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SYNTHESIS OF NEW CYCLOPROPARENES

by

ROBERT WAGNER

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
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APPROVED, THESIS COMMITTEE

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Abstract

Synthesis of new Cycloproparenes

by

Robert Wagner

The [2.2]paracyclocophane-annelated cycloproparenes 1 and 2 were prepared by treating the Diels-Alder adducts of 1-bromo-chlorocyclopropene and either 1-vinyl[2.2]paracyclophane-1-ene (3) or 1,2-dimethylene[2.2]paracyclophane (4) with potassium t-but-oxide in THF. Using the same approach the new cycloproparenes 5 and 6 were obtained from the [2.2]paracyclophanetetraenes 7 and 8.

[Chemical structures with reaction equations]
The silver-ion catalyzed polymerization of the dicyclopentrabenzoperylenes 9 and 10 was also studied. This method has shown to be an alternative to the repetitive Diels-Alder reaction in the synthesis of ladder polymers. The ladder polymers 11 and 12 were obtained and characterized by IR, solid-state $^{13}$C-NMR and thermogravimetric analysis (TGA).
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The Synthesis of new Cycloproparenes

INTRODUCTION

In 1964 Anet and Anet synthesized the first member of the cycloproparene family 13 via photolysis of the 3H-indazole 14. Cycloproparenes have become of particular interest for organic chemists. Their chemistry is characterized by the interplay of two contradictory effects, namely aromaticity which is generally known to stabilize compounds, and strain which is destabilizing.

Thus the determination of the strain energy of benzocyclopene (15) and cyclopropa[b]naphthalene (16) gave a value of 68 kcal/mol and 65-67 kcal/mol, respectively. For the dicyclopropa[b,g]naphthalene (17) a value of 166 kcal/mol was found. Despite these high values of strain energy compounds 15 to 17 are remarkably stable and have unusual physical and chemical properties that might be caused by a disruption of the aromatic sextet.
The first synthesis of cyclopropabenzene (15) itself was reported by Vogel et al.\textsuperscript{5} in 1965. His approach involves the Diels-Alder addition of dimethyl acetylenedicarboxylate (DMAD) to 1,6-methano[10]annulene (18). When the resulting adduct 19 was subjected to pyrolysis, cyclopropabenzene (15) was obtained as product of a retro-Diels-Alder reaction.

\begin{center}
\begin{tikzpicture}
  \node[draw] (a) at (0,0) {\textbf{18}};
  \node[draw] (b) at (3,0) {\textbf{19}};
  \node[draw] (c) at (1,-2) {\textbf{15}};

  \draw[->] (a) -- node[above] {DMAD} (b);
  \draw[->] (b) -- node[above] {\Delta} (c);
\end{tikzpicture}
\end{center}

This approach has also successfully been used in the synthesis of cyclopropa[a]naphthalene (20)\textsuperscript{6} and cyclopropa[l]phenanthrene (21)\textsuperscript{7}. 

\begin{center}
\begin{tikzpicture}
  \node[draw] (a) at (0,0) {\textbf{20}};
  \node[draw] (b) at (3,0) {\textbf{21}};
\end{tikzpicture}
\end{center}
A more general approach to cycloproparenes uses halogenated bicyclo[4.1.0]heptanes such as 22 and 23 as precursors. The tetrahalogenated derivatives 22 can be easily prepared via Diels-Alder addition of a tetrahalocyclopropene 24 to a 1,3-diene 25. The dihalogenated compounds of type 23 can be obtained by addition of a dihalocarbene 26 to a cyclohexadiene (RR = H) or a benzoannelated cyclohexadiene (RR = benzo) 27 (Scheme I).

Scheme I

\[
\begin{align*}
25 & \quad + \quad \begin{array}{c}
24 \\
\end{array} \quad \rightarrow \quad \begin{array}{c}
22 \\
\end{array} \\
\begin{array}{c}
27 \\
\end{array} & \quad + \quad :C_X_2 \quad \rightarrow \quad \begin{array}{c}
23 \\
\end{array}
\end{align*}
\]

\(X = \text{Br, Cl}
\)
\(Y = \text{Cl, F}
\)

Dehydrohalogenation of the Diels-Alder adduct 22 leads, as shown in scheme II, to the dihalocycloproparene 28, while treatment of the dihalogenated bicyclo[4.1.0]heptanes 23 with base gives the cycloproparene 28.
Scheme II

Thus the parent compound benzocyclopropene (15) has been prepared using the precursor 30 as well as its isomer 31.\textsuperscript{9}

The following mechanism has been proposed by Prestien and Günther\textsuperscript{10} to account for the formation of benzocyclopropene (15) from the precursor 31 (Scheme III).
Scheme III

$$\text{Cl} \quad \text{Cl} \quad \xrightarrow{t\text{-BuOK}} \quad \text{Cl} \quad \text{Cl}$$

$$\text{31} \quad \xrightarrow{\text{DMSO}} \quad \xrightarrow{\text{15}}$$

However, attempts to prepare cycloprop[b]anthracene (32) and cyclopropa[b]phenanthrene (33) using the gem-dichloro precursors have shown to be unsuccessful.

$$\text{32} \quad \text{33}$$

Treatment of 34 with potassium t-butoxide in THF gave only 2-chloromethylanthracene (35)$^{11}$ as product, while compound 36 yielded a mixture of the two isomer chloromethylphenanthrenes 37 and 38.$^{12}$

$$\text{34} \quad \xrightarrow{t\text{-BuOK}} \quad \text{35}$$
When the gem-dichloro compound 39 was treated with potassium t-butoxide in THF, the desired cyclopropa[b]naphthalene (16) was obtained in 65% yield together with small amounts of the t-butylether 40.\textsuperscript{13} Formation of this ether 40 can be rationalized by reaction of initially formed 2-chloromethylnaphthalene (41) with excess potassium t-butoxide.

The mechanism presented in scheme IV has been proposed to explain the formation of the chloromethyl compounds 35, 37, 38 and 41:\textsuperscript{14}
Scheme IV

\[ \text{Ar Ar} = \text{benzo or naphtho} \]

The key step of this mechanism is the deprotonation of 42 to a cyclopropylcarbiny1 anion 43 that undergoes ring-opening to the chloromethyl species 44. This anion 43 is stabilized by resonance with the adjacent aromatic ring system. One should expect this resonance stabilization to be greater for ArAr = naphtho than for ArAr = benzo. Therefore the formation of this anion 43 is more likely to occur from the gem-dichloro precursors 34 and 36 than from 39.

Billups and coworkers have shown that 1-bromo-2-chlorocyclopropene (44) can be used as a powerful synthon in the preparation of cycloproparenes 29.\textsuperscript{15} As it has been shown in scheme I for the tetrahalocyclopropenes 22, 1-bromo-2-chlorocyclopropene (44) can be added to 1,3-dienes and the resulting adducts 45 can be
subjected to dehydrohalogenation to yield cyclopropenes 29 (Scheme V).

Scheme V

\[
\begin{align*}
\text{25} & \quad + \quad \text{44} \quad \xrightarrow{\text{THF} \ -20^\circ C} \quad \text{45} \\
& \quad \xrightarrow{t-\text{BuOK} \ \text{THF}} \quad \text{29}
\end{align*}
\]

1-Bromo-2-chlorocyclopropene (44) can be prepared via the following sequence of steps: \(^{15}\)

\[
\begin{align*}
\text{TMS} & \quad \xrightarrow{1. \text{Br}_2 \ \text{CH}_2\text{Cl}_2} \quad \text{TMS} \\
& \quad \xrightarrow{2. \text{HNEt}_2} \quad \text{Br} \\
& \quad \xrightarrow{\text{CCI}_2} \quad \text{46}
\end{align*}
\]

\[
\begin{align*}
\text{47} & \quad \xrightarrow{\text{NBu}_4\text{F, THF} \ -20^\circ C} \quad \text{Br} \\
& \quad \xrightarrow{\text{Cl}} \quad \text{44}
\end{align*}
\]

Addition of the carbene to 46 is most effectively achieved using the organomercury compound PhHgCCl_2Br. \(^{16}\) Dehalosilylation of 47 to 44 is usually carried out by Bu_4NF in THF \(^{15}\), but CsF in
acetonitrile or in DMSO has also been used.\textsuperscript{17} 44 is an unstable compound that decomposes readily above -20°C. The first step is probably the ring opening of 44 to a carbene 48, as it has been observed for other cyclopropenes.\textsuperscript{18} However, the successive products of this initial rearrangement are unknown.

\[
\begin{array}{c}
\text{Br} \\
\text{Cl} \\
\text{44}
\end{array} \xrightarrow{\Delta} \begin{array}{c}
\text{X} \\
\text{48}
\end{array}
\]

44 has been used to synthesize cycloprop[b]anthracene (32)\textsuperscript{19} and cyclopropa[b]phenanthrene (33)\textsuperscript{15} that are inaccessible via the \textit{gem}-dichloro approach. In addition a number of fused benzocyclopropenes has been synthesized using this method. Examples are 49, 50, 51\textsuperscript{20} and 52\textsuperscript{21} which is the most strained cycloproparene that has been prepared.

