

Novel pentafulvenes – versatile building blocks in π -perimeter chemistry

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Abstract – Kinetically stabilized 6-halopentafulvenes provide access to numerous new derivatives of the cross-conjugated system, which proved to be useful building blocks for polycyclic hydrocarbons and other π -electron systems. Their transformation into pentafulvene carbenoids as well as carbenes and the rearrangement of these into benzyne will be reported. From 6-chloropentafulvenes a stabilized 5-vinylidencyclopentadiene could be obtained. The allene dimerizes in a solid state reaction to a tetraquinane derivative, and by its oxidative coupling a pentafulvenoid cumulene became accessible.

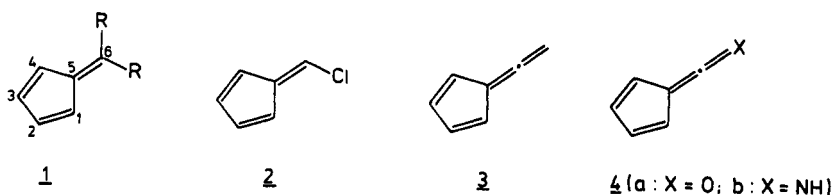
INTRODUCTION

Since Thiele's (ref. 1) discovery of pentafulvenes **1**, these π -electron systems have been a focus of interest as prototypes of cyclic cross-conjugated molecules, and because of their unique physical and chemical properties (ref. 2). In accord with theoretical considerations (ref. 3,4), the reactivity of pentafulvene itself **1** (R=H) as well as its derivatives, alkylated or arylated in 6-position, will be determined by the cis-1,3-diene system. This means predominantly electrophilic 1,4-additions as well as Diels-Alder reactions take place and, with strong nucleophiles, also additions at the exocyclic C-atom (ref. 2a). On the other hand, pentafulvenes with N- or even O-functions at the exocyclic carbon – which increases the polarizability of the cross-conjugated system show – like the isomeric anilines or phenols – a pronounced tendency for electrophilic and nucleophilic substitution reactions (ref. 2b). Moreover, they are also capable of periselective [6+2]- as well as [6+4]-cycloaddition reactions, thus remarkably increasing the synthetic potential of these compounds (ref. 4).

Pentafulvenes of the latter type were studied by us and other groups in the last two decades and could be converted into numerous interesting pentafulvenoid compounds, of which some proved to be versatile intermediates for the synthesis of new carbo- as well as heterocyclic conjugated π -electron systems, containing one or more 5-membered rings (ref. 5). For their synthesis cyclizing condensations, electrocyclic reactions and [6+4]- as well as [6+2]-cycloadditions of the pentafulvenoid systems proved to be general principles, which allow annelation of 5- or 7-membered rings to an existing mono- or polycycle (ref. 6). However, in spite of the broad applicability of these methods, several polycyclic conjugated π -electron systems are inaccessible by these synthetic routes.

In order to develop further building blocks for the construction of new π -perimeters with novel bonding systems, we recently undertook studies on the synthesis and properties of some until now scarcely or even never at all accessible functionalized pentafulvenes. To these belong not only derivatives of the cross-conjugated system with strong electron withdrawing substituents at the exocyclic carbon atom, but also those where the pentafulvenoid moiety is connected with cumulative double bonds.

Most interesting representatives of this class of compounds are 6-halopentafulvenes and pentafulvenoid allenes as well as ketenes, from which Bergman et al. (ref. 7) and also Neuenchwander et al. (ref. 8) generated for the first time the extremely unstable 6-chloropentafulvene **2** with less than 10% yield as a yellow oil. Wentrup et al. (ref. 9), Hedaya et al.

