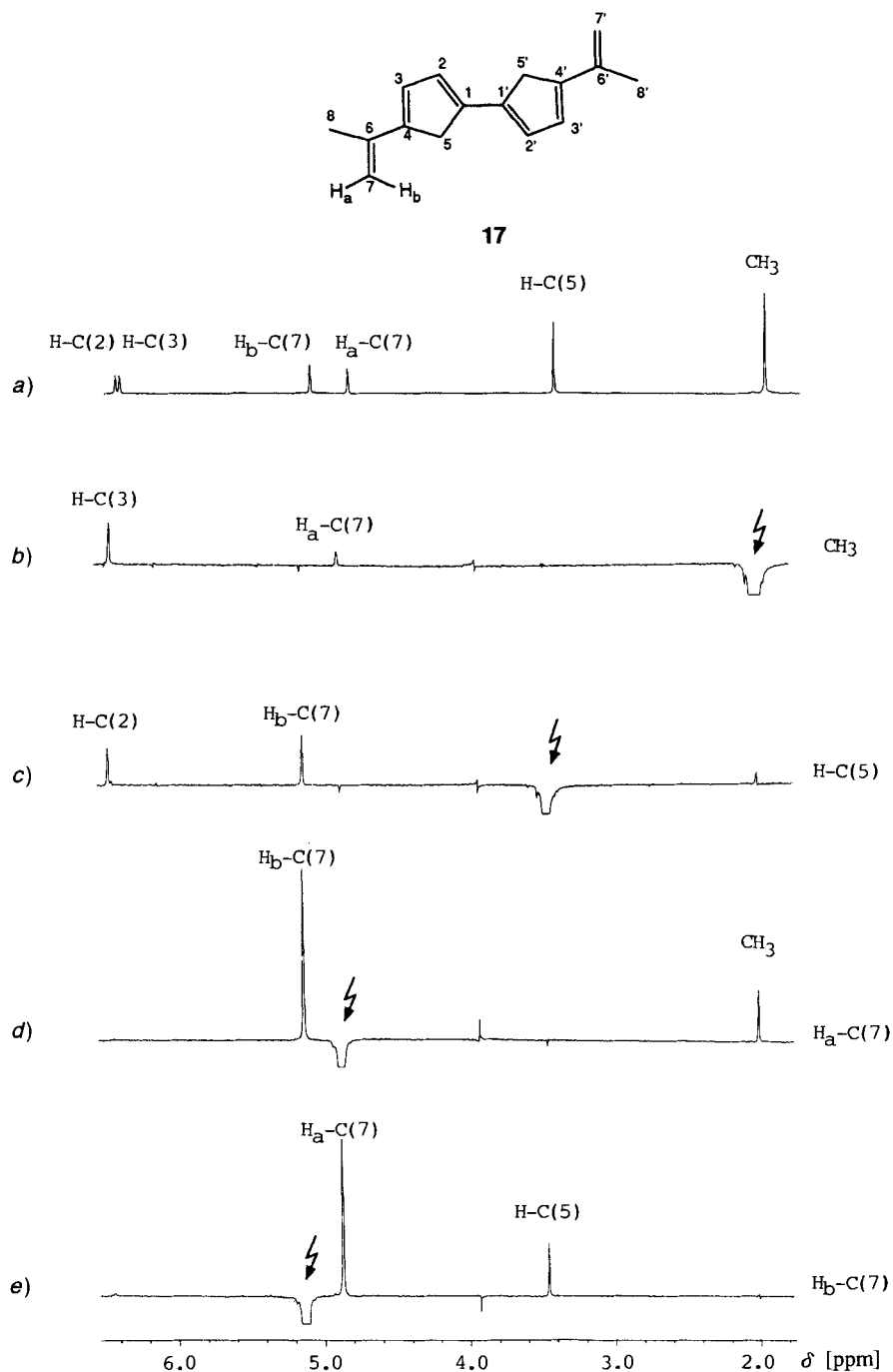


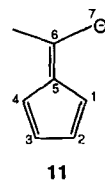
Fig. 3. Reference $^1\text{H-NMR}$ spectrum of **17** (400 MHz, CDCl_3 , (a)) and NOE-difference spectra obtained by irradiating the CH_3 (b), CH_2 (c), and terminal vinylic protons $\text{H}_a\text{-C}(7)$ (d) and $\text{H}_b\text{-C}(7)$ (e)