\[
\begin{array}{cccc}
\text{49} & \text{50} & \text{51} & \text{52}
\end{array}
\]

Recently the Billups method has been used to synthesize the two dicyclocproparenes 53 and 54\textsuperscript{22} as well as the triscyclo-proparenes 55 and 56.\textsuperscript{23}
One of the problems associated with the Diels-Alder additions based on 44 is the low reactivity of halogenocyclopropenes towards dienes: Thus, a high excess of 44 and prolonged reaction times (several weeks) were necessary to convert the hexaene 57 into the tris-adduct 58, the precursor for the above triscyclopropene 58.\textsuperscript{23}

Another example is the oxo-bridged tetraene 59: Reaction of 59 with a high excess of 44 yielded only the monoadduct 60.\textsuperscript{14}
Müller has tried to overcome this problem by using furans or isobenzofurans instead of dienes in cycloaddition reactions with 44. The aromatization of the resulting adducts can be achieved by using a low-valent titanium reagent. Thus Müller and coworkers were able to synthesize the cyclopropaisoquinoline 60 as well as cyclopropa-[b]naphthalene 16.\textsuperscript{24}

One drawback of Müller's approach is that the aromatization of the Diels-Alder adducts does not always give the desired cycloproparene, but rather proceeds under rearrangement of the starting material: Treatment of the adduct 61 with low-valent titanium yielded a mixture of benzocyclopropene 15 and the
dihalocycloheptatriene 62. When 63 was reacted under the same conditions only the rearranged material 64 was isolated.\textsuperscript{25}

\[
\begin{array}{c}
\text{Me} \quad \text{Cl} \\
\text{Br} \quad \text{Cl} \\
\text{Me} \\
\text{Br}
\end{array}
\xrightarrow{\text{TiCl}_3, \text{LiAlH}_4}
\begin{array}{c}
\text{Me} \\
\text{Cl} \\
\text{Me} \\
\text{Br}
\end{array}
\quad + 
\begin{array}{c}
\text{Me} \\
\text{Cl} \\
\text{Me} \\
\text{Br}
\end{array}
\]

61  15  62

\[
\begin{array}{c}
\text{Me} \quad \text{Cl} \\
\text{Me} \\
\text{Cl} \\
\text{Me} \\
\text{Br} \quad \text{Br}
\end{array}
\xrightarrow{\text{TiCl}_3, \text{LiAlH}_4}
\begin{array}{c}
\text{Me} \\
\text{Me} \\
\text{Br} \\
\text{Br}
\end{array}
\]

63  64

Cycloadditions of furans to tetrahalogenocyclopropenes can equally be achieved. However, all attempts to aromatize the resulting adducts with low-valent titanium gave only decomposed starting materials and afforded no cyclopropenes.\textsuperscript{26}
Attempts to prepare 1H-cycloprop[a]azulene and 3-methoxy-1H-cycloprop[a]azulene

BACKGROUND

There have been no reports describing the synthesis of non-benzenoid cycloproparenes. Azulene (65), a classical non-benzenoid aromatic system, has long been of interest to organic chemists. The first successful synthesis was reported in 1936 by Pfau and Plattner27 and the chemistry of azulene and its derivatives has been investigated thoroughly during the past fifty years.28

![Diagram of azulene (65)]

It would be interesting to synthesize the ring system of cycloprop[a]azulene (66), because this would provide the first cycloproparene with a methylene-fusion on a five-membered ring and an increased strain energy compared to benzenoid cycloproparenes should be expected.
One approach towards the synthesis of 1,2-disubstituted azulenes uses the [8 + 2]-cycloaddition of a dienophile to a heptafulvene.\textsuperscript{29} This route was used by Kitahara and coworkers to prepare the two azulenes 67 and 68 in low yield via [8 + 2]-cycloaddition of the dienophiles 69 and 70 to 8-bromo-8-cyanoheptafulvene (71)\textsuperscript{30} and 8-cyanoheptafulvene (72)\textsuperscript{31}, respectively.

\[
\begin{align*}
\text{NCBr} & \quad \text{CO}_2\text{Me} \\
\text{71} & \quad \text{CO}_2\text{Me} \\
\text{NC} & \quad \text{H}
\end{align*}
\]

\[
\begin{align*}
1. \text{DMAD} & \quad 2. \text{-HBr} \\
\text{69} & \quad \text{67}
\end{align*}
\]

\[
\begin{align*}
\text{NC} & \quad \text{H} \\
\text{72} & \quad \text{O} \\
\text{70} & \quad \text{CN}
\end{align*}
\]

\[
\begin{align*}
1. \text{toluene, reflux} & \quad 2. \text{p-chloranil, PhH} \\
\text{68}
\end{align*}
\]

The Heptafulvenes reported so far can be classified into two groups:\textsuperscript{32} Heptafulvenes containing electron-withdrawing groups at the exocyclic carbon atom (heptafulvenes with "normal" ring-
polarization) and heptafulvenes bearing electron-donating groups at C-8 (heptafulvenes with "inverse" ring-polarization). The compounds of the first group are generally more stable toward oxidation then members of the latter one and are better represented by resonance structure 73a than by structure 73b. The heptafulvenes with inverse ring polarization have a more pronounced polyolefin character (resonance structure 73a).

\[ \text{R} \]
\[ \text{R} \]
\[ 73a \]

\[ \text{R}^- \text{R} \]
\[ \text{R} \]
\[ 73b \]

[8 + 2]-Cycloadditions with heptafulvenes of the first group, i.e., 71 and 72, usually require electron-rich dienophile partners and elevated temperatures (refluxing toluene or xylene) to proceed smoothly. The unstable and very reactive parent compound 73 has not found wide use as a synthon for the preparation of substituted azulenes since it is difficult to prepare and to handle. Daub and coworkers have synthesized several heptafulvenes with inverse ring-polarization. 8-Methoxyheptafulvene (74)\textsuperscript{33} is the best known member of this group and its [8 + 2]-cycloaddition chemistry has been intensively studied; two examples are illustrated below:\textsuperscript{34}
This makes 74 a very interesting starting material for the synthesis of a cycloprop[a]azulene-system: Reaction of 74 with 1-bromo-2-chlorocyclopropene (44) should provide the adduct 75, that could then be subjected to dehydrohalogenation to give 3-methoxy-1H-cycloprop[a]azulene (76). Furthermore, reaction of the parent compound 73 with 44 would provide a direct pathway to the unsubstituted 1H-cycloprop[a]azulene 66 via the adduct 77.
Earlier work in this laboratory on the synthesis of the parent compound 73 was carried out by Rodin. However, his attempt to prepare heptafulvene according to the method described by Neuenschwander was unsuccessful. In Neuenschwander's synthesis, tropone (78) is reacted with acyliumtetrafluoroborate (79) to give the acylium salt (80) which upon treatment with MeLi in CH₂Cl₂ forms a mixture of the isomer acetates 81. Flash vacuum pyrolysis of this product yields heptafulvene 73 as a red oil that polymerizes quickly above -20°C.

In our hands, the tropylium salt 80 could not be converted to the desired product 81. Three other syntheses of 73 have been
described in literature: The method described by Doering\textsuperscript{37} uses a Hoffman-elimination of the quarternary ammonium salt 82 in vacuo. The product is obtained as a mixture with water and triethylamine.

\[ \begin{array}{c}
\text{CH}_2\text{NMMe}_3 \\
\text{82}
\end{array} \xrightarrow{\text{Ag}_2\text{O, H}_2\text{O}} \begin{array}{c}
\text{73}
\end{array} \]

A third synthesis has recently been published by Neuenschwander et al.:\textsuperscript{38} Reaction of tropylium tetrafluoroborate (83) with bromomethylmagnesiumbromide yields the unstable bromomethylcycloheptatriene (84). Dehydrobromination of this compound with potassium t-butoxide in THF provides heptafulvene (73).

\[ \begin{array}{c}
\text{BF}_4^- \\
\text{83}
\end{array} \xrightarrow{\text{BrCH}_2\text{MgBr, THF}} \begin{array}{c}
\text{CH}_2\text{Br} \\
\text{84}
\end{array} \xrightarrow{\text{t-BuOK, THF}} \begin{array}{c}
\text{73}
\end{array} \]

This synthesis could be reproduced, though low temperature chromatography (-40°C) of the intermediate 84 was difficult and resulted in loss of most of the product due to polymerization.