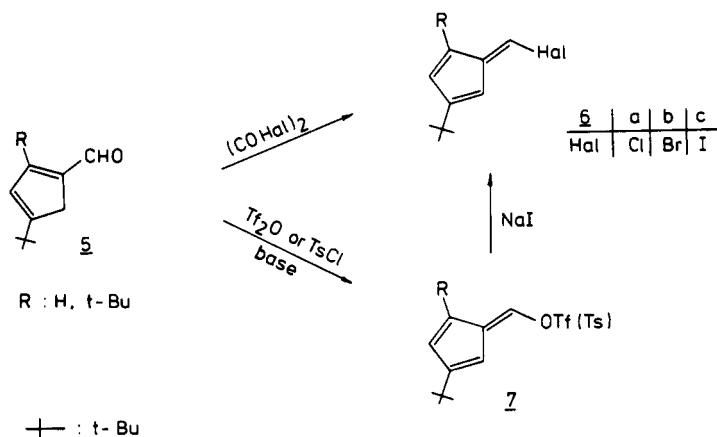


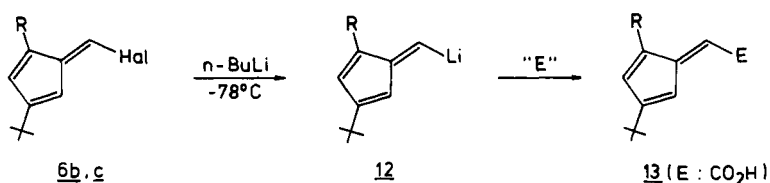
(ref. 10) and others (ref. 11) obtained pentafulvene allene **3** by high temperature flash pyrolysis or by photolysis of different phenylcarbene progenitors as a short lived intermediate, characterizable by spectroscopic methods. The pentafulvene ketene **4a** and its imine **4b** were postulated as intermediates in the gas-phase pyrolysis of some benzenoid precursors, but never detected (ref. 12).

Due to their high thermal instability, information on the bonding situation and the chemical properties of these pentafulvene derivatives is exceedingly scarce. These difficulties could easily be overcome by kinetic stabilization of the pentafulvene system with one or two bulky alkyl substituents, which exhibit only a slight electronic influence on the cross-conjugated system. This concept allowed us to open up not only efficient pathways to several new pentafulvenes with unexpected properties, sometimes in a surprisingly simple manner, but also their conversion into π -electron systems hitherto inaccessible.

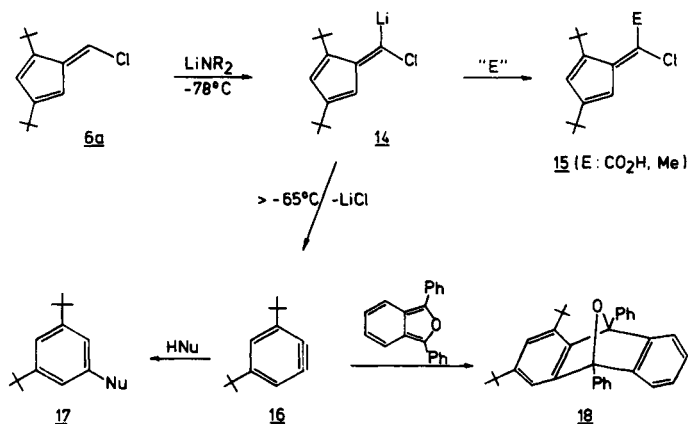
CHEMISTRY OF 6-HALOPENTAFULVENES

The kinetically stabilized 6-halopentafulvenes **6** are accessible on a 100 g scale by reaction of formylcyclopentadienes **5**, simply prepared by formylation of the respective cyclic dienes, with phosgene or oxalyl halides in 90% yield (ref. 13). Likewise, formylcyclopentadienes **5** react via their enolates with tosyl chloride or trifluoromethane sulfonic acid anhydride to the 6-pseudohalopentafulvenes **7**, which on treatment with sodium iodide are converted into the 6-iodopentafulvenes **6c** (ref. 14).



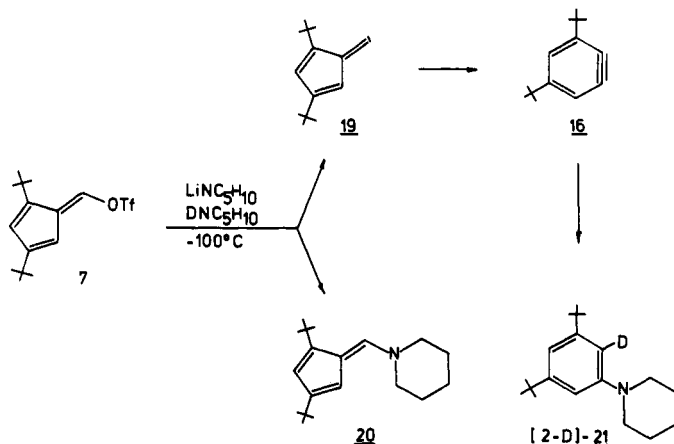


Furthermore, 6-chloropentafulvene 6a (R= t-Bu) can be easily metallated with mainly retention of configuration by treatment with lithium dialkylamides at -78°C to the interesting pentafulvene carbenoid 14. This reacts with electrophiles stereoselectively to the substitution products 15, but with nucleophiles to a small extent only (ref. 14), unlike other alkylidene carbenoids that undergo ambiphilic reactions. Above -65°C the cross-conjugated carbenoid rearranges by elimination of LiCl to benzyne 16, which could be trapped to 17 or 18 by addition of a sec. amine or thiophenolate, or by [4+2]-cycloaddition with 1,3-diphenyliso-