ments and splitting patterns: irradiating the Me group at 1.97 ppm (*Fig. 3, b*) induces a NOE for $H_a-C(7)$ at 4.84 ppm and for $H-C(3)$ at 6.41 ppm. On the other hand, irradiation of the ring CH_2 group at 3.42 ppm (*Fig. 3, c*) induces a NOE for $H_b-C(7)$ at 5.10 ppm as well as for $H-C(2)$ at 6.43 ppm. Similarly, if $H_a-C(7)$ at 4.84 ppm is irradiated, a NOE is observed for the Me signal at 1.97 ppm as well as for $H_b-C(7)$ (*Fig. 3, d*) while irradiation of $H_b-C(7)$ at 5.10 ppm produces NOE effects of the CH_2 group at 3.42 ppm as well as of $H_a-C(7)$ (*Fig. 3, e*). These experiments clearly show that the C skeleton of **17** is nearly coplanar (in order to maximize π -overlap of the π -system), while the CH_2 groups as well as the isopropenyl units are arranged in a conformation with a minimum steric overlap (see *Formula* in *Fig. 3* and *Scheme 4*).

4. Regioselectivity of the Oxidative Coupling of Anion **11**⁹⁾. – According to *Scheme 4* the observed reaction products **15**, **16**, and **17** are different from primary coupling products expected to be formed under kinetic control (see *Scheme 4*, in brackets). They are obtained from these primary coupling products by base-catalyzed tautomerizations or by a series of 1,5-H shifts¹²⁾. It is obvious that in equilibria of that type products with a maximum π -overlap like **17** are favored. Furthermore, it is well known that 5-alkylcyclopentadienes rapidly tautomerize to an equilibrium in which 1-alkyl- and 2-alkylcyclopentadienes are strongly favored [26]. This means that the observed product distribution of tautomeric mixtures **15/16** matches the expectation.

According to *Scheme 4* and *Table 2*, the following dimers have been spectroscopically identified and their yields have been analytically approximated: **13** (17.6%), **14** (15.7%), **15** (36.5%), **16** (5.2%), **17** (6.0%). These results may be handled in two ways to give

Table 2. Analytical Yields of Products **13–17** as well as Coupling Sites and Relative Importance of Sites in Oxidative Coupling of Anion **11**



Compound	Anal. yield ^{a)} [%]	Coupling sites involved ^{b)}	Relative importance of			
			Site 1/4 ^{c)}	Site 2/3 ^{d)}	Site 5	Site 7
13	17.6	[7-7]	–	–	–	2 × 17.6
14	15.7	[7-5]	–	–	15.7	15.7
15	36.5	[7-2/3]	–	0.5 × 36.5	–	36.5
16	5.2	[5-2/3]	–	0.5 × 5.2	5.2	–
17	6.0	[2/3-2/3]	–	2 × 0.5 × 6.0	–	–
Sum	81.0%	– ^{e)}	–	26.8	20.9	87.4
Reactivity index		–	–	0.198	0.155	0.647

^{a)} Averaged yields of three independent runs, in which a THF solution of anion **11** was added to a slurry of $CuCl_2$ in THF. The determined yields are **13**: 17.3/17.8/17.6%; **14**: 15.1/15.6/16.5%; **15**: 35.1/38.8/35.6%; **16**: 4.9/5.2/5.5%; **17**: 6.3/6.5/5.1%.

^{b)} [7-5] means coupling of two anions **11** at C(5) and C(7).

^{c)} Traces of a [7-1] coupling product have been identified.

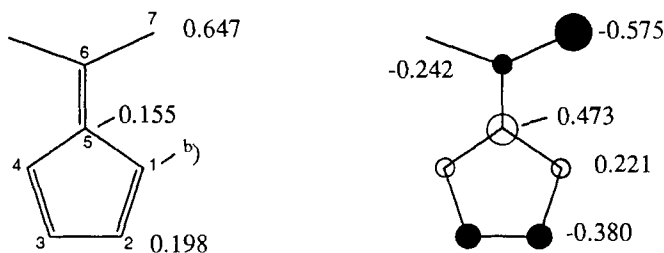
^{d)} Statistically, there are two equivalent positions available.

^{e)} Relative to a total reactivity of 1.

informations on regioselectivities: on one side, reactivity indexes of the C-atoms of anion **11** (or radical **12**)¹⁸⁾ may be derived, and on the other hand, the experimental product distribution (*Scheme 4*) may be compared with the expected product distribution according to a model based on extended frontier-orbital arguments. The following discussions are based on simple *Hückel* calculations.