The most efficient synthesis of heptafulvene was the method described by Parker and Jones:\textsuperscript{39} Addition of monochlorocarbene to
cycloheptatriene (85) resulted in the formation of a mixture of the endo- 86a and exo-adduct 86b, the combined yield being 11% (endo/exo = 75/25 %). When a solution of this material in tetraglyme was added rapidly to a suspension of potassium t-butoxide in tetraglyme at 90°C in vacuo a red condensate could be isolated in a liquid nitrogen trap. Parker and Jones have shown that only the exo-adduct 86b is responsible for the formation of heptafulvene:

\[
\text{CH}_2\text{Cl}_2, \text{MeLi, RT} \quad \xrightarrow{85} \quad \begin{align*}
\text{endo: 75 \%} & \quad \text{86a} \\
\text{exo: 25 \%} & \quad \text{86b}
\end{align*}
\]

\[
\text{86b} \quad \xrightarrow{\text{tetraglyme, } \text{t-BuOK, 1 Torr, 90°C}} \quad \text{73}
\]

Compound 73 prepared this way could be trapped with DMAD to yield the dehydroazulene 87\[37, 38\]
In order to prepare the addition product 1-bromo-2-chlorocyclopropene (44) was freshly prepared and added to a solution of 73 in THF. After the mixture was stored overnight in the freezer at -20°C, the red color of the fulvene 73 had dissapeared. Workup of the mixture resulted in isolation of a white polymer that rapidly turned yellow in the air. None of the desired [8 + 2]-addition product could be detected by 1H-NMR. When this experiment was repeated in n-pentane, the red solution decolorized more slowly, but on workup a white polymer was found. No trace of the desired product could be isolated. In a final experiment, CH₂Cl₂ was used as solvent yielding again only a polymeric material as product.

Disappointed by these results, further experiments focused on the reaction of 8-methoxyheptafulvene (74) with 44 in order to prepare the substituted cycloprop[a]azulene 76. 74 was synthesized from cyclooctatetraene (88) according to Daub's procedure and purified by Kugelrohr distillation.33, 41 The compound was obtained as a deep-red liquid that polymerized quickly to a yellow resin when exposed to air.
In a control experiment, a solution of 74 in CH₂Cl₂ was stirred with DMAD 69 overnight at room temperature. Upon workup the [8 + 2]-cycloaddition product 89 was obtained in 21% yield.  

The attempted reaction of 8-methoxyheptafulvene (74) with 1-bromo-2-chlorocyclopropene (44) was, however, not successful: Addition of 44 to the fulvene 74 in THF and storage in the freezer at -20°C for 1 day resulted only in formation of polymeric material. This polymerization seemed to be slowest in pentane (decolorization after 2 days) and fastest in CH₂Cl₂ (complete decolorization of the red solution after only 1h at -20°C). Daub and coworkers observed a similar behaviour of 8-methoxy-heptafulvene (74) in the attempted [8 + 2]-cycloaddition with fumaronitrile (90) and dimethyl fumarate (91). In both cases only polymerization products of the fulvene 74 could be obtained.

\[
\begin{align*}
74 &+ 69 \xrightarrow{\text{CH₂Cl₂, RT, 24H}} 89 \\
\text{polymerization of the fulvene} &
\end{align*}
\]
A satisfactory explanation for this behaviour has not yet been found. The reactivity of the polyenophiles 90, 91 and 44 obviously seems to be too low under these reaction conditions to achieve an [8 + 2]-cycloaddition.
The Synthesis of [2.2]Paracyclophane-annelated Cycloproparenes

BACKGROUND

[2.2]Paracyclophane (92) and its derivatives have long been of interest to organic chemists. This interest results from two special characteristics of the [2.2]paracyclophane-system: the interaction between the π-electron-systems of the two benzene ring-planes and the deformation of the two benzene rings.

The interaction between the two benzene ring π-systems leads to a novel, extended electron system. Its highest occupied molecular orbital (HOMO) is higher than that of the corresponding alkylbenzene (p-diethylbenzene), while its lowest unoccupied molecular orbital (LUMO) lies at a lower level than that in the open chain reference molecule. Thus, the net-effect is a narrowing of the HOMO-LUMO-gap in [2.2]paracyclophane compared to benzene. X-ray crystal structure analyses have shown that the two benzene rings are not planar but
rather distorted. The four aromatic bridgehead atoms C3, C6, C11 and C14 are bent out of plane of the remaining benzene carbon atoms, thus deforming the aromatic nuclei into a boat conformation. The distance of the central carbon atoms of the benzene rings is considerably smaller (308-309 pm) than the normal van der Waals separation between parallel benzene rings (340 pm). This is caused by the transannular $\pi-\pi$-overlap. A similar $\pi-\pi$-interaction, though weaker, is found for [3.3]paracyclophane (93), but is absent in [4.4]paracyclophane (94) whose benzene rings behave as separated systems.

![Diagram](image)

PE and ESR studies by Gleiter have shown that there is a significant $\sigma-\pi$-overlap between the 1,2- (9,10-) $\sigma$-bonds and the $\pi$-orbitals of the benzene rings in 92. Considering this effect, 1:2,9:10-dibenzo-[2.2]paracyclophane-1,9-diene (95) is of special interest: there is no conjugation in a classical sense between the outer benzene rings, but the high $\pi$-electron density of the paracyclophane-unit should enable some kind of electronic interaction between them. Recently de Meijere and coworkers have prepared several substituted dibenzo[2.2]paracyclophanes. ESR,
NMR and cyclovoltametric studies show that these compounds are interesting models for charge storage systems.

De Meijere and König also proposed the structure of a poly(anthraceno[2.2]paracyclophanediene) (96).\textsuperscript{47,48} A ladder polymer of this type should be more stable than the polyacen-system 97 since the conjugation of the benzene rings is interrupted by the [2.2]paracyclophane-units. However, the whole system has a high $\pi$-electron density. Doping of this polymer with alkali metals could lead to a material with high electrical conductivity as it has been observed for doped polythiophenes\textsuperscript{49} and polyacetylenes.\textsuperscript{50}
During the past ten years the synthesis of new dicycloprenenes and the study of their silver-ion catalyzed polymerization has been a major goal in this laboratory. We have found that this reaction is an interesting alternative to the repetitive Diels-Alder reaction in the synthesis of ladder polymers.\textsuperscript{51}

The synthesis of the [2.2]paracyclophe-annelated cycloprop-arenes 1, 2, 98 and 99 would therefore not only provide a new group of theoretically interesting molecules, but also yield potential precursors for molecular systems like 96.

Synthesis of these new compounds might be accomplished via the Billups' approach using the dienes 3\textsuperscript{47}, 4\textsuperscript{52} and tetraenes 7\textsuperscript{47}, 8\textsuperscript{52} as starting materials.
RESULTS AND DISCUSSION

Our experiments were initiated with the synthesis of 1-vinyl[2.2]paracyclophane-1-ene (1) which was prepared in four steps according to Hopf and Psiorz: Photobromination of [2.2]paracyclophane with one equivalent of bromine yielded a mixture of 1-bromo[2.2]paracyclophane (100) and 1,2-dibromo[2.2]paracyclophane (101).

Treatment of the crude mixture of 100 and 101 with copper cyanide in N-methylpyrrolidone resulted in a mixture of the nitriles
102 and 103. Separation of these compounds could be accomplished by column chromatography.\textsuperscript{52}

Reduction of 102 with DIBAH in benzene gave the aldehyde 104 in 44\% yield. The desired diene 3 could be obtained from 104 by Wittig-reaction in 70\% yield.\textsuperscript{52}

When 3 was added to a freshly prepared solution of 44 in THF (twentyfold excess) and the resulting mixture was stored at -20°C for 3 days, none of the desired cycloaddition material 105 could be detected by TLC. However, when the reaction mixture was slowly
warmed to 0°C and kept at this temperature for two days the desired product 105 could be obtained in 9% yield. When the reaction mixture was immediately warmed to room temperature after the addition of 3 only traces of the product could be observed. Most of the cyclopropene 44 decomposed under these conditions.

Attempts to increase the yield of 105 by using a higher excess of 44 proved to be unsuccessful. A fortyfold excess of the cyclopropene 44 resulted in the formation of more polymeric byproducts. Attempts to catalyze the Diels-Alder reaction with Lewis-acids (BF₃ · Et₂O) were also unsuccessful.

Bauld and coworkers have reported, that the addition of the stable cation-radical salt (p-BrC₆H₄)₃NSbCl₆ can be used effectively to catalyze Diels-Alder reactions involving neutral or electron rich-dienophiles. The catalyst transforms the dienophile into the more reactive radical-anion. To check if this catalyst would improve the yield of 105, a small amount was added to a solution of 3 and 44 in CH₂Cl₂ at -20°C. The initially blue color of the solution disappeared overnight. After 2 days at 0°C and workup, no cycloaddition product
105 could be detected. The TLC showed only decomposition products of 44 next to unreacted diene 3.

The $^1$H-NMR spectrum of 105 exhibits, as expected, two doublets at 1.69 and 2.29 ppm for the protons attached to the cyclopropane ring. Complex multiplets are found for the protons of the ethylene bridge and the aromatic protons of the two benzene rings at 3.00 - 3.15 ppm and 6.35 - 6.71 ppm, respectively.

The $^{13}$C-NMR spectrum shows twelve signals for aliphatic carbon-atoms and 24 signals for sp$^2$-hybridized carbon atoms. This can be rationalized by the fact that compound 105 is probably a mixture of the isomers 105a to 105d and their enantiomers. However, it was not possible to separate this mixture into its components.