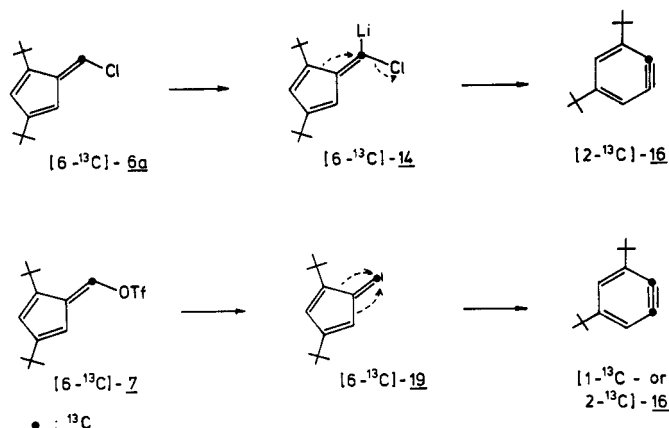
benzofuran (ref. 15). Ab initio calculations of Houk (ref. 16) let assume that, due to thermodynamic as well as kinetic considerations, the rearrangement of carbenoids of this type does not proceed via a carbene intermediate, hence, a synchronous elimination of LiCl and ring enlargement to the benzyne seems to be obvious.

On the other hand, Stang et al. (ref. 17) could show that alkylidene carbenes are generated by reaction of primary alkenyl triflates with appropriate bases. Therefore, we reacted also the pentafulvenyl triflate 7 (R=t-Bu) with lithium piperidide at -100°C in the presence of N-deuterated piperidine and obtained 60% of the o-deuterated N-phenylpiperidine 21 besides a small amount of the 6-piperidinopentafulvene 20. Obviously, an α -elimination of the triflate yields the pentafulvenylidene 19, which immediately rearranges to the benzyne 16. Such a course is in good agreement with predictions of Apeloig et al. (ref. 18), based on ab

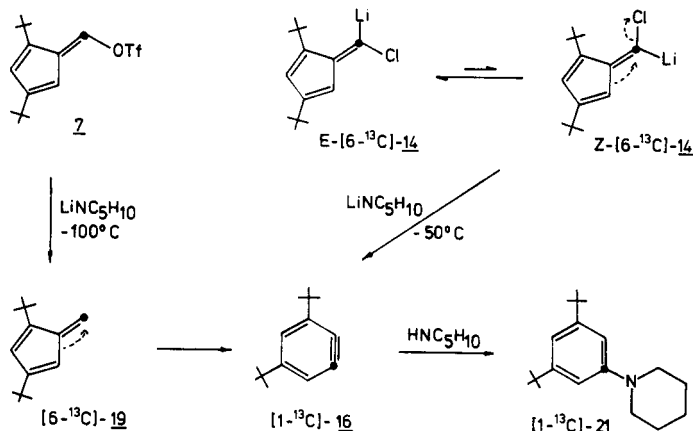


initio calculations. According to these, the heat of formation of benzyne should be ca. 14 kcal·mol⁻¹ lower than that of pentafulvenylidene. Therefore, it can be expected that the carbene rearranges immediately after its formation, even at very low temperatures, while the benzyne formation via the carbenoid requires a higher activation energy and proceeds only above -65°C. All attempts to trap the pentafulvenoid carbene **19** by cycloaddition with olefins have failed so far, thus not revealing the nature of this interesting carbene. In line with these findings, Brown et al. (ref. 19), who suggested the unsubstituted pentafulvenylidene as an intermediate in the formation of biphenylene and triphenylene by flash vacuum pyrolysis of polycyclic malonic acid derivatives, also failed to secure information on this short-lived intermediate.

In order to learn more about the mechanistic pathway of the rearrangements of the cross-conjugated carbenoid **14** as well as carbene **19** into the benzyne **16**, we studied these reactions with [6-¹³C]-labeled 6-chloropentafulvene **6a** and the corresponding triflate **7**. In case of a synchronous rearrangement of the carbenoid, only the substituent in anti-position to the leaving chloride should be shifting according to the results obtained by Köbrich et al. (ref. 20) with alkylidene carbenoids. Contrary to that, in case of a pentafulvenylidene intermediate both carbon-shifts should be observed. Against all expectations, both



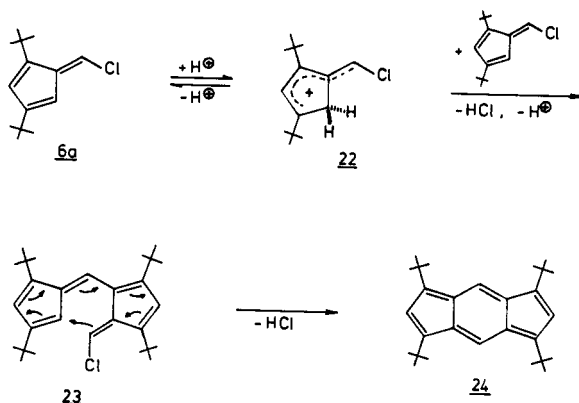
pentafulvenes, the 6-chloroderivative [6-¹³C]-**6a** as well as the triflate [6-¹³C]-**7** react with lithium piperidide to the *N*-phenylpiperidine **21** labeled at 1-position. Probably the regioselectivity of the rearrangement of the carbene **19**, generated at -100°C, is influenced by steric and electronic effects of the cross-conjugated system. In contrast, in case of the carbenoid **14** a primary *E*/*Z*-isomerization could be assumed. Detailed ¹³C-NMR studies between -100 and -70°C on a [6-¹³C, ⁶Li]-carbenoid **14**, wherein, besides the signal of C-6 at 242.0 ppm (triplett, *J* = 13.2 Hz) with high intensity for the *E*-isomer, a second triplett at 241.3 ppm (*J* = 17.0 Hz) of low intensity can be detected at about -90°C, are well



in accord with this. In view of the close chemical shifts and coupling constants of both signals, the second one of low intensity obviously belongs to the *Z*-isomer **14**, which rearranges to the benzyne **16** after its formation. Assuming the rearrangement of the *Z*-carbenoid **14** into the benzyne **16** to be first-order, the free activation enthalpy of this

process should be $\Delta G^\ddagger_{-65^\circ\text{C}} = 14\text{--}15.5 \text{ kcal}\cdot\text{mol}^{-1}$ (ref. 14). This is in good agreement with calculations of Houk (ref. 16) for the rearrangement of 1-lithio-1-fluoroethylene into an acetylene-lithium fluoride complex, for which $\Delta G^\ddagger = 19 \text{ kcal}\cdot\text{mol}^{-1}$ was calculated.

Besides this interesting rearrangement of 6-chloropentafulvene **6a** (R=t-Bu) and the corresponding triflate **7** into the benzyne **16**, these compounds proved to be particularly versatile progenitors for several new polycyclic π -electron systems, containing one or even more 5-membered rings. A most surprising reaction of this cross-conjugated halide is its spontaneous self-condensation in the presence of traces of proton or Lewis acids in boiling methanol. Apparently, a pentafulvene cation **22** is formed first on reversible protonation.

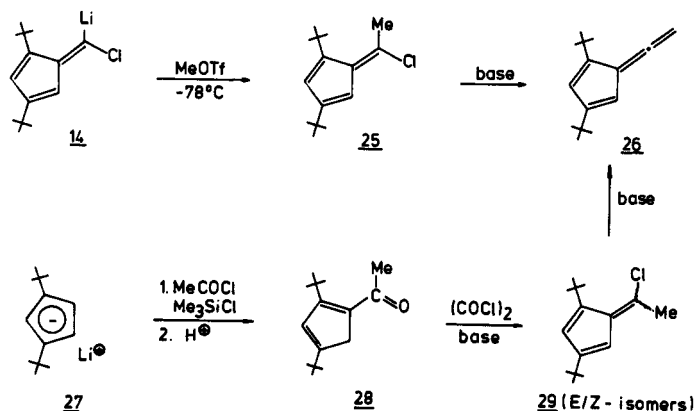


This alkylates a second molecule of the starting material to give the obviously highly reactive 6-chloro-1-(6-pentafulvenyl)-pentafulvene **23**, whose 12π -electrocyclization with subsequent elimination of HCl leads, in an overall yield of higher than 90%, to the crystalline deep-red thermally stable s-indacene **24** (ref. 21). The same hydrocarbon can be synthesized also with other pentafulvenes, bearing a good leaving group in 6-position like **7**. Particularly the 6-alkoxy-pentafulvenes proved to be a preferred starting material, because no acidic product is formed by its self-condensation, and, hence, no decomposition of the tricyclic hydrocarbon **24** takes place (ref. 14).

Extended theoretical as well as experimental studies of the s-indacene proved its exceptional position among the so far known $4n$ π -electron systems (ref. 21,22).

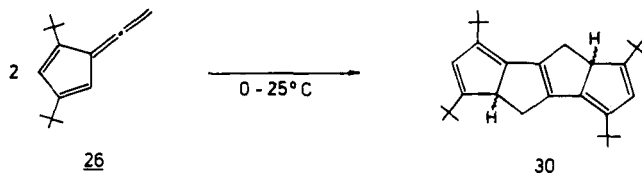
CHEMISTRY OF PENTAFULVENE ALLENES

Another, entirely different transformation of the 6-halopentafulvenes **6** provided access to representatives of two other fairly new groups of π -electron systems, namely tetraquinanes and pentafulvenoid cumulenes. As already mentioned, metallated 6-chloropentafulvene **14** reacts with electrophiles by substitution in 6-position. With methyl triflate the carbenoid yields the 6-chloro-6-methylpentafulvene **25**, which easily reacts with bases by elimination of HCl to the crystalline, yellow 5-vinylidencyclopentadiene **26** (ref. 23). This can



also be prepared in good yields by acetylation of lithium cyclopentadienide 27, subsequent chlorination of the keton 28 to 29 and elimination of HCl (ref. 24). The stable pentafulvene allene 26 obtained by these procedures allowed for the first time a detailed study of its physical and chemical properties. It displays an abundant reactivity leading to a variety of new interesting π -electron systems.

Chemically, one of the most remarkable and surprising property of the 1,3-di-*t*-butylpentafulvene allene 26 is its dimerization in a solid-state reaction between 0°C and 25°C, with increasing rate within a couple of days, to give the tetrahydrodicyclopenta[*a,e*]pentalene 30, which is not formed in solution, even at elevated temperatures (ref. 24). This opens up an unexpected simple entry to the hitherto largely unexplored linear annelated tetraquinanes (ref. 23,25).



During the dimerization, which yields about 50% of the tetracyclic system 30, the crystals of 26 become opaque, and a slight depression of the melting point is observable. For detailed X-ray crystal structure analysis of the allene 26 at room temperature several single crystals were used, as these decay within a few hours (ref. 26). A second data set was measured at -135°C (ref. 27). The molecular geometry of the pentafulvenoid allene 26 does not show any surprising features (Fig. 1). Both X-ray analyses show the same packing within

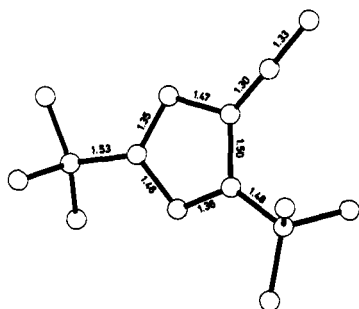


Fig. 1. Molecular geometry of 26

the space group P2₁, with a distance of approximately 3.6 Å between the allene moieties stacked along the monoclinic axis, for which the *t*-butyl groups are probably responsible (Fig. 2). In extensive studies Schmidt (ref. 28), one of the pioneers of the chemistry of solid state reactions, and others (ref. 29) demonstrated that such topochemical processes are strictly controlled by the packing arrangement of molecules in crystals. In agreement with this, a corresponding dimerization of the 2-*t*-butyl-5-vinylidenecyclopentadiene or of a 1,3-di-*t*-butyl-pentafulvene allene, methylated at the terminal allene position, is not observed (ref. 24).

The correlation of the solid state chemical reactivity of the pentafulvenoid allene 26 with X-ray crystal structure data has provided a valuable insight into the dimerization reaction.

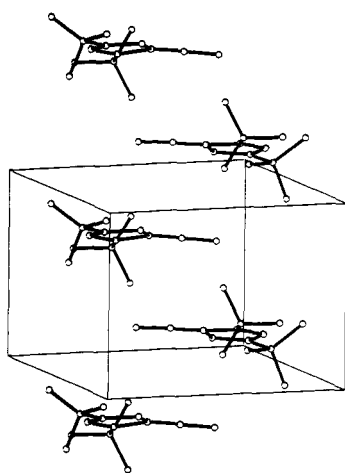


Fig. 2. Crystal packing of 26:
Stacking along the b-axis

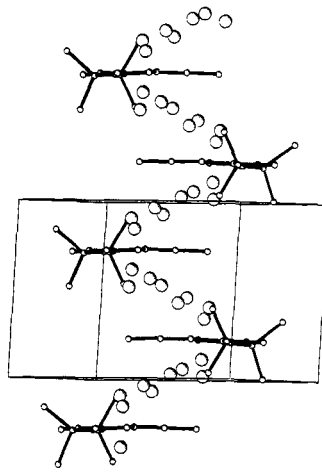


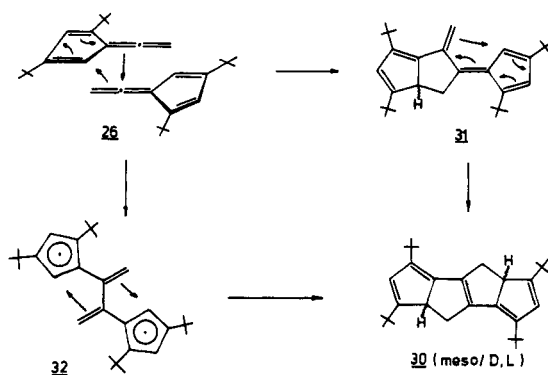
Fig. 3. Stacking of 26 along the b-axis
with maxima of residual electron densities
between the molecules

The topochemical principle states that such a reaction in the solid state is preferred and occurs with a minimum amount of atomic or molecular movement. This implies that a certain amount of motion of various atoms in the crystal lattice is tolerable.

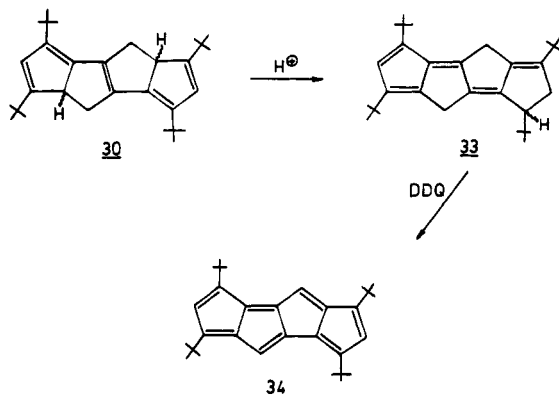
Detailed inspection of the electron density map shows residual electron densities between the allene molecules, which indicate the existence of about 10% of the dimer 30 in the single crystals (Fig. 3) (ref. 26). The view on the decks shows that the displacement of the reacting atoms takes place only along the monoclinic axis in full agreement with the topochemical principle. If the dimerization between two neighboring monomers arises in this manner, the dimer should have meso configuration. Although many [2+2]-photodimerizations in the solid state (ref. 28,29) have been extensively investigated, a comparable example for such a defined thermally induced solid state reaction was – as far as we know – only observed with suitable substituted diacetylenes (ref. 30). The only example for a ground-state nontopochemically controlled reaction of cycloheptatrienethione in the crystalline state, leading to a novel [8 π +8 π]-cyclodimer with syn configuration was reported just recently by Machiguchi et al. (ref. 31).

In case of the solid state dimerization of the pentafulvene allene 26, the nature and stereochemistry of the product should be precisely determined by the crystal packing within the monomer lattice.

So far it could not be finally ruled out, that instead of a completely synchronous dimerization of 26 the formation of three new σ -bonds takes place within a two-step process with a pentafulvenoid or even a biradical intermediate. In case of a two-step process, the reaction could be brought about by a [6+2]-cycloaddition of the terminal double bond of the allene 26 to the pentafulvene moiety of a second molecule to give the tetrahydropentalene derivative 31. This subsequently undergoes, like other 6-vinylpentafulvenes (ref. 32), an 8 π -electro-

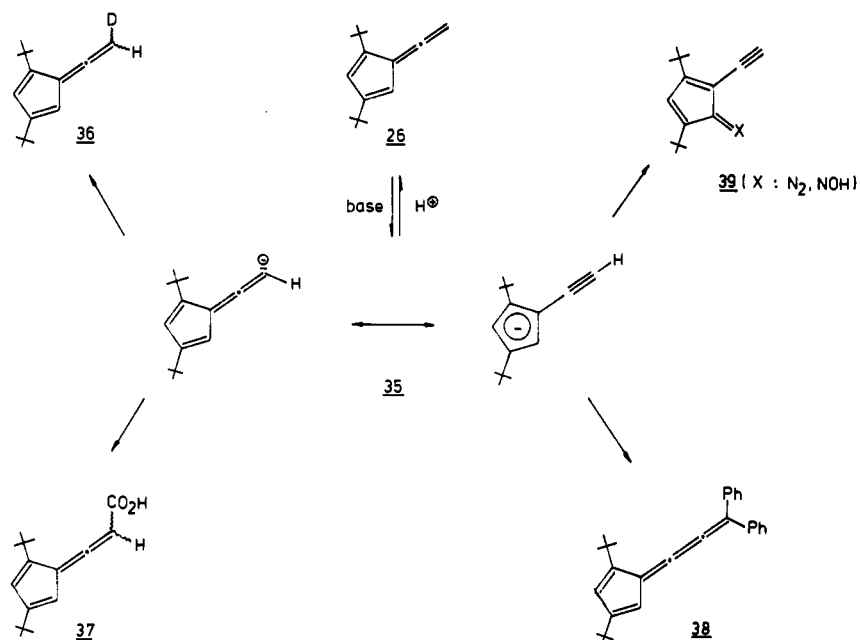


cyclization to the tetraquinane derivative 30. Alternatively, a two-step dimerization of the pentafulvenoid allene 26 could also proceed via the resonance-stabilized diradical 32 by formation of a σ -bond between the sp-bonded central carbons of two allenes and, following ring closure, to the tetracyclic system 30. From both nonsynchronous pathways, however, a 1:1-mixture of two stereoisomeric hydrocarbons 30 (meso and D,L) should be expected if the dimerization occurs without steric restriction; this, however, was not observed.

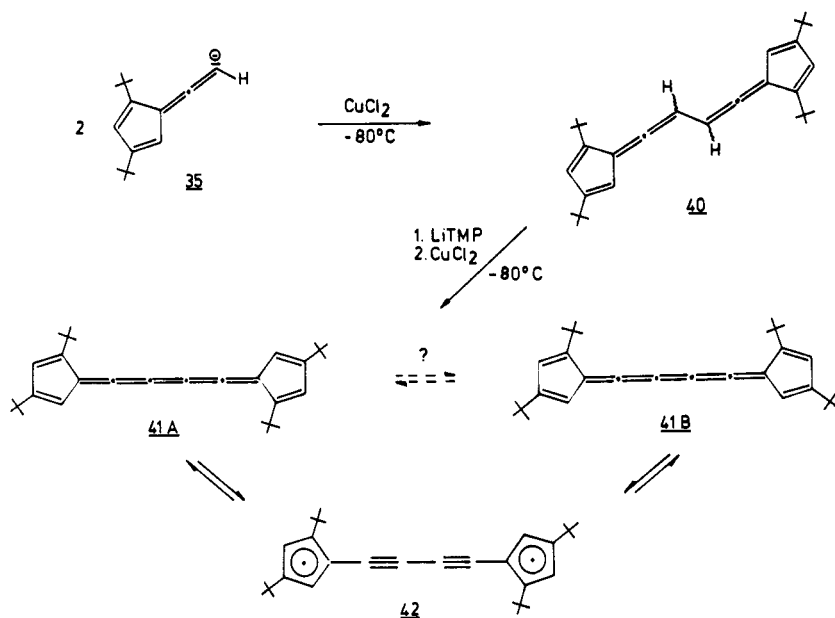


The proton-catalyzed tautomerization of the tetracyclic hydrocarbon 30 leads to the isomeric system 33 with a 6-butadienylpentafulvene moiety, which can easily be dehydrogenated to the fully conjugated tetracycle 34, the first example of a π -electron system with a $[4n+2]$ -perimeter having $[4n]$ partial structures (ref. 23).

A representative of a second class of new compounds, a pentafulvenoid cumulene, became accessible due to the reversible deprotonation of the 5-vinylidenecyclopentadiene 26, which easily takes place with strong bases. The resonance stabilized anion 35 reacts with electrophilic reagents, preferably at the terminal carbon, to the chiral substitution products, i.e. to the deuterated allene 36, carboxylic acid 37, or even to the achiral black crystalline butatriene derivative 38. Alkyl nitrites or tosylazide, however, attack the allene anion 35 at the 5-membered ring to form the corresponding ethynylpentafulvenes 39 (ref. 33).

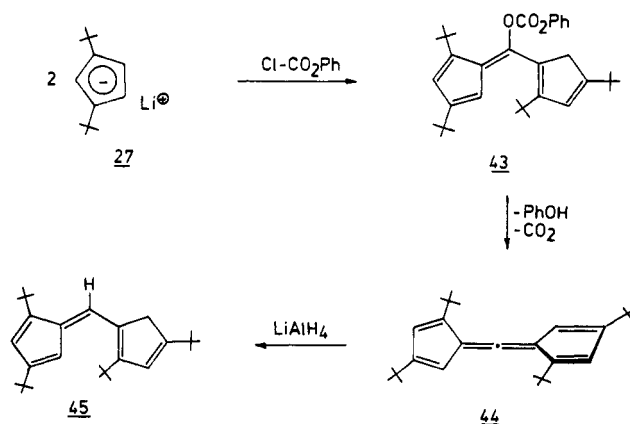


The oxidative coupling of the allene anion 35 with $CuCl_2$ yields a 1:1-mixture of the diastereomers of the yellow bis-allene 40. Deprotonation with lithium 2,2,6,6-tetramethylpiperidide to the dianion and repeated oxidation with $CuCl_2$ finally leads to the 1,4-bis-(1,3-di-*t*-butylcyclopentadienylidene)-1,2,3-butatriene 41 as black crystals with



lustre. One of the most remarkable properties of this interesting cumulene is its thermal stability up to 300°C. Its UV/VIS-spectrum (in n-hexane) shows in the visible region a strong absorption at $\lambda = 442$ nm ($\epsilon = 88\,700$) besides a longest-wavelength, low-intensity band at $\lambda = 532$ nm ($\epsilon = 5090$) (ref. 33). The simple $^1\text{H-NMR}$ spectrum with a doublet and a broad singlet between 5.7 and 6.2 ppm for the 4 ring protons seems to indicate a fast equilibrium between the two possible E/Z-stereoisomers 41A and B of the cumulene, which are expected for unsymmetrically substituted cumulenes with an even number of carbon atoms and an odd number of double bonds. In contrast, cumulenes of this type with an odd number of carbon atoms and an even number of double bonds should be obtained as enantiomeric mixtures. Final experimental proof for the expected equilibrium of the diastereoisomers 41A and B, which could involve a diradical intermediate 42 (ref. 34), is still missing.

Recently, also the simplest member of this series of pentafulvenoid cumulenes, bis-(1,3-di-*t*-butylcyclopentadienylidene)-methane 44, could be synthesized by reaction of lithium 1,3-di-*t*-butylcyclopentadienide 27 with phenyl chloroformate via the pentafulvene derivative 43 (ref. 33,35). The $^1\text{H-}$ and $^{13}\text{C-NMR}$ -spectra of the pale yellow crystalline 1,2-propadiene 44



confirm the symmetric structure of this chiral allene. Final proof of the molecular geometry of 44 is provided by an X-ray structure analysis of the compound, which shows the two 5-membered rings with bond fixation in perpendicular planes and carbon-carbon bond length for the allene moiety of 1.31 Å (ref. 26).

The allene 44 is thermally rather stable and chemically surprisingly inert. While it does not react with lithium alkyls, it can be reduced with LiAlH_4 to the pentafulvene derivative 45.

CONCLUSION

The syntheses and reactions of pentafulvenes presented in this survey reveal anew the high potential of this class of compounds as building-blocks in the chemistry of π -electron systems. The versatile, sometimes rather unexpected reactivity of functionalized pentafulvenes opens the prospect that not only new polycyclic systems such as polyquinanes and multi-annelated hydrocarbons with extended π -electron systems will materialize, but also those with new dynamic as well as mechanistic aspects. On the other hand, some of the compounds described may be suitable for further transformation into molecules, like charged species or transition metal complexes, with interesting chemical and physical properties.

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35. Likewise **44** also the bis-(1,2,3,4-tetraphenylcyclopentadienylidene)-methane (orange crystals, m.p. 296-298°C) was obtained from tetraphenylcyclopentadiene.