4.1. *Regioselectivity of Different Sites of Radical 12*¹⁹⁾. All the dimers **13–17** may be formally split into the corresponding fulvenyl radicals so that in each case the positions which reacted together may be determined. Then the appropriate analytical yield is assigned to each site. For instance, since compound **13** (17.6% yield) has been formed by formal reaction of C(7) of both fulvenyl radicals **12**, the assigned 'reactivity number' is 2×17.6 . In the case of **14** (15.7% yield), C(7) of one radical **12** has been connected with C(5) of the second, so that a 'reactivity number' of 15.7 is assigned to both sites. Statistical corrections are necessary for cases in which monomers were reacting with C(2)/C(3) or C(1)/C(4). By adding up the 'reactivity numbers' of each position, a reactivity index of each site may be derived (*Table 3*).

Table 3. *Reactivity Indexes Derived from Analytical Yields (left) and Hückel Coefficients of the SOMO of Radical 12*^{a)}



^{a)} Note that the *Hückel* coefficients of the SOMO of radical **12** are identical to those of the HOMO of anion **11**.

^{b)} Traces of a [7-1] coupling product have been identified.

In the case that fulvenyl radicals **12** should play an important role in oxidative couplings of anion **11**, the frontier orbital (SOMO) of radical **12** would be important in recombination reactions of the type $2 \times \mathbf{12} \rightarrow \mathbf{13}$ to **17**. According to the *Hückel* coefficients of the frontier orbital (the SOMO of the radical **12**; *Table 3*), reactivity is expected to decay in the series site 7 > site 5 > sites 2/3 > sites 1/4. If one takes into account that coupling at site 5 interrupts the π -system in a very unfavorable position, the experimental product distribution, which decays in the series site 7 > sites 2/3 > site 5 > sites 1/4, seems to give a reasonable fit with qualitative expectations based on frontier-orbital interactions of fulvenyl radical **12**, provided that the coupling reaction is frontier orbital controlled.

¹⁸⁾ Note that the *Hückel* coefficients of the SOMO of radical **12** are identical to those of the HOMO of anion **11**. Despite the fact that the mechanism is not yet known^{b)}, we assume that fulvenyl radical **12** plays an important role in oxidative coupling of anion **11**.

¹⁹⁾ Numbering see *Formula* in *Table 2*.

4.2. *Expected Product Distribution According to a Model Based on Extended Frontier-Orbital Arguments.* As a result of perturbation theory, Klopman [32] and Salem [33] derived an expression for the energy gained and lost, when orbitals of two reactants are overlapping. If we neglect the closed-shell repulsion term (taking account for the interaction of filled orbitals), and considering the fact that both SOMO's of radical **12** are of the same energy, this equation has the form

$$\Delta E = \frac{Q_a \cdot Q_b}{\varepsilon \cdot R_{a,b}} - 2 \cdot C_a \cdot C_b \cdot \beta_{a,b}$$

Coulomb SOMO-SOMO
Repulsion Interaction

where a and b are the two reaction sites, R and β the distance and resonance integral, respectively, between these sites, Q and C the corresponding charges and coefficients of the SOMO, respectively, and ε the dielectric constant.

As this is a frontier-orbital-controlled reaction [32], it may be assumed that SOMO-SOMO interaction will be a very important factor in coupling reactions of radicals. Despite the fact that two radicals are combining, *Coulomb* repulsion should be considered. Furthermore, we should consider the very different loss of conjugation for the different transition states. All these effects might influence regioselectivity and product distribution.

SOMO-SOMO Interaction. This type of interaction will certainly be very important if two radicals are recombining. The predictions concerning regioselectivity are easily derived by calculating $|C_a \cdot C_b|$ of each combination. Couplings at C(6) are excluded, because they would give rise to diradicals. For comparisons one has to weigh the different products due to the different ways reactions can occur. For instance, if there is only one equivalent reaction site on both molecules as in [7-7] or [5-5], and the sites are the same on both reagents, there is only one combination possible for the reaction, whereas in the case [7-5] site 5 of molecule a might react with site 7 of molecule b or *vice versa*. If equivalent sites on one molecule as site 1/4 or site 2/3 are reacting there are even more combinations possible. The resulting statistical weights are listed in *Table 4*.

It is interesting to see that the statistically corrected yields are decreasing in the series [7-7] >> [7-2] > [7-5] >> [2-2] ~ [5-2], while products of *Hückel* coefficients $|C_a \cdot C_b|$ are decreasing in the row [7-7] > [7-5] > [5-5] > [7-2] > [5-2] > [2-2] according to *Table 4*. With exception of the combination [5-5], all the combinations with large $|C_a \cdot C_b|$ products have been isolated. Furthermore, C(7) and C(2) are obviously reacting together more easily than expected. All the other products are in the predicted row, and no combination being characterized by small $|C_a \cdot C_b|$ values has been found.

Coulomb Forces. According to the charge-density distribution of the 'fulvenyl radical', C(7), C(6), C(5) have a positive charge decreasing in the series from 0.211 to 0.075 and 0.060, while C(1)/C(4) and C(2)/C(3) have a negative charge of -0.139 and -0.033. So, for all the 'HOMO couplings' of identical C-atoms, charge repulsion should be operative and decrease in the row [7-7] > [1-1] > [5-5] > [2-2]. Obviously *Coulomb* forces are not the dominating factor, since then the yields should decay in the sequence [2-2] > [5-5] > [1-1] > [7-7] which is in clear contradiction to the experimental sequence in which the [5-5] product is missing, while the [7-7] product is favored.

Table 4. Coupling Sites of Fulbenyl Radical 12. Experimental and Calculated Yields

Product	Yield [%]	Stat. weight	Weighted yield %	In of rel. W.Y. ^{a)}	$C_a \cdot C_b$	$cc/rel.^b)$	$Q_a \cdot Q_b^c)$	$qq/rel.^d)$	res./rel. ^{e)}	Calc. ln of rel. W.Y. ^{a)}	Calc. W. yield [%]	Calc. yields [%]
[7-7]	17.6	1	17.6	0.0	0.331	0.0	+0.0444	0.0	0.0	0.0	17.6	17.6
[7-5]	15.7	2	7.85	0.8074	0.272	-0.059	+0.0126	-0.0318	-0.994	-0.959	6.75	13.5
[7-2]	36.5	4	9.125	-0.6569	0.219	-0.112	-0.0070	-0.0514	-0.567	-0.619	9.48	37.9
[5-2]	5.2	4	1.3	-2.6055	0.180	-0.151	-0.0020	-0.0464	-1.561	-2.449	1.52	6.1
[2-2]	6.0	4	1.5	-2.4624	0.145	-0.186	+0.0011	-0.0433	-1.134	-2.565	1.35	5.4
[7-1]	traces ^{f)}	4			0.127	-0.204	-0.0293	-0.0737	-0.478	-1.126	5.71	22.8
[5-1]	§)	4			0.104	-0.226	-0.0083	-0.0527	-1.472	-3.227	6.98	2.7
[2-1]	§)	8			0.084	-0.247	+0.0047	-0.0397	-1.045	-3.442	0.56	4.5
[1-1]	§)	4			0.049	-0.282	+0.0194	-0.0250	-0.956	-4.304	0.24	1.0
[5-5]	§)	1			0.224	-0.107	+0.0036	-0.0408	-1.988	-2.483	1.47	1.5

^{a)} Natural logarithm of the weighted yield divided by the one of the [7-7] compound.

^{b)} $|C_a \cdot C_b| - |C_a \cdot C_b|$ of the [7-7] compound.

^{c)} +: repulsion; -: attraction.

^{d)} $Q_a \cdot Q_b - Q_a \cdot Q_b$ of the [7-7] compound.

^{e)} Resonance energy of the product minus the one of the [7-7] compound.

^{f)} Traces identified by ¹H-NMR.

^{§)} Not found so far.

For mixed couplings (of different C-atoms of the two molecules), the [7-1] product should be strongly favored due to *Coulomb* attraction, and in the case of a dominating *Coulomb* effect, the expected series is [7-1] > [5-2] ~ [5-1] > [7-2] > [2-1] > [7-5], which once again does not correlate with the experimental results [7-2] > [7-5] > [5-2] > [7-1] and [5-1] (not found). It is interesting to note that the favored product [7-1] has been observed, although the yield is very small.

Although *Coulomb* forces do not seem to be very important in couplings of fulvenyl radicals **12**, they may be operative besides the dominating SOMO-SOMO interaction.

Loss of Conjugation. Whereas the above two terms are adequate for a discussion of substitution reactions, we should additionally consider in the present case the loss of conjugation for different transition states. Assuming that the transition state has in this respect some similarity to the product, we have to add two independent *Hückel* energies (which we will call resonance energies, in a slightly sluggish way) for the two parts of the product. Depending on the reaction site these individual energies have the following values: site 7 (7.47β (fulvene)) > site 1 (6.99β (hexa-1,3,5-triene)) \approx site 2 (6.90β (2-vinylbuta-1,3-diene)) > site 5 (6.47β (butadiene + ethene)).

Summing up the two parts, we get the following sequence [7-7] > [7-1] \approx [7-2] > [1-1] \approx [7-5] \approx [2-1] \approx [2-2] > [5-1] \approx [5-2] > [5-5], which might explain why [5-5] has not been found.

Combining the Three Terms in a Simple Model. As all three terms are representing energies, we might try to find a kind of *Boltzmann* relationship between them and the yield for the different products. If we arbitrarily divide all yields by the yield of the [7-7] product, *i.e.* choose the yield of the [7-7] combination as 1, and subtract from all the energetical terms the corresponding term of the [7-7] product, *i.e.* choose the energies of [7-7] combination as 0, then we can make the following approximation:

$$\ln(\text{relative weighted yield}) = a_1 \cdot cc/\text{rel.} + a_2 \cdot qq/\text{rel.} + a_3 \cdot \text{res.}/\text{rel.}$$

where a_i are fit parameters and *cc/rel.*, *qq/rel.* and *res./rel.* stand for the above defined relative SOMO-SOMO, *Coulomb*, and resonance interactions, respectively. All the data needed for this fit are given in *Table 4*. Only the first five compounds (which were experimentally found with a reproducible yield) were used for the fit giving the following parameters: $a_1 = 14.2$, $a_2 = -31.4$, and $a_3 = 1.13$. With the fitted parameters, the yields were then recalculated for all the products including the ones experimentally not found. The calculated yields are given in the last column of *Table 4* and need some comment.

It is not surprising that the yields of the experimentally found compounds are modelled fairly well, as we used three parameters for five values. However, it is interesting to see, that, with the exception of compound [7-1], a small yield is predicted for all products which were not found. Compound [7-1] was found in traces, while the model predicts a high yield. This only contradiction cannot be explained presently. It seems that a further factor is of importance here which we do not know. Steric hindrance does not seem to explain the result, as we confirmed with molecular-mechanics calculations.

The parameters given above are not very conclusive about the relative importance of the different terms. However, if we multiply them by the range of the corresponding property (*e.g.* $a_1 = a_1(cc/\text{rel.}_{\text{max}} - cc/\text{rel.}_{\text{min}}) = 14.2 \cdot 0.282 = 4.0$), we obtain the following absolute values: $a_1 = 4.0$, $a_2 = 2.3$, $a_3 = 2.3$, which show the relative importance of the

different factors. As qualitatively discussed above, the SOMO-SOMO interaction is dominating, whereas the other two factors are of similar size but less important.

Conclusions. To our opinion the experimental results obtained so far²⁰⁾ are in agreement with the following postulates. 1) The central effect governing regioselectivity is the SOMO-SOMO interaction of the fulvenyl radicals **12**. 2) *Coulomb* interactions and loss of conjugation are secondary effects which may influence the sequence predicted by $|C_a \cdot C_b|$ values.

There are several attractive arguments in support of postulate 1: first of all, all the products [5-1], [2-1], [1-1] being characterized by a $|C_a \cdot C_b|$ product smaller than 0.10 are missing. Second, all the products with a large SOMO overlap have been found, with one important exception concerning the [5-5] product, which is easily explained by an exceptionally high loss of conjugation. The only contradiction between the experimental findings and the above model is the high yield predicted for product [7-1], which, although showing a smaller SOMO-SOMO interaction than the [2-2] product (which was found with a yield of 6%), should be favored by a considerable *Coulomb* interaction and less loss of conjugation.

In summary, our results suggest that SOMO-SOMO interaction of the approaching fulvenyl radicals **12** is the most important effect governing regioselectivity and product distribution observed in oxidative couplings of anion **11**, while *Coulomb* interactions and loss of conjugation are secondary effects.

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Experimental Part

General. All the procedures were realized in abs. solvents and under Ar. Since most of the coupling products are thermally unstable and will polymerize at a considerable rate even around 0°, their isolated yields will be somewhat lower than the analytical yield of products in the reaction mixture. Therefore, isolated yields were not optimized. Product composition was determined from the ¹H-NMR spectra (300 MHz) of three independent runs by adding MeNO₂ as an internal standard after filtration and evaporation of the crude mixture.

Procedure. – A 50-ml two-necked flask fitted with a magnetic stirrer, septum, and Ar bubbler was flame-dried and flushed with Ar. The flask was charged with 1.4 ml (1.01 g, 10 mmol) of anh. (*i*-Pr)₂NH and 5 ml of THF. At –10°, 7.2 ml (10 mmol) of *t*-BuLi (1.4M in pentane) were dropwise added within 10 min by means of a syringe. After stirring the mixture for 30 min at r.t., the resulting LDA soln. was again cooled to –10°, and 0.96 g (9 mmol) of freshly distilled 6,6-dimethylfulvene, dissolved in 5 ml of 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 ¹H-NMR spectrum of the almost colorless soln. showed that 6,6-dimethylfulvene had been consumed, while anion **11** had been formed.

A second flame-dried two-necked flask fitted with a magnetic stirrer, septum, and Ar bubbler was charged with 1.34 g (10 mmol) of anh. CuCl₂ as well as with 15 ml of THF and cooled at –78°. To the yellow-brown suspension the freshly prepared soln. of **11** (see above) was added dropwise within 10 min at –78° by means of a syringe. After addition was complete, stirring was continued for 15 min at –78° 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 35 g of Et₃N-deactivated silica gel, elution was realized (under slight Ar pressure) by means of pentane. At –30°, ca. 60 ml of a red fraction were collected and concentrated at 0°/0.3 mbar to give 0.882 g of an orange

²⁰⁾ Due to the fact that the reaction mixture is extremely complex and not easily separated, it is possible that products being present in small amounts have not been detected.

oil²¹): The oil was dissolved in 20 ml of Et₂O and kept at -70° overnight, while 57 mg (6.0%) of yellow crystals of dimers 7 were precipitating. Recrystallization from Et₂O gave pure, thermally instable dimer 17.

The filtrate was concentrated at 0°/0.3 mbar and separated by flash chromatography with pentane/Et₂O 200:1 over 100 g of Et₃N-deactivated silica gel to give three fractions: the first fraction (R_f 0.84) contained pure 16 (46 mg, 4.8%) as a tautomeric mixture; the second fraction (464 mg, 48.8%) was a mixture of 14 as well as of tautomers 15, while the third fraction (R_f 0.53) gave yellow crystals of thermally instable dimer 13 (156 mg, 16.3%) after evaporation. Repeated HPLC or MPLC of 150 mg of the second fraction with pentane over 70 g of Et₃N-deactivated silica gel resulted in the separation of 14 and 15a, while 15b was obtained as a mixture together with 14.

Analytical and Spectroscopic Data of Compounds 13–17^{22,23}. – 2,5-Di(cyclopenta-2,4-dien-1-ylidene)hexane (13). M.p.: sinters at 48°, becomes totally brown at 150°. UV (hexane): 255 (19640, sh), 263 (26490), 278 (28230), 360 (690). IR (film): 3115w, 3100w, 3068w, 2990w, 2930w, 2908w, 2865w, 2850w, 1635s, 1615w–m, 1470m, 1458m, 1434w–m, 1368s, 1265w, 1148w, 1098w, 1089m, 994w, 922w, 890w, 860w–m, 810w, 768s, 762s, 631m–s, 620w–m. MS: 211 (12), 210 (65, M⁺), 209 (5), 196 (16), 195 (99), 183 (16), 182 (84), 181 (22), 180 (58), 179 (27), 178 (17), 169 (16), 168 (16), 167 (75), 166 (31), 165 (72), 155 (13), 154 (18), 153 (33), 152 (18), 145 (21), 141 (18), 130 (17), 129 (29), 128 (18), 117 (18), 105 (34), 104 (9), 103 (41), 91 (27), 90 (14), 89 (19), 79 (74), 78 (21), 77 (100), 65 (23), 53 (11), 51 (12), 43 (8), 41 (13), 39 (15). HR-MS: 210.1416 (C₁₆H₁₈, M⁺; calc. 210.1409).

5-[2-(Cyclopenta-2,4-dien-1-ylidene)propyl]-5-isopropenylcyclopenta-1,3-diene (14). UV (hexane): 270 (17195), 350 (380, sh). IR (neat): 3100w, 3090w, 3070w, 2970w, 2950w, 2920w–m, 2860w, 1633s, 1615w, 1470m, 1450w–m, 1370s, 1253w, 1150w, 1100w, 1090w–m, 994w, 976w, 930w, 920w, 890m, 859w, 810w, 802w, 770s, 750m–s, 715w, 663w–m, 620m. MS: 211 (8), 210 (43, M⁺), 209 (5), 196 (17), 195 (100), 194 (8), 182 (16), 181 (21), 180 (58), 179 (25), 178 (12), 168 (15), 167 (55), 166 (29), 165 (70), 155 (12), 154 (23), 153 (35), 152 (20), 145 (6), 144 (6), 143 (11), 142 (9), 141 (15), 130 (12), 129 (25), 128 (20), 127 (6), 123 (5), 118 (5), 117 (10), 115 (17), 106 (5), 105 (31), 104 (8), 103 (36), 102 (5), 92 (7), 91 (20), 90 (11), 89 (21), 81 (8), 80 (6), 79 (70), 78 (19), 77 (90), 76 (5), 65 (21), 65 (7), 53 (12), 51 (14), 41 (11), 39 (18). HR-MS: 210.1409 (C₁₆H₁₈, M⁺; calc. 210.1409).

1-[2-(Cyclopenta-2,4-dien-1-ylidene)propyl]-4-isopropenylcyclopenta-1,3-diene (15a). UV (hexane): 268 (20870), 308 (9030, sh), 380 (500, sh), 404 (326, sh). IR (neat): 3085m, 3070m, 2990w–m, 2970w–m, 2950m, 2922m, 2900w–m, 2850w, 1640s, 1618m–s, 1603m, 1598m, 1530m, 1470m–s, 1453m, 1440m–s, 1369s, 1269w, 1250w, 1089m, 992w–m, 898m–s, 870m–s, 858m–s, 830w–m, 808w, 765s, 635m, 612m–s. MS: 211 (14), 210 (67, M⁺), 209 (6), 196 (10), 195 (62), 194 (7), 193 (11), 182 (15), 181 (23), 180 (50), 179 (33), 178 (20), 169 (19), 168 (10), 167 (40), 166 (28), 165 (100), 155 (13), 154 (18), 153 (41), 152 (33), 151 (7), 143 (10), 142 (9), 141 (17), 130 (6), 129 (14), 128 (20), 127 (7), 117 (10), 115 (25), 105 (10), 103 (10), 102 (4), 91 (17), 90 (5), 89 (15), 79 (17), 77 (45), 76 (9), 65 (5), 63 (9), 53 (6), 51 (8), 41 (7), 39 (7). HR-MS: 210.1402 (C₁₆H₁₈, M⁺; calc. 210.1409).

3-[2-(Cyclopenta-2,4-dien-1-ylidene)propyl]-1-isopropenylcyclopenta-1,3-diene (15b). UV (hexane): 272 (20540), 360 (443). IR (neat): 3100w, 3090w, 3070w, 2970w, 2950w, 2921w, 2858w, 1632s, 1615w, 1602w, 1470m, 1440w–m, 1369s, 1100w, 1089w–m, 890m, 858w–m, 810w, 770s, 750m, 715w, 663w–m, 620m. MS: 211 (15), 210 (74, M⁺), 196 (14), 195 (100), 194 (14), 182 (13), 181 (25), 180 (70), 179 (48), 178 (22), 169 (26), 168 (17), 167 (57), 166 (32), 165 (85), 155 (12), 154 (27), 153 (40), 152 (36), 143 (11), 141 (16), 129 (21), 128 (22), 117 (9), 115 (14), 105 (14), 103 (14), 91 (18), 89 (18), 79 (28), 77 (38), 65 (13), 63 (6), 51 (4), 28 (13), 18 (45). HR-MS: 210.1405 (C₁₆H₁₈, M⁺; calc. 210.1409).

Tautomeric Mixture of 5-Isopropenyl-5-(1-isopropenylcyclopenta-2,4-dien-1-yl)cyclopenta-1,3-dienes (16a, b, c). UV (hexane): 295 (9330), 364 (113, sh). IR (neat): 3112w, 3085m, 3075m, 3002w, 2972m, 2962m, 2945m, 2920m, 2895w, 2850w, 1640m, 1620m, 1600m, 1585w, 1525w, 1455m, 1440m, 1380m, 1370m, 1316w–m, 1265w, 1248w–m, 1185w, 1140w, 1085w, 1018w, 978w, 961w, 890m, 851m, 835m, 819m, 800w, 765w, 715m–s, 663w, 630w–m. MS: 211 (16), 210 (94, M⁺), 209 (8), 196 (16), 195 (100), 194 (11), 193 (5), 182 (5), 181 (20), 180 (58), 179 (32), 178 (15), 169 (16), 168 (11), 167 (46), 166 (28), 165 (69), 155 (15), 154 (24), 153 (44), 152 (29), 151 (5), 143 (13), 142 (9), 141 (19), 130 (7), 129 (25), 128 (32), 127 (12), 126 (7), 115 (22), 105 (6), 103 (7), 102 (5), 91 (11), 90 (7), 89 (9), 79 (12), 77 (21), 65 (7), 63 (4), 53 (4), 51 (4), 41 (12), 39 (9). HR-MS: 210.1401 (C₁₆H₁₈, M⁺; calc. 210.1409).

NMR Data of Tautomers 16a, b, c²⁴: 16a: ¹H-NMR (400 MHz, CDCl₃): 6.525 (m, 2 H); 6.333 (m, 2 H); 6.265 (m, 1 H); 6.230 (m, 1 H); 5.010 (m, 1 H); 4.902 (m, 1 H); 4.778 (m, 1 H); 4.771 (m, 1 H); 3.138 (m, 2 H); 1.927 (m,

²¹) For ¹H-NMR spectrum, see Fig. 1.

²²) For ¹H-NMR as well as ¹³C-NMR data, see Table I.

²³) For a more detailed compilation of spectroscopic data as well as for illustrations of spectra, see [3].

²⁴) Identified in the mixture. Some ¹³C-signals of 16c are overlapping with those of 16a/b. Assignment of quaternary C-atoms to tautomers is tentative.

3 H); 1.726 (*m*, 3 H). ¹³C-NMR (400 MHz, CDCl₃): 147.06 (*s*); 146.02 (*s*); 145.81 (*s*); 142.40 (*d*); 139.25 (*s*); 129.45 (*d*); 128.22 (*d*); 128.17 (*d*); 111.21 (*t*); 109.91 (*t*); 68.07 (*s*); 41.61 (*t*); 20.95 (*q*); 20.25 (*q*). **16b**: ¹H-NMR (400 MHz, CDCl₃): 6.530 (*m*, 2 H); 6.378 (*m*, 2 H); 6.308 (*m*, 1 H); 5.982 (*q*, 1 H); 5.075 (*m*, 1 H); 4.925 (*m*, 1 H); 4.820 (*m*, 1 H); 4.810 (*m*, 1 H); 3.14 (*m*, 2 H); 1.949 (*m*, 3 H); 1.706 (*m*, 3 H). ¹³C-NMR (400 MHz, CDCl₃): 148.29 (*s*); 145.17 (*s*); 144.64 (*s*); 141.79 (*d*); 139.30 (*s*); 130.05 (*d*); 129.87 (*d*); 125.01 (*d*); 111.81 (*t*); 110.48 (*t*); 67.33 (*s*); 39.97 (*t*); 20.59 (*q*); 20.49 (*q*). **16c**: ¹H-NMR (400 MHz, CDCl₃): 6.545 (*m*, 2 H); 6.530 (*m*, 1 H); 6.340 (*m*, 2 H); 6.155 (*q*, 1 H); 5.186 (*m*, 1 H); 4.973 (*m*, 1 H); 4.893 (*m*, 1 H); 4.770 (*m*, 1 H); 3.056 (*m*, 2 H); 1.976 (*m*, 3 H); 1.726 (*m*, 3 H). ¹³C-NMR (400 MHz, CDCl₃): 147.30 (*s*); 146.25 (*s*); 142.47 (*d*); 138.64 (*s*); 126.33 (*d*); 126.05 (*d*); 112.05 (*t*); 42.95 (*t*); 20.52 (*q*).

1,1'-Bi(4-isopropenylcyclopenta-1,3-diene-1-yl) (**17**). UV (hexane): 210 (16 110), 223 (18 120), 294 (5370), 382 (14460, sh), 400 (19050), 423 (15810). IR (KBr): 3085_w, 3075_w, 2975_w, 2945_w, 2920_w, 2915_w, 2855_w, 1610_m, 1552_w, 1487_{w-m}, 1450_w, 1430_w, 1383_m, 1370_m, 1293_w, 1255_w, 1097_w, 1033_{w-m}, 978_w, 901_{m-s}, 875_s, 820_s, 690_w. MS: 211 (17), 210 (100, M⁺), 209 (7), 196 (13), 195 (85), 194 (6), 181 (15), 180 (39), 179 (22), 178 (12), 169 (10), 167 (30), 166 (18), 165 (45), 155 (8), 154 (12), 153 (25), 152 (13), 143 (7), 142 (4), 141 (8), 129 (11), 128 (12), 115 (8), 105 (8), 91 (4), 89 (3), 79 (4), 77 (6). HR-MS: 210.1406 (C₁₆H₁₈, M⁺; calc. 210.1409).

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