To synthesize the cyclopropane 1 compound 105 was treated with a fivefold excess of potassium $t$-butoxide in THF at low temperatures (-50 to -20°C). After removal of the solvent in vacuo
the residue was extracted with *n*-pentane. After passing the combined extracts over a florisil column and removing the solvent in vacuo compound 1 was obtained as very fine, colorless solid that decomposed upon heating (> 200°C) without melting.

\[
\begin{array}{c}
\begin{align*}
\text{105} & \quad \xrightarrow{\text{t-BuOK, THF}} \quad 50\% \\
X = \text{Br, Cl}
\end{align*}
\end{array}
\]

The \(^1\)H-NMR spectrum of 1 exhibits the following pattern of signals: 3.13 (s, 4H, CH\(_2\)CH\(_2\)), 3.42 (s, 2H, CH\(_2\)), 6.56 (s, 4H, p-ArH), 6.59 (s, 4H, p-ArH), 7.28 (d, 1H, o-ArH), 7.49 (d, 1H, o-ArH). The assignments of these signals were made by comparison with the chemical shifts exhibited by benzo[2.2]paracyclophane\(^{45}\) and various benzocyclopropenes.\(^2\) The \(^{13}\)C-NMR spectrum shows, as expected, three signals for sp\(^3\)-hybridized carbon atoms and fourteen signals for sp\(^2\)-carbon atoms. The signal at 19.7 ppm is typical of the carbon atom of the methylene-fusion in cyclopropenes. The signals at 34.8 and 34.9 ppm can be attributed to the carbon atoms of the ethylene bridge. The high field shift at 113.3 ppm can be assigned to the tertiary carbon atom ortho to the cyclopropyl-ring. For benzocyclopropene (15)\(^2\) this signal is found at 114.7 ppm.
The ease of the synthesis of 1 lead to the investigation of its structural isomer 2. The diene 4 was prepared after a method that has been recently described by de Meijere and König.\(^{47}\) The crude mixture of the mono- and dibromides was treated with potassium \(t\)-butoxide in DMSO to yield [2.2]paracyclophane-1-ene 106.

\[
\begin{align*}
100 & \xrightarrow{t\text{-}BuOK, \text{DMSO}} 106 \\
\end{align*}
\]

Bromination of 106 gave the dibromoadduct 107.

\[
\begin{align*}
106 & \xrightarrow{\text{Br}_2, \text{CH}_2\text{Cl}_2} 107 \\
\end{align*}
\]

However, when this material was treated with potassium \(t\)-butoxide in \(t\)-butanol under reflux, as described by Psiorz\(^{52}\), only traces of the desired 1-bromo[2.2]paracyclophane-1-ene (108) could be isolated. When the dehydrobromination was carried out under less harsh conditions in methyl \(t\)-butyl ether (MTBE) at room temperature, the product 108 was isolated in 88% yield.
Bromination of 108 in CH₂Cl₂ gave the tribromophane 109 in 81 % yield which upon treatment with potassium t-butoxide in t-butanol yielded 1,2-dibromo[2.2]paracyclophane-1-ene (110) in 90 % yield.

Methylation of 110 was achieved using a methylvcuprate in THF that was prepared in situ from copper iodide and methylmagnesium bromide. The 1,2-dimethyl[2.2]paracyclophane-1-ene (111) was isolated in 51 % yield and contained about 10 % (by ¹H-NMR) of the monomethylated product 112 that could not be removed by column chromatography.
Bromination of 111 in CH$_2$Cl$_2$ using 2 equivalents of bromine gave the bromomethyl compound 113 in 50 % yield. Reduction of this material with activated zinc$^{88}$ in dry $p$-dioxane in an ultrasound bath$^{56}$ provided dimethylene[2.2]paracyclophe (4) in 64 % yield.

When 4 was reacted under the same conditions that had been used to prepare 105 the cycloaddition product 114 was isolated in 30% yield (colorless crystals, m.p. 185°C). Again, addition of Lewis-acid catalysts to the reaction mixture had no influence on the yield.
The $^1$H-NMR-spectrum of 114 exhibits the expected pattern with two doublets at 1.65 and 1.95 ppm (cyclopropane CH$_2$) and one singlet at 3.01 ppm (-CH$_2$-CH$_2$-). For the allylic CH$_2$-groups and the aromatic protons two multiplets are found at 3.45-3.67 ppm and 6.22-6.48 ppm, respectively. The $^{13}$C-NMR-spectrum displays fifteen signals. Only the signals at 25.9 ppm (cyclopropane CH$_2$) and at 34.6 ppm (-CH$_2$-CH$_2$-) could be assigned by comparison with the $^{13}$C-NMR-data of [2.2]paracyclophane (92)$^{42}$ and the Diels-Alder adducts 115 and 116.$^{22}$

Dehydrohalogenation of 114 gave the cycloproparene 2 in 67 % yield.
The $^1$H-NMR of 2 displays the following signals: 3.10 (s, 4 H, -CH$_2$-CH$_2$-), 3.42 (s, 2 H, CH$_2$), 6.54 (s, 8 H, p-ArH), 7.51 (s, 2 H, o-ArH). The $^{13}$C-NMR spectrum shows signals at 20.1 (cyclopropyl CH$_2$), 34.8 (-CH$_2$-CH$_2$-), 113.5 (C's ortho to cyclopropyl), 124.8, 132.2, 132.8, 139.2, 140.7, 139.2, 140.7 and 146.9.

Elemental composition was provided by high resolution mass spectrometry; calculated for C$_{21}$H$_{16}$: 268.1252; found: 268.1249.

Next the reaction of the tetraenes 7 and 8 with 44 was investigated. 7 was synthesized in four steps from [2.2]paracyclopnone (92). Photobromination of 92 with four equivalents of bromine yielded a mixture of the two isomer tetrabromides$^{57}$ 117 that upon treatment with CuCN in N-methylpyrrolidine gave the two isomer dinitriles 118 in 19 % combined yield.$^{52}$
Reduction of 118 with DIBAH in benzene gave a 3:1 mixture of the dialdehydes 119 and 120 that were separated by column chromatography using CH₂Cl₂. The 1,9-isomer 119 was isolated in 12% yield.⁵²

Transformation of 119 into the divinylphane 7 was then achieved by Wittig reaction in 48% yield.

The isomer tetramethylene[2.2]paracyclophane (8) was prepared in an eight step synthesis from the mixture of the tetrabromides 117.⁴⁷ Dehydrohalogenation of 117 with potassium t-butoxide in
MTBE lead to a mixture of the dibromo[2.2]paracyclopandedienes 121 in 73 % combined yield.

Bromination of this mixture provided the hexabromides 122 (58 % yield) that were then transformed into 1,2,9,10-tetrabromo-[2.2]paracyclophanediene (123) in 59 % yield.\textsuperscript{46}

Methylation of 123 gave the tetramethylparacyclophane 124 in 31 % yield.
Reaction of 124 with bromine in CH₂Cl₂ in at -25°C resulted in the formation of a white precipitate of 125. Careful temperature control was necessary to obtain a good yield.

Attempts to prepare the tetraene 8 from 125 via reduction with activated zinc in p-dioxane as described by König⁴⁷ were however not successful. Even after two days of sonification in an ultrasound bath only traces of the desired product 8 were formed. Conversion of 125 to 8 was quickly achieved when 125 was suspended in a solution of sodium iodide in acetone⁵⁸ and sonicated in an ultrasound bath for 3 hours at room temperature.
When the tetraenes 7 and 8 were were added to a twentyfold excess of 44 in THF only one product was isolated in each case next to the unreacted starting materials. In both cases these products were identified as the monoadducts 126 and 127 by their $^1$H-NMR-spectra: 126: $\delta = 1.70$ (d, 2J=7.5 Hz, 1 H, cyclopropane CH$_2$), 2.27 (d, 2J=7.5 Hz, cyclopropane CH$_2$), 3.23 (m, allyl CH$_2$), 4.28 (m, CH) 5.41 (m, H$_2$C=CH-), 5.82 (m, C=CH-CH$_2$-), 6.31 (m, ArH), 6.52-6.67 (m, ArH), 6.79 (dd, 3J$_{cis}$=12.5 Hz, 3J$_{trans}$=17.5 Hz, HC=C-CH=CH$_2$), 6.88 (m, ArH) and 7.12 (s, H C=C-CH=CH$_2$); 127: $\delta = 1.65$ (d, 2J=7.5 Hz, cyclopropane CH$_2$), 1.93 (d, 2J=7.5 Hz, cyclopropane CH$_2$), 3.45-3.70 (m, allyl CH$_2$), 5.32 (d, 2J=1.7 Hz, C=CH$_2$), 5.67 (d, 2J=1.7 Hz, C=CH$_2$) and 6.30-6.61 (m, ArH).

126 is probably again a mixture of different isomers as can be concluded from its $^{13}$C-NMR-spectrum. But this shall be ignored for the further discussion.
The yields of 125 (8%) and 126 (24%) were similar to the yields of 105 (9%) and 114 (30%), thus speaking for a lesser reactivity of the vinylphanes 3 and 7 compared to the di- and tetramethylenephanes 4 and 8. Attempts to prepare the bisadducts 127 and 128 by using a higher excess of the cyclopropene 44 or adding catalysts like BF₃·Et₂O or ZnCl₂ were unsuccessful. Nor was an increased reaction time the solution.

![Diagram of 127 and 128]

X = Cl, Br

When the purified monoadducts 125 and 126 were again added to a twentyfold excess of 44 workup of the reaction mixtures gave only the monoadducts back while none of the desired products 127 and 128 were formed. The reactivity of 125 and 126 toward the cyclopropene 44 can be compared to the reactivity of the oxobridged monoadduct 60 mentioned previously on page 11. No satisfactory explanation has been found so far that shows why the addition of a second molecule of 44 to the monoadducts 125, 126, and 60 is difficult and doesn't proceed in the temperature range from -20 to 0°C. If the formation of the bisadducts could be achieved under high pressure needs to be explored.
When 125 and 126 were treated with potassium t-butoxide in THF the cyclopropenanes 5 and 6 were obtained in 68 and 57 % yield.

The \textsuperscript{1}H-NMR-spectrum of 5 displays the following signals: \( \delta = 3.42 \) (s, cyclopropene \( \text{CH}_2 \)), 5.44 (m, \( \text{H}_2\text{C} = \text{CH} \)), 6.53-6.71 (m, p-ArH), 6.82 (dd, \( ^3J_{\text{cis}} = 10 \) Hz, \( ^3J_{\text{trans}} = 17 \) Hz, HC=CH=CH\(_2\)), 7.15 (s, HC=C-CH=CH\(_2\)), 7.30 (d, \( ^3J = 7.5 \) Hz, o-ArH) and 7.51 (d, \( ^3J = 7.5 \) Hz, o-ArH). For the isomer compound 6 peaks at \( \delta = 3.42 \) (s, cyclopropene \( \text{CH}_2 \)), 5.39 (d, \( ^2J = 1.5 \) Hz, C=CH\(_2\)), 5.72 (d, \( ^2J = 1.5 \) Hz, C=CH\(_2\)), 6.63 (m, p-ArH) and 7.55 (s, o-ArH) are found. Elemental composition of both compounds was proven by high-resolution mass spectrometry: calculated for \( \text{C}_{23}\text{H}_{16} : 292.1252 \); found: 292.1250 (5) and 292.1251 (6). Both compounds form fine white crystals that decompose without melting at 170\(^\circ\)C (5) and 150\(^\circ\)C (6). 1, 2, 5 and 6 exhibit the typical foul smell of cyclopropenanes, however subdued due to their low volatility. Further work in our group is continued toward the synthesis of new dicyclopropenanes.
The Polymerization of Dicycloprenanes

INTRODUCTION

Ladder (ribbon) polymers consist of cyclic subunits, connected by two links which are attached to different sites of the respective subunits. Thus ladder polymers have two independent strands of bonds that are tied together regularly and do not cross or merge into a single or double bond. Cleavage of several single bonds in the same strand will not result in a decrease of the molecular weight as is commonly observed for single-stranded polymers.

Scheme VI: Scission of ladder polymer chains

\[ \begin{array}{ccc}
\text{---} & \text{---} & \text{---} \\
\text{---} & \text{---} & \text{---} \\
\text{---} & \text{---} & \text{---} \\
\text{---} & \text{---} & \text{---} \\
\end{array} \]

This results in greater resistance of ladder polymers to mechanical, thermal, and chemical degradation. One problem associated with many ladder polymers is their insolubility in
organic solvents and their infusibility. This makes it difficult to characterize and to process them. These properties are caused by strong intermolecular interactions among their more or less planar backbones. So far two general methodologies for the synthesis of ladder polymers have been developed.\textsuperscript{60} The first approach (Scheme VII) uses the reaction of two tetrafunctional monomers to form each of the strands from the very beginning. However, it is nearly impossible to achieve a linkage of the monomers in the desired way throughout the length of the band. Incorrect linkages lead rather to a cross-linked polymer.

**Scheme VII**

![Scheme VII diagram]

The above approach has been used by Vögtle and coworkers to prepare the [3.3]metacyclophane oligomer 129.\textsuperscript{61}
In the second method, shown in scheme VIII, a single stranded polymer is synthesized first and the second strand is then formed by reaction of suitable functional groups that are attached to the first strand. Ideally this reaction should proceed like a zipper from one terminus of the chain to the other. However, for statistical reasons this is very unlikely to happen since the reactions among functional groups occur more or less randomly leading to imperfect ladders.

Scheme VIII
This approach is illustrated in the cyclization of poly(methylvinylketone) \(130\)^{62}.

Marvel and Levesque obtained the polymer \(131\) by heating the polyketone \(130\) to 300°C. The cyclization was only 86% complete.

The problem of cross-linked polymer formation associated with the first approach can be overcome when Diels-Alder cyclizations are used to connect the monomers: The transition state of the Diels-Alder reaction is stabilized by electron delocalization and forces the reactants into an ideal geometry. The two strands of the ladder are formed simultaneously. Thus the reaction is regiospecific and side reactions are suppressed. This method was used as early as
1954 by Bailey and coworkers\textsuperscript{63} who obtained an almost perfect ladder polymer \textbf{132} from 2-vinylbutadiene (\textbf{133}) and \(\rho\)-benzoquinone (\textbf{134}). The average molecular weight was found to be \(M_n = 7000 \text{ g/mol}\).

\[
\begin{align*}
\text{133} & \quad + \quad \text{134} \\
& \quad \rightarrow \\
\text{132}
\end{align*}
\]

However, the material \textbf{132} was infusible and insoluble in common organic solvents which prevented technical applications. Recently, Schlüter\textsuperscript{60} has prepared several new ladder polymers using the Diels-Alder route. The problem of low solubility was overcome by attaching flexible alkyl side chains to the monomers. This prevented the growing polymers from early precipitation and led to polymers with about 50 repeat units. In the case of the polymer \textbf{135} an average molecular weight of \(M_n = 100,000 \text{ g/mol}\) was found!
The synthesis of fully conjugated ladder polymers has become a major topic of research during the past fifteen years. These are potentially interesting materials for applications in areas such as electrical conductivity, nonlinear optics and photovoltaics. The polyacene-system (97) has attracted much attention in this regard. 97 is a model for a one dimensional conductor and might exhibit some interesting properties such as high temperature superconductivity and ferromagnetism.$^{64-66}$

Numerous attempts to prepare 97 and similar systems$^{67-69}$ have been reported in literature. Thus Kiji and Iwamoto obtained a black, insoluble, heat resistant polymer 136 via oxidation of cyclized 1,2 polybutadiene (137) with chloranil that probably contains polyacene-subunits.$^{70}$
In a more recent approach, Ozaki and coworkers prepared a polymer with polyacene-like structure 138 via pyrolysis of poly(ethynylacetylene) (139). This material shows a weak electrical conductivity that is, however, far from being metallic.\textsuperscript{71}

Schlüter synthesized the polyacene precursor 140 by reduction of the polymer 141 with trimethylsilyliodide.\textsuperscript{60} Support for the structure 140 came from the solid-state $^{13}$C-NMR spectrum.
Despite these attempts, the synthesis of a pure polyacene in the sense of structure 97 has not yet been achieved and theoretical calculations predict the fully conjugated species to be very sensitive toward oxygen.

The synthesis of a fully unsaturated ladder polymer 142 that consists of pyracylene and oligoacene subunits was recently reported by Schlüter et al.\textsuperscript{72} Dehydration of the prepolymer 143 with p-TsOH in toluene gave an orange product whose spectroscopic data (\textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR, UV) are consistent with formula 142.
The use of flexible dodecyl side chains makes this polymer soluble in organic solvents in contrast to the polymers 136 and 138.
As was already mentioned on page 26, the silver-ion catalyzed polymerization of dicyclopophrenes can be used as an alternative to the repetitive Diels-Alder reaction in the synthesis of ladder polymers.\textsuperscript{51} The reaction probably arises via the cationic intermediates 144 and 145 that result from addition of the silver ion to the sigma electrons of the cyclopropenyl ring,\textsuperscript{73-81} as is demonstrated below for the dimerization of benzocyclopropene (15) to 9,10-dihydroanthracene (146).

\[
\begin{align*}
\text{15} \xrightarrow{\text{AgBF}_4} \text{144} & \xrightarrow{\text{CHCl}_3} \text{145} \\
& \quad \downarrow \\
& \text{146}
\end{align*}
\]

So far the polymers 147 and 148 have been prepared from the dicyclopophrenes 17 and 53, respectively.
Both polymers have been characterized to some extent by solid state nuclear magnetic resonance spectroscopy. In a cross polarization experiment polymer 147 exhibited aromatic signals at 132.3 and 126.1 ppm as well as an aliphatic signal at 37.0 ppm.\textsuperscript{51,82} The corresponding spectrum of 148 shows aromatic signals at 140.0, 125.0 ppm as well as three signals for aliphatic carbon atoms at 55.0, 45.0 and 40.0 ppm.\textsuperscript{83} The three different aliphatic signals have been attributed to crystal packing effects. When the polymerization of 17 was monitored by \textsuperscript{1}H-NMR spectroscopy the dimer 149 was observed as an intermediate. However, attempts to separate this dimer 149 from the monomer 17 failed.\textsuperscript{84}

Dimers 150\textsuperscript{82} and 151\textsuperscript{83} were observed when the polymerisation of the dicycloprenes 9 and 10 was studied by
$^1$H-NMR, while no intermediates could be detected in the course of the polymerisation of the anthracene 53.$^{82}$

It was the goal of this thesis to prepare the polymers 11 and 12 in larger quantities for characterization and to isolate and characterize the intermediates 150 and 151.
RESULTS AND DISCUSSION

The dicyclopentane 10 was prepared in two steps according to Luo\textsuperscript{83,84} from 2, 3, 5, 6-tetramethylidene[2.2.2]bicyclooctane (152)\textsuperscript{85} and cyclopropene 44: Conversion of 152 to the bisadduct 153 was complete when a twentyfold excess of 44 was used and a small amount of BF\textsubscript{3} \cdot Et\textsubscript{2}O was added to the reaction mixture. Elimination of 153 to the dicyclopentane 10 was achieved by treating 153 with an excess of potassium t-butoxide (84% yield).

\[
\begin{align*}
\text{152} & \quad \xrightarrow{44, \text{THF}, \text{BF}_3 \cdot \text{Et}_2\text{O}, -20^\circ \text{C}} \quad \text{153} \\
& \quad \xrightarrow{t-\text{BuOK}, \text{THF}, \text{84%}} \quad \text{10}
\end{align*}
\]

Dicyclopenta[b,h]phenanthrene 9 was synthesized as described by Haley:\textsuperscript{22,86} Reaction of 1,2,3,4-tetramethylenecyclohexane (154)\textsuperscript{87} with cyclopropene 44 gave a mixture of the monoadduct 155 and the desired bisadduct 156. Separation of the products was achieved by column chromatography and afforded 156 as colorless
crystals in only 10 % yield. 156 was then oxidized with DDQ in benzene to yield 116. Dehydrohalogenation of 116 with potassium t-butoxide yielded the dicyclopentayne 9.

![Chemical diagram]

In order to prepare the polymers 11 and 12 solutions of the cyclopropylenes in 9 and 10 in dry CDCl3 were added to AgBF4 (several flicks) under an argon atmosphere and the reaction was monitored by 1H-NMR spectroscopy. The initially colorless solutions rapidly turned yellow. Traces of the dimer 151 were already visible in the 1H-NMR after 10 minutes. After three hours the solution of 10 turned cloudy and the polymer 12 started to precipitate. After another 5 hours no more starting material or dimer could be detected. The polymerization of the dicyclopenta[b,h]phenanthrene 9 proceeded much more slowly under the same conditions: Traces of the dimer 150 could be detected after 4.5 hours. The reaction
mixture turned cloudy after 12 hours and after 36 hours a precipitate of the polymer 11 had formed. The reaction was completed after 4 days.

Infrared spectroscopy of the powdery solids showed the expected aromatic and aliphatic absorbances. Polymer 11 was further characterized by solid-state $^{13}$C-NMR spectroscopy. The cross-polarization experiment revealed an aromatic signal at 127 ppm and an aliphatic signal at 27 ppm. These signals are consistent with the assigned structure 11. Thermogravimetric analysis (TGA) of both polymers showed them to be reasonable stable up to 250 °C (argon flow). Between 273 and 642°C 12 experienced a weight loss of 17.3 % that might be caused by a loss of the ethylene-bridges of the bicyclo[2.2.2]octane-units. A similar weight loss (17 %) was observed for polymer 11 between 244 and 622°C. An X-ray powder diagram of polymer 11 suggests that this material might be partially crystalline and shows that elemental silver (from the reduction of AgBF$_4$) has been incorporated into the polymer.

In order to isolate the dimers 150 and 151 samples of the dicycloproparylenes 9 and 10 in CDCl$_3$ were again added to AgBF$_4$. When the maximum concentrations of the dimers had built up (~ 2.5 - 3 hours for 151, 28 hours for 150) the polymerization was terminated by removing the AgBF$_4$ by filtration through a florisil plug. Separation of the dimer 151 from the monomer 10 was then achieved by preparative TLC, using a deactivated silica gel plate. The dimer 151 was obtained as the third zone after the monomer and an
unidentified impurity. The $^1$H-NMR spectrum of 151 exhibits the following signals:

$\delta = 1.68$ (s, 8 H, -CH$_2$-CH$_2$), 3.11 (d, 2H, J = 2.5 Hz, cyclopropyl CH$_2$), 3.23 (d, 2 H, J = 2.5 Hz, cyclopropyl CH$_2$), 3.80 (s, 4H, -CH$_2$-), 4.34 (s, 4H, tert.-H), 7.16 (m, 8 H, ArH). Assignments of these signals was based on comparison with the $^1$H-NMR data of the starting material 10. The singlet at 3.80 ppm indicates that 151 actually is the transoid compound 151b. The cisoid compound 151a should exhibit two singlets for the protons of the bridging methylene groups.

Attempts to isolate the dimer 150 using the same technique that had been successful for 151 failed. The material 150 was too sensitive for chromatography on deactivated silica gel plates. However, separation of 150 from the monomer 9 was achieved on a small florisil column: The monomer 9 eluted first with n-pentane; the dimer was then isolated as the next fraction using CHCl$_3$ as eluting solvent. The product obtained in this manner was free of the
monomer, but contained still other impurities. 150 has shown to be very air and temperature sensitive but can be stored in CDCl$_3$ solution in the freezer for a few days. The $^1$H-NMR-spectrum of 150 displays four singlets in the aliphatic region at 3.59, 4.33, 4.41 and 4.49 ppm. In the aromatic region signals at 7.76-7.81 (m), 7.88 (d), 8.57 (s) and 8.77 (d) are found. The ratio of the integrals of the aliphatic signals is 4 : 1 : 2 : 1. This can be rationalized by assuming that 150 is a 1 : 1 mixture of the cisoid isomer 150a and the transoid isomer 150b. 150a should show two signals for the protons of the central ring while for 150b only one singlet should be found. Both isomers exhibit one common singlet at 3.59 ppm for the cyclopropyl CH$_2$-group. An exact assignment of the aromatic signals was not possible.

![Diagram of 150a and 150b]

Future research in this field should focus on the synthesis of soluble polymers since this would enable the determination of their molecular weight by methods such as size exclusion chromatography (SEC). In addition soluble polymers could be characterized by standard $^1$H- and $^{13}$C-NMR-spectroscopy in solution instead of using
the solid-state technique. Soluble polymers could be obtained by using Schlüter's concept of adding flexible alkyl-side chains to the backbones of the polymers. The unknown cyclopropene 152 might be an interesting synthon to achieve this goal.
Experimental

GENERAL

$^1$H- and $^13$C-NMR-spectra were recorded using a Bruker 250 MHz spectrometer ($^1$H: 250 MHz, $^13$C: 62.9 MHz) and were obtained in deuterochloroform. Chemical shifts (δ) are expressed in ppm downfield from tetramethysilane using the residual chloroform as internal standard ($^1$H: 7.26, $^13$C: 77.0). Infrared spectra of the compounds were recorded in a Nicolet 205 FT-IR as KBr pellets. Mass spectra were recorded on a Finnigan MAT 95. Melting points were determined on a Fischer-Johns apparatus and are uncorrected.

8-Chlorobicyclo[5.1.0]octa-2,4-diene was prepared as a 3 : 1 mixture of the endo- (86a) and exo-isomer (86b) as described by Merenyi.40

8-Methoxyheptafulvene (74) was synthesized according to Daub and coworkers.33 [2.2]Paracyclopahne was bought from Aldrich (98 % pure). The vinylphanes 3 and 7 were prepared according to the procedure by Hopf and Psiorz.47 For the preparation of the methylene[2.2]paracyclophanes 4 and 8 the methods developed by de Meijere and König were followed.52 Dicyclopropa[b,h]phenanthrene (54) was prepared as outlined in Haley's thesis.86 2,3,5,6-tetramethylidene[2.2.2]bicyclooctane (152) was synthesized according to Vogel et al.85
All reactions that involved metalorganic reagents were carried out under an argon atmosphere in flame-dried glassware. Tetrahydrofuran, benzene and methylene chloride were distilled from calcium hydride under an argon atmosphere. Carbon tetrachloride was distilled from phosphorous pentoxide. The silver tetrafluoroborate used in the polymerization reactions was handled and stored in a dry box under argon. The polymerization reactions were carried out in deuterochloroform that had been distilled twice from phosphorous pentoxide and was stored over molecular sieves. All other chemicals and solvents for column chromatography were of reagent grade quality and used as obtained from the manufactures without further purification. For column chromatography silica gel grade 60 from Spectrum was used. Whatman precoated analytical silica gel plates (silica gel 60 K6F) were used for analytical and small scale preparative thin layer chromatography.

1-Bromo-1-trimethylsilyl-2,2-dichlorocyclopropane (47)

A mixture of PhHgCCl₂Br¹⁶ (52.2 g, 0.12 moles), (1-bromovinyl)-trimethylsilane (46)¹⁵ (20.1 g, 0.11 moles) and 200 ml dry benzene was refluxed for 4 hours while stirring with a magnetic stirrer. A colorless precipitate of phenylmercuricbromide formed as the mixture foamed vigorously. The precipitate was removed by
filtration and the filtrate was then concentrated in vacuo. Vacuum distillation (bp: 65-68°C, 3 Torr) of the residue gave 18.5 g (63%) of the pure product 47.

$^1$H-NMR: $\delta = 0.29$ (s, 9 H), 1.74 (d, 1 H, J=8.5 Hz), 1.94 (d, 1 H, J=8.5 Hz)

1-Bromo-2-chlorocyclopropane (44)$^{15}$

A 50 ml three-necked round bottom flask was charged with tetra $n$-butylammoniumfluoride (7 g, 22 mmoles), topped with a small distillation bridge, rubber septum and glass stopper and equipped with a magnetic stirrer. A 25 ml round bottom flask was then attached to the other end of the distillation bridge. The apparatus was kept under argon. THF (15 ml) was then added via syringe to the tetra $n$-butylammoniumfluoride and the resulting solution was cooled to -40°C (bath temperature). The cyclopropane 47 (3.75 g, 14.3 mmoles) was then added via syringe to this solution followed by a rinse of THF (2 ml). The mixture was now stirred for an hour and the temperature was raised to -25°C. The rubber septum was then quickly exchanged for a glass stopper and the apparatus was gradually evacuated to 0.3 Torr avoiding too vigorous foaming of the mixture. The product 44 and THF were collected in the 25 ml flask that was cooled with liquid nitrogen. After one hour the cooling bath was removed and the 50 ml flask was allowed to warm to room temperature. After another 20 min the vacuum pump was shut off,
the liquid nitrogen bath was removed and the 25 ml flask was
warmed to -78°C (acetone/dry-ice bath). The apparatus was then
vented with argon and the 25 ml flask was quickly removed from the
distillation apparatus and capped with a rubber septum. A
characterization of the instable product 44 was not performed and
the yield was not determined.

Synthesis of heptafulvene (73)\textsuperscript{39} and its characterization as
Dimethyl 3,8a-dihydro-1,2-azulene dicarboxylate (87)\textsuperscript{36,37}

For the preparation of heptafulvene (73) the same apparatus was
used as for the preparation of 1-bromo-2-chlorocyclopropene (44)
(see above) with the only difference that the rubber septum was
exchanged for a 25 ml addition funnel. The 50 ml flask was then
charged with potassium t-butoxide (0.8g, 14 mmol), dry
tetraglyme(5 ml, Aldrich) and equipped with a magnetic stirrer. The
addition funnel was charged with a mixture of endo/exo
chlorobicyclo[5.1.0]-octa-2,4-diene (86a/b)\textsuperscript{40} (1 g, 7 mmoles) in
tetraglyme (5 ml). The apparatus was evacuated to 1 Torr and the 50
ml flask was heated to 90°C (bath temperature). The 25 ml flask was
cooled in a liquid nitrogen bath. The solution of compound 86a/b
was then rapidly added under stirring to the potassium t-butoxide.
As the mixture foamed vigorously a red condensate formed in the 25
ml flask. When no further formation of condensate was observed, the
oil bath was removed. The 25 ml flask was warmed to -78°C, the apparatus was vented with argon and the 50 ml three-necked flask was then exchanged for a 25 ml flask containing THF (10 ml). The THF was then slowly condensed into the 25 ml flask containing the heptafulvene (73). Repeated evacuation of the apparatus and warming the flask with the THF by hand were herefore necessary.. The apparatus was then vented with argon and the flask containing the heptafulvene/THF mixture was quickly removed, capped with a septum and immersed in an acetone/dry-ice bath (-78°C). The yield of the unstable heptafulvene was not determined and no spectra were recorded. However, characterization of the product 73 was performed in the following way. A solution of of DMAD (200mg, 14 mmoles) was added via a syringe and the deep-red solution was slowly warmed to 0°C and placed in the refrigerator (-0°C) overnight. The solvent was then removed in vacuo and the residue was dissolved in diethyl ether (20 ml). This solution was washed with water (3x 20 ml) and dried over anhydrous MgSO₄. After the solvent had been removed in vacuo the residue was purified by preparative TLC on silica gel using ether/hexanes (2 : 8).

The yield of the product 87 was not determined.

¹H-NMR: δ = 3.36 (s, 1H, 8a-H), 3.66 (s, 2H, 3-H), 3.81 (s, 3H, CO₂CH₃), 3.83 (s, 3H, CO₂CH₃), 5.21 (m, 1H, 8-H), 6.12 and 6.52 (m, 4H, 4-H - 7-H).
Attempted reaction of heptafulvene (39) with 1-bromo-2-chlorocyclopropene (44)

Heptafulvene (73) was prepared as described above from potassium t-butoxide (0.8 g, 14 mmol) and compound 86a/b (1 g, 7 mmol). THF (10 ml) was condensed into the trap. The flask with the heptafulvene (73) was then immersed in an acetone/dry-ice bath (-78) and quickly connected to the distillation apparatus used to prepare 1-bromo-2-chlorocyclopropene (44). Compound 44 was then prepared from the cyclopropane 47 (1.3 g, 5.0 mmol) and tetra n-butyl-ammoniumfluoride (2.4 g, 7.5 mmoles) in THF (10 ml) and distilled into the flask containing the heptafulvene solution. The mixture was warmed to -20°C and placed into the freezer overnight at this temperature. The red mixture decolorized completely and turned cloudy. It was then warmed to room temperature. The solvent was removed in vacuo yielding a colorless, solid residue that was not soluble in THF, n-pentane or CHCl₃. This polymeric residue was extracted with CDCl₃ (~2 ml). The ¹H-NMR of this extract gave no evidence for the formation of the desired Diels-Alder addition product 77. This experiment was repeated using solutions of heptafulvene (73), prepared from the same amount of starting materials, in n-pentane (10 ml) and CH₂Cl₂ (10 ml). In both cases no formation of the desired product 77 could be observed by ¹H-NMR spectroscopy.
Dimethyl 3,8a-dihydro-3-methoxy-1,2-azulene dicarboxylate (89)\textsuperscript{33}

A solution of DMAD (745 mg, 5.24 mmol) in dry CH\textsubscript{2}Cl\textsubscript{2} (5 ml) was added via a syringe to a solution of 74\textsuperscript{33} (703 mg, 5.24 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (25 ml) under argon. The mixture was stirred overnight whereby the deep-red solution disappeared. For workup the solvent was removed in vacuo and 100 ml of Et\textsubscript{2}O/n-pentane (1:1) were added to the residue whereby a white precipitate (polymerized fulvene 74) formed. This was removed by filtration and the filtrate was concentrated in vacuo yielding the crude addition product 89. This material was purified by column chromatography on silica gel using Et\textsubscript{2}O/hexanes (1 : 9).

Yield: 430 mg (29\%) colorless crystals.

\textsuperscript{1}H-NMR: $\delta = 3.33$ (s, 3H, OCH\textsubscript{3}), 3.49 (m, 1H, 8a-H), 3.84 (s, 3H, CO\textsubscript{2}CH\textsubscript{3}), 3.87 (s, 3H, CO\textsubscript{2}CH\textsubscript{3}), 5.18 (dd, 1H, 8-H), 5.42 (t, 1H, 3-H), 6.0 - 6.8 (m, 4H, 4-H - 7-H).

Attempted reaction of 8-methoxyheptafulvene (74) with 44

44 was prepared from 47 (1.3 g, 5 mmoles) and tetra n-butyl ammoniumfluoride (1.6 g, 5 mmoles) in THF (5 ml) as described above and distilled into a trap (cooled with liquid N\textsubscript{2}) containing the fulvene 74 (433 mg, 3.23 mmoles) in THF (25 ml). The mixture was then thawed in an acetone/dry-ice bath (-78°C) and warmed to -20°C
and placed in the freezer (-20°C). The red solution decolorized almost completely after one day. For workup the solvent was removed in vacuo yielding a colorless residue that probably consisted of the polymerized fulvene 74. This residue was extracted with CDCl₃ (~2 ml). The ¹H-NMR spectrum of this solution showed no evidence for the formation of the addition product 75. The reaction was repeated with solutions of the same amount of 8-methoxyheptafulvene (74) in n-pentane (25 ml) and CH₂Cl₂ (25 ml). Decolorization of the CH₂Cl₂ solution was complete after only one hour in the freezer at -20°C. When n-pentane was used as solvent the red color persisted for about two days and a colorless precipitate formed. Removal of the solvent in vacuo yielded in both cases colorless residues that were extracted with CDCl₃ (~2 ml). None of the desired addition product 75 could be detected by ¹H-NMR spectroscopy.

1-Bromo[2.2]paracyclophane (100) and 1,1-dibromo[2.2]para-cyclophane (101)⁵³

[2.2]Paracyclophane (92) (5g, 24 mmoles) was dissolved in CCl₄ (600 ml) by heating to reflux. The heater was then removed and the solution was irradiated with a 500 Watt halogen sunlight-lamp. A solution of bromine (4.7g, 29.5 mmoles) in CCl₄ (20 ml) was then slowly added over a period of 30 min. After the addition of the
bromine was completed the mixture was irradiated for another 15 min. The solution was then reduced (in vacuo) to a volume of 50 ml whereby unreacted [2.2]paracyclopahne precipitated. This precipitate was removed by filtration and the filtrate was evaporated to dryness yielding 4.95 g of a brown solid. According to Psiorz\textsuperscript{53} the product obtained in this manner is a mixture of 1-bromo-[2.2]paracyclophane (100), 1,1-dibromo[2.2]paracyclophane (101), higher brominated compounds and unreacted starting material. It was used without further purification for the synthesis of 102 and 103.

[2.2]Paracyclophane-1-ene-1-carbonitrile (102)\textsuperscript{52}

Copper cyanide (6.28g, 70 mmoles) was dissolved in dry N-methylpyrrolidone by heating the mixture to 140ºC. A crude mixture (4.95 g) of 1,1-dibromo[2.2]paracyclophane (100) and 1-bromo[2.2]paracyclophane (100) prepared as described above was then added in small amounts between 140 and 150ºC. After the addition was completed the mixture was stirred at 140ºC for another 4 hrs, cooled to room temperature and poured into 320 ml of 4% NaCN-solution. This precipitate was collected by vacuum filtration, washed with water and dissolved in CHCl₃. The resulting brown solution was dried over anhydrous MgSO₄ and concentrated in vacuo yielding an oily brown residue that was chromatographed on silica
gel using CH₂Cl₂. The product 102 eluted first, giving 271 mg of yellow crystals, followed by the saturated nitrile 103 (243 mg of yellow crystals). A calculation of the %-yield was not possible since the exact composition of the mixture of the bromides 100 and 101 was unknown.

¹H-NMR for 102: δ = 3.12 (s, 4H), 6.53 (AB-q, 4H), 6.58 (AB-q, 4H), 8.09 (s, 1H).

¹H-NMR for 103: δ = 3.14 (m, 4H), 3.38 (dd, 1H), 3.62 (dd, 1H), 4.22 (dd, 1H), 6.56 (m, 7H), 6.93 (dd, 1H).

[2.2]Paracyclophane-1-ene-1-carbaldehyde (104)⁵²

A solution of the nitrile 102 (271 mg, 1.17 mmol) in dry benzene (30 ml) was cooled to 5°C. A solution of 1.5 M DIBAH in toluene (0.9 ml, 1.35 mmol) was then added via a syringe. The mixture was stirred for an additional hour at 5°C and then for two hours at room temperature. The mixture was then hydrolysed with water (20 ml) and acidified with 10 % HCl (~5 drops). The organic layer was separated and the aqueous layer was extracted three times with CH₂Cl₂. The combined organic layers were dried over anhyd. MgSO₄ and the solvent was removed in vacuo. The crude aldehyde obtained in this manner was purified via column chromatography on silica gel using CH₂Cl₂. Yield: 122 mg (43 %), colorless crystals.

¹H-NMR: δ = 3.06 (s, 4H), 6.50 (m, 8H), 8.15 (s, 1H), 9.91 (s, 1H).
1-Vinyl[2.2]paracyclophane-1-ene (3)$^{52}$

Methyltriphenylphosphonium bromide (356 mg, 0.97 mmol) was suspended in dry THF (25 ml). A solution of 2.0 M n-BuLi in hexane (0.5 ml, 1.0 mmol) was then added via a syringe at room temperature. The resulting orange solution was stirred for an additional 2 hrs and then cooled to 10°C. A solution of the aldehyde 104 (122 mg, 0.52 mmol) in THF (5 ml) was then added and the mixture was warmed to room temperature and stirred for an additional hr. The mixture was then poured into a small beaker. Upon contact with air a white precipitate formed that was removed via vacuum filtration using a small glass frit. The precipitate was washed 4x with 10 ml of THF. The filtrate and the combined washings were evaporated to dryness and the residue was chromatographed on silica gel using hexanes.

Yield: 99 mg (82%), colorless powder

$^1$H-NMR: δ = 3.05 (s, 4H), 5.38 (dd, 1H), 5.42 (dd, 1H), 6.48 (AB-q, 4H), 6.50 (AB-q, 4H), 6.83 (dd, 1H), 7.16 (s, 1H).

[2.2]Paracyclophane-1-ene (106)$^{52}$

The crude mixture of 100 and 101 (4.557 g) was dissolved in 40 ml of dry DMSO using a magnetic stirrer and warming to ~40°C. Potassium t-butoxide (11.46 g, 102 mmol) was then added at once.
The mixture became very hot and turned black. After cooling to room temperature saturated aqueous NH$_4$Cl-solution (100ml) was slowly added and the mixture was extracted overnight with toluene (500 ml). The organic layer was separated, dried over anhyd. MgSO$_4$ and the solvent was removed in vacuo. The residue was dissolved in CH$_2$Cl$_2$ and filtered over a short column of neutral aluminum oxide. Evaporation of the solvent yielded light-brown crystals of 106 (2 g) that were used for the next step without further purification.

1,2-Dibromo[2.2]paracyclophane (107)$^{52}$

The crude [2.2]paracyclophane-1-ene (106) (2 g, 10 mmole) was dissolved in CH$_2$Cl$_2$ and a solution of bromine (1.6 g, 10 mmole) in CH$_2$Cl$_2$ (20 ml) was then added until the brown color persisted. The solvent was then removed in vacuo and the brown residue was chromatographed on silica gel using CH$_2$Cl$_2$/hexanes (1:2). After evaporation of the solvent compound 107 was obtained as colorless crystals. Yield: 1.307 g (36 %)

$^1$H-NMR: $\delta = 3.06$ (m, 4H), 5.68 (s, 2H), 6.54 (m, 6H), 7.26 (dd, 2H).
1-Bromo[2.2]paracyclophe-1-ene (108)$^{52}$

Compound 107 (1.307 g, 3.57 mmoles) was suspended in MTBE (30 ml) and potassium $t$-butoxide (512 mg, 4.56 mmoles) was then added. The mixture was stirred at room temperature for 7 hrs. The mixture was then filtered and the filtrate washed with water (10 ml), saturated aqueous NH$_4$Cl-solution (10 ml) and dried over anhyd. MgSO$_4$. Removal of the solvent in vacuo yielded 900 mg (88%) of 108 as colorless crystals.

$^1$H-NMR: $\delta$ = 3.05 (s, 4H), 6.49 (AB-q, 4H), 6.56 (AB-q, 4H), 7.55 (s, 1H).

1,1,2-Tribromo[2.2]paracyclophe (109)$^{52}$

A solution of bromine (600 mg, 3.75 mmoles) in CH$_2$Cl$_2$ (10 ml) was added slowly to a solution of 108 (900 mg, 3.16 mmoles) in 30 ml CH$_2$Cl$_2$. The solvent was removed in vacuo yielding 1.342 g (81 %) of brownish crystals that were used without further purification.

$^1$H-NMR: 2.88 (m, 2H), 3.26 (m, 2H), 5.74 (s, 1H), 7.06 (m, 2H), 7.64 (dd, 1H).
1,2-Dibromo[2.2]paracyclophane-1-ene (110)^{52}

A solution of the bromide 109 (1.342 g, 3.04 mmol) in dry t-butanol (150 ml) was heated to reflux. Potassium t-butoxide (7.43 g, 66.3 mmol) was then added and the mixture was refluxed for 1 hr. After cooling to room temperature, CCl₄ (125 ml) was added and the mixture was washed 3x with water (100 ml). After drying the organic layer with anhyd. MgSO₄ the solvent was removed in vacuo. The residue was chromatographed on silica gel using CH₂Cl₂/hexanes (1 : 3) yielding 985 mg (90 %) colorless crystals. ^{1}H-NMR: 3.06 (s, 4H), 6.58 (AB-q, 8H).

1,2-Dimethyl[2.2]paracyclophane-1-ene (111)^{47}

Copper iodide (927 mg, 4.87 mmol) and the dibromide 110 (985 mg, 2.72 mmol) were suspended in THF (65 ml). The suspension was cooled to -78°C and MeMgBr 3.1 M in Et₂O (5.2 ml, 16.2 mmol) was added via a syringe. The mixture was stirred for an additional 10 min at -78°C and then warmed to room temperature. After stirring for 16 hrs, methanol (2 ml) was added and the black precipitate was removed by vacuum filtration. The filtrate was diluted with CH₂Cl₂ (200 ml) and washed 3x with water (100 ml). The organic layer was dried with anhyd. MgSO₄. After removal of the solvent in vacuo the yellow residue was chromatographed 2x on
silica gel with hexanes yielding 111 as a fine colorless powder (343 mg, 54 %). The material obtained in this way contained about 10 % (by $^1$H-NMR) of the monomethylated product 112 which could not be removed by column chromatography.

$^1$H-NMR: $\delta = 2.22$ (s, 6H), 3.01 (s, 4H), 6.39 (AB-q, 8H).

1,2-Dibromomethyl[2.2]paracyclophane-1-ene (113)$^{47}$

A solution of the phane 111 (125 mg, 0.54 mmoles) in CH$_2$Cl$_2$ (20 ml) was cooled to -15$^\circ$C. 2.8 ml (1.1 mmoles) of a solution of Br$_2$ in CH$_2$Cl$_2$ (1 : 50, v/v) were then slowly added and the mixture was stirred for an additional 30 min at -15$^\circ$C. The mixture was washