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## Oxidative Coupling of 6,6-Dimethylfulvenyl Anion [1]

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**Abstract.** Oxidative treatment of anion **1** (obtained by deprotonation of 6,6-dimethylpentafulvene) with  $\text{CuCl}_2$  gives a very complex mixture of coupling products **3** (18%), **4** (16%), **5** (36%), **6** (5%), and **7** (6%) (Scheme 2). This result shows that the reactive intermediate obtained by oxidation of **1** (which is believed to be fulvenyl radical **2**) 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 1), while simple frontier orbital considerations of radical **2** would suggest the sequence  $\text{C}(7) > \text{C}(5) > \text{C}(2)/\text{C}(3) > \text{C}(1)/\text{C}(4)$ . The experimental result is in agreement with a considerable steric shielding of  $\text{C}(5)$  of **2**.

pling mode' as well as regioselectivity of the coupling reaction are strongly dependent on the number  $n$  of  $\text{CH}_2$  groups between the cyclopentadienide units. While intramolecular coupling is still important for  $n = 1$  [7], intermolecular coupling (to give reactive polymers with cyclopentadiene rings in the polymer chain) dominates for  $n > 2$  [2].

Deprotonated 6,6-dimethylpentafulvene (**1**) is a very attractive ambident anion for oxidative couplings, because the delocalized anion **1** as well as the fulvenyl radical **2** (which is assumed to be formed after withdrawal of one electron from **1** [8]) have several reactive sites (Scheme 1). So, regioselectivity of the  $\text{Cu}^{\text{II}}$  induced coupling of **1** is very interesting, which may take place at  $\text{C}(1)$ – $\text{C}(5)$  and  $\text{C}(7)$ . If reactivity of all these C-atoms would be

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### Introduction

It is well known today that oxidative coupling of indenide [3] cyclopentadienide [4], and cyclononatetraenide [5] proceeds nearly quantitatively in the presence of  $\text{Cu}^{\text{II}}$  salts at low temperatures, thus providing a straightforward access to pentafulvalenes [4] and nonafulvalene [6]. If the reaction is applied to  $\alpha,\omega$ -di(cyclopentadienyl)alkyl-diides, then the 'cou-

Scheme 1 ([8][10])

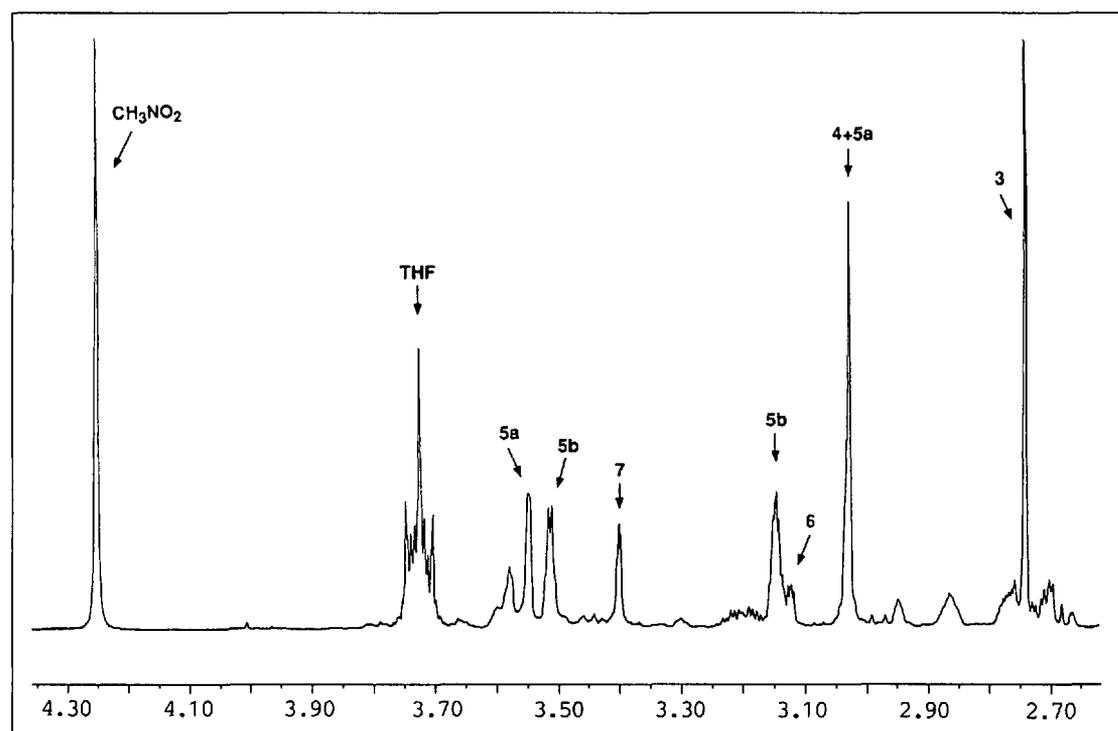
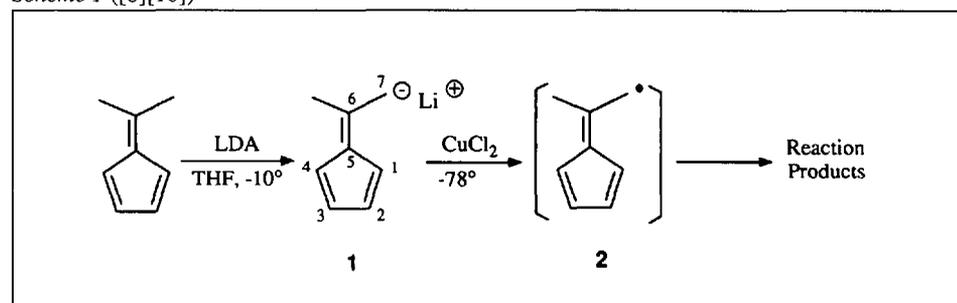


Figure.  $\text{CH}_2$ -Range (2.7–3.6 ppm) of the  $^1\text{H}$ -NMR spectrum (300 MHz,  $\text{CDCl}_3$ ) of the crude reaction mixture together with some THF and the reference signal of  $\text{MeNO}_2$

similar, 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 [9].

## Results

Anion **1** is easily prepared by reacting 6,6-dimethylfulvene at  $-10^\circ$  with 1.1 equiv. of LDA [11]. Subsequently, the solution of **1** is added dropwise to the stirred brownish slurry of anhydrous  $\text{CuCl}_2$  in THF at  $-78^\circ$  [12]. During reaction,  $\text{CuCl}_2$  dissolves to finally give a dark green-brown solution which is filtered over deactivated silica gel at  $-30^\circ$ . After elution, the red solution is carefully concentrated ( $0^\circ/0.2$  mbar) to give a 92% yield of the crude mixture of dimers [12].

Spectroscopic investigations [13] show that the mixture of coupling products is extremely complex. So, the  $^1\text{H-NMR}$  spectrum (300 MHz,  $\text{CDCl}_3$ ) displays several signals in the range of vinylic cyclopentadiene ring protons (ca. 5.9–6.7 ppm), of terminal vinylic protons (ca. 4.7–5.2 ppm), of cyclopentadiene  $\text{CH}_2$  or  $\text{CH}$  (ca. 3.1–3.6 ppm), of  $\text{CH}_2\text{-C=C}$  (ca. 2.8–3.1 ppm) and of  $\text{CH}_3\text{-C=C}$  (ca. 1.7–2.3 ppm). A typical expansion of the range between 2.7 and 3.7 ppm, together with the reference signal of  $\text{CH}_3\text{NO}_2$ , is given in the Figure [13].

Separation of the main components from the reaction mixture proved to be

extremely difficult due to the fact that most products are thermally unstable hydrocarbons of the same molecular weight, while complexity of the mixture is increased by easily occurring tautomerizations of compounds with cyclopentadiene units [14][15]. Nevertheless, pure samples of **3,4, 5a, 6** [15], and **7** have been obtained by low-temperature crystallization (**7**), flash chromatography (**3, 4, and 6** [14]) and HPLC or MPLC (**5a**) (see *Exper. Part*).

Despite the complexity of the reaction mixture, the relative amount of **3–7** could be determined by adding a small amount of  $\text{CH}_3\text{NO}_2$  as a reference to the evaporated crude reaction mixture. After dilution with  $\text{CDCl}_3$ ,  $^1\text{H-NMR}$  integrals of all the  $\text{CH}_2$  signals between 2.70 and 3.60 ppm were recorded at 300 MHz (see *Fig.*) and compared with the integrals of the reference at 4.27 ppm. These analytical yields are given in *Scheme 2* and *Table 1*, the total analytical yield of **1–7** amounting to 81%. According to these results, tautomeric mixture **5** is predominantly formed, followed by **3** and **4**. On the other hand, tautomers **6** as well as **7** are less important. The qualitative conclusion is that oxidative coupling takes mainly place at C(7) of anion **1** (or fulvenyl radical **2**, respectively).

## Discussion

According to *Scheme 2*, the observed reaction products **5, 6, and 7** are different

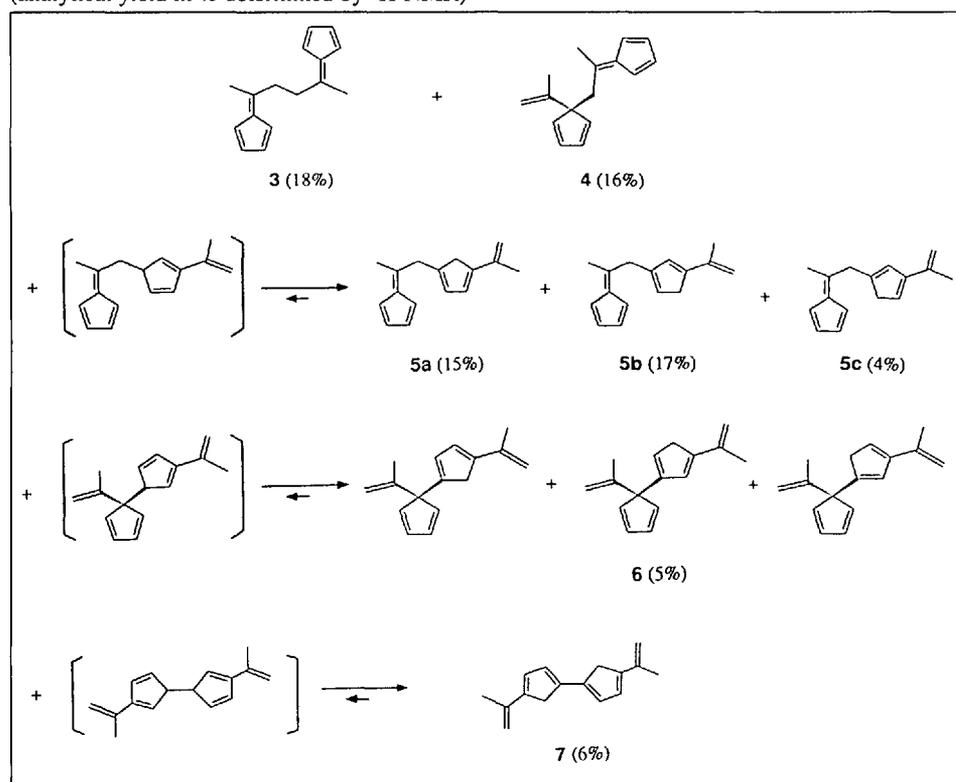
from primary coupling products expected to be formed under kinetic control (see *Scheme 2*, in brackets). They are easily derived from those primary products by based-catalyzed tautomerizations or by a series of 1,5-H shifts [14]. It is obvious that in equilibria of that type products with a maximum  $\pi$ -overlap like **7** are favored. Furthermore, it is well known that 5-alkylcyclopentadienes rapidly tautomerize to an equilibrium in which 1-alkyl- and 2-alkyl-cyclopentadienes are strongly favored [9]. This means that the observed product distribution of tautomeric mixtures **5** and **6** matches the expectation.

According to *Scheme 2* and *Table 1*, the following dimers have been spectroscopically identified and their approximate yields analytically determined: **3** (18%); **4** (16%); **5** (36%); **6** (5%); **7** (6%). These results may be handled in the following way in order to get informations about regioselectivities: first of all, the dimers may be formally split into the corresponding fulvenyl radicals **2** 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 **3** (18%) has been formed by formal reaction of C(7) of both fulvenyl radicals **2**, the assigned 'reactivity number' is  $2 \times 18$ . In the case of **4** (16%), C(7) of one radical **2** has to be connected with C(5) of the second, so that a 'reactivity number' of 16 is assigned to both sites. Statistical corrections are necessary for cases in which monomers were reacting at C(2)/C(3) of **1/4**. By adding up the 'reactivity numbers' of each position, a reactivity index of each site may be derived (*Table 1*).

In the case that fulvenyl radicals **2** should play an important role in oxidative couplings of anion **1** [8], the frontier orbital (SOMO) of radical **2** would be important in recombination reactions of type  $2 \times 2 \rightarrow 3-7$ . According to Hückel coefficients of the SOMO of **2** (*Table 2*), reactivity is expected to decay in the series site 7 > site 5 > sites 2/3 > sites 1/4, provided that the coupling reaction is frontier orbital controlled [16]. The experimental sequence is site 7 > sites 2/3 > site 5 > sites 1/4, it obviously includes steric interactions as well, which are expected to discriminate oxidative couplings at C(5) of fulvenyl radical **2**: if one takes into account that site 5 of **2** is sterically strongly shielded compared with all other sites, then there seems to be a reasonable fit between the experimental product distribution and qualitative expectations based on frontier orbital interactions of fulvenyl radical **2**.

In summary, oxidative coupling of 6,6-dimethylfulvenyl anion **1** proceeds in a high yield (> 81%) in the presence of

Scheme 2. Reaction Products Obtained by Oxidative Coupling of Anion **1** with  $\text{CuCl}_2$  in THF (analytical yield in % determined by  $^1\text{H-NMR}$ )



CuCl<sub>2</sub> to give a very complex product mixture in which compounds **5**, **3**, and **4** are important. Oxidative coupling takes mainly place at C(7) of **1** or **2**, respectively, followed by C(2)/C(3) and C(5). Product distribution qualitatively matches reactivities derived from frontier-orbital considerations with exception of C(5) which is probably less reactive due to steric shielding.

## Experimental

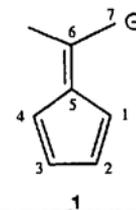
**General.** All the procedures were realized in abs. solvents and under Ar. Since most of the coupling products **3–7** are thermally unstable and will polymerize at a considerable rate even around 0°, their isolated yields will be considerably lower than the analytical yield of products **3–7** in the reaction mixture. Therefore, isolated yields were not optimized. Product composition was determined from the <sup>1</sup>H-NMR spectra (300 MHz) of three independent runs by adding MeNO<sub>2</sub> 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)<sub>2</sub>NH 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 syringe within 15 min. After addition was complete, stirring was continued for 15 min at r.t. The <sup>1</sup>H-NMR spectrum of the almost colorless soln. showed that 6,6-dimethylfulvene had been consumed, while anion **1** 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. CuCl<sub>2</sub> as well as with 15 ml of THF and cooled at -78°. To the yellow-brown suspension the freshly prepared soln. of **1** (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 darkgreen 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 Et<sub>3</sub>N-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 oil [17]. The oil was dissolved in 20 ml of Et<sub>2</sub>O and kept at -70° over night, while 57 mg (6.0%) of yellow crystals of dimer **7** were precipitating. Recrystallization from Et<sub>2</sub>O gave pure thermally instable dimer **7**.

The filtrate was concentrated at 0°/0.3 mbar and separated by flash-chromatography with pentane/Et<sub>2</sub>O 200:1 over 100 g of Et<sub>3</sub>N-deactivated silica gel to give three fractions: the first fraction (*R<sub>f</sub>* 0.84) contained pure **6** (46 mg, 4.8%) as a tautomeric mixture; the second fraction (464 mg, 48.8%) was a mixture of **4** as well as of tautomers

Tab. 1. Analytical Yield of Products **3–7** as well as Coupling Sites and Relative Importance of Sites in Oxidative Coupling of Anion **1**



Compound	Anal. yield <sup>a)</sup>	Coupling sites involved <sup>b)</sup>	Relative importance of			
			Site 1/4 <sup>c)</sup>	Site 2/3 <sup>d)</sup>	Site 5	Site 7
<b>3</b>	17.6%	[7–7]	–	–	–	2x17.6
<b>4</b>	15.7%	[7–5]	–	–	15.7	15.7
<b>5</b>	36.5%	[7–2/3]	–	0.5x36.5	–	36.5
<b>6</b>	5.2%	[5–2/3]	–	0.5x5.2	5.2	–
<b>7</b>	6.0	[2/3–2/3]	–	2x0.5x6.0	–	–
Sum	81.0%	– <sup>e)</sup>	–	26.8	20.9	87.4
Reactivity Index <sup>e)</sup>		–	–	0.198	0.155	0.647

<sup>a)</sup> Averaged yields of three independent runs, in which a THF solution of anion **1** was added to a slurry of CuCl<sub>2</sub> in THF. The determined yields are: **3**: 17.3/17.8/17.6%; **4**: 15.1/15.6/16.5%; **5**: 35.1/38.8/35.6%; **6**: 4.9/5.2/5.5%; **7**: 6.3/6.5/5.1%.

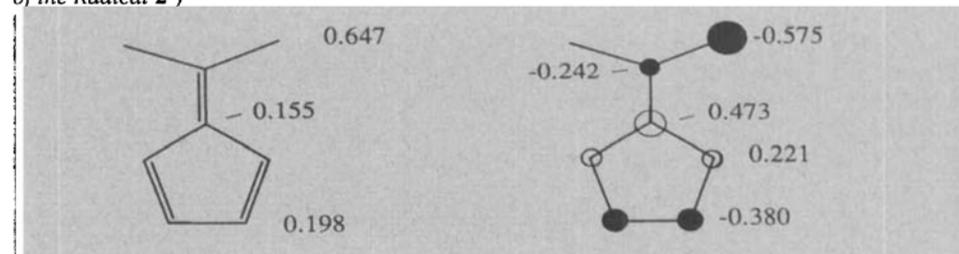
<sup>b)</sup> [7–5] means coupling of two anions **1** at C(5) and C(7), respectively.

<sup>c)</sup> Traces of a [7–1] coupling product have been identified.

<sup>d)</sup> Statistically, there are two equivalent positions available.

<sup>e)</sup> Relative to a total reactivity of **1**.

Table 2. Reactivity Indexes Derived from Analytical Yields (left) and Hückel Coefficients of the SOMO of the Radical **2**<sup>a)</sup>



<sup>a)</sup> Note that the Hückel coefficients of the SOMO of radical **2** are identical to those of the HOMO of anion **1**.

**5**, while the third fraction (*R<sub>f</sub>* 0.53) gave yellow crystals of thermally instable dimer **3** (156 mg, 16.3%) after evaporation. Repeated HPLC or MPLC chromatography of 150 mg of the second fraction with pentane over 70 g of Et<sub>3</sub>N-deactivated silica gel resulted in the separation of **4** and **5a**, while **5b** was obtained as a mixture together with **4**.

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- [10] Note that the  $\pi$ -system of fulvenyl anion **1** as well as of fulvenyl radical **2** is considerably delocalized according to HMO calculations.
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- [12] Oxidative coupling may be realized by adding anh.  $\text{CuCl}_2$  to the cooled ( $-78^\circ$ ) solution of anion **1** as well. While product distribution is similar to that of *Table 1*, the total anal. yield (determined by  $^1\text{H-NMR}$ ) drops to 68%.
- [13] Spectroscopic structure elucidation of compounds **3–7** will be discussed in a full paper (in preparation for *Helv. Chim. Acta*). Spectra of purified compounds are given in [1].
- [14] Tautomerizations of products with cyclopentadiene units (see **5–7**) may occur at low temperature by base catalysis or, in many cases, at ambient temperature, by concerted 1,5-H shifts [9].
- [15] While HPLC allowed to separate tautomers **5a** and **5b**, the mixture of tautomers **6** could not be separated.
- [16] Coupling at C(6) of **2** would produce a diradical and is, therefore, considered to be energetically very unfavorable.
- [17] An adequate portion of this oil was used for NMR analysis at 300 MHz after adding a balanced amount of  $\text{MeNO}_2$  as an internal standard for integration.

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## Synthese und Röntgenstruktur einer Triafulvalen-Vorstufe [1]

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**Abstract.** Triafulvalene precursors **3b** and **3c** have been synthesized by  $\text{Cu}^{\text{II}}$ -catalyzed 'carbene dimerization' of cyclopropyl carbenoids (obtained by halogen-lithium exchange of 1,1-dibromo-2-(phenylthio)-3-(trimethylsilyl)cyclopropane (**2b**; see *Scheme 2*) in moderate yields. Diastereoselectivity of the central step **2b**  $\rightarrow$  **3b** is low. An X-ray analysis of the predominantly formed *trans-anti* isomer has been performed.

### Einleitung

Triafulvalen (Bi(cyclopropenyliden)); **1**) ist als gespanntes cyclisch gekreuzt konjugiertes System sowohl bindungstheoretisch wie spektroskopisch von grossem Interesse. Bis heute sind weder der Grundkörper **1**, noch einfache Derivate, oder aussichtsreiche Vorstufen von **1** bekannt. Wir berichteten kürzlich von einer präparativ sehr einfachen Umsetzung von 1,1-Dibromo-2-(phenylthio)cyclopropan (**2a**) zum Diastereoisomerengemisch der Bi(cyclopropylidene) **3a** [3]. Dabei wurde das unter kinetischer Kontrolle aus **2a** mit  $\text{BuLi}$  erzeugte Gemisch der 1-Bromo-1-lithio-2-(phenylthio)cyclopropane mittels  $\text{CuCl}_2$  in einer formalen 'Carben-Dimerisierung' zu **3a** umgesetzt. Die präparativen Ausbeuten der Reaktion **2a**  $\rightarrow$  **3a** sind sehr stark von den Reaktionsbedingungen abhängig. Das Resultat ist deshalb überraschend, weil 'Hückel-Anionen' wie Cy-

clopentadienid unter analogen Bedingungen oxidative Kupplungen zu 1,1'-Bi(cyclopentadienylen) eingehen [4][5].

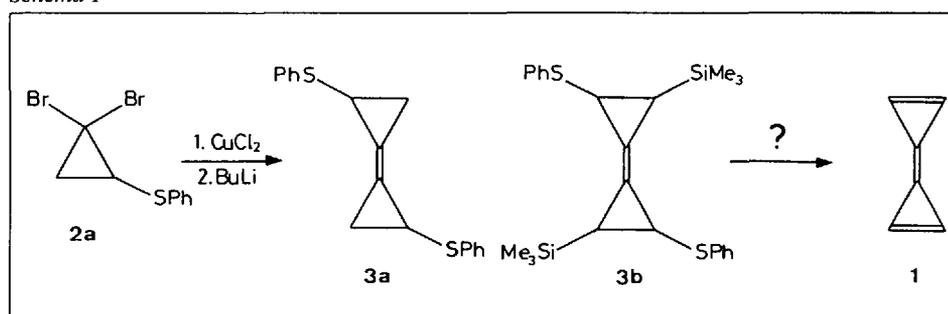
Mit dieser einfachen Eintopf-Reaktion **2a**  $\rightarrow$  **3a** bietet sich erstmals die Möglichkeit, aussichtsreiche Vorstufen des Grundkörpers Triafulvalen (**1**) zu synthetisieren (*Schema 1*). Einerseits könnte versucht werden, die PhS-Gruppen von **3a** in gute Abgangsgruppen umzuwandeln, was nach unseren früheren Erfahrungen mit analogen Triafulven-Vorstufen nicht so einfach ist [6]. Andererseits wäre die Einführung zweier sich bei der geplanten Elimination unterstützender Abgangsgruppen attraktiv. Eine kürzlich erschienene

Arbeit über die Synthese des instabilen Spiro-pentadiens [7] veranlasst uns, im folgenden kurz über die erfolgreiche Synthese von Bi(cyclopropylidenen) des Typs **3b** zu berichten.

### Synthese der Triafulvalen-Vorstufen **3b** und **3c**

*trans*-1,1-Dibromo-2-(phenylthio)-3-(trimethylsilyl)cyclopropan (**2b**) ist weder nach *Makosza* [8] noch nach *von Doering* und *Hoffmann* [9] zugänglich und liess sich schliesslich aus dem entsprechenden Olefin nach *Seyferth* und Mitarbeitern [10] mittels (Tribromomethyl)(phenyl)quecksilber herstellen. Wird **2b** zunächst bei  $-95^\circ$  mit  $\text{BuLi}$  und dann mit  $\text{EtOH}$  behandelt, wird unter (Br-Li)-Austausch in über 70% Ausbeute das erwartete Gemisch zweier diastereoisomerer *trans*-1-Bromo-2-(phenylthio)-3-(trimethylsilyl)cyclopropane isoliert [11]. Trotzdem ist die nachfolgende 'Carben-Dimerisierung', welche durch  $\text{CuCl}_2$  katalysiert wird [3], sehr problematisch: Unter 'thermodynamischer Kontrolle' [12] liegen die maximalen Ausbeuten an **3b** bei 2%. Sie steigen unter 'kinetischer Kontrolle' [12] auf 17%, falls katalytische Mengen (rund 0,1 mol-equiv.)  $\text{CuCl}_2$  verwendet werden, und auf 21% (GC), falls 1 mol-equiv.  $\text{CuCl}_2$  zugegeben wird. Im Gegensatz zu **2a**  $\rightarrow$  **3a** sinkt die Ausbeute der Umsetzung **2b**  $\rightarrow$  **3b**, wenn anstelle von THF als Lösungsmittel  $\text{Et}_2\text{O}$  verwendet wird. Sonst sind die Ausbeuten in beiden Fällen von denselben Parametern abhängig (Details vgl. [3]), wobei vor

*Schema 1*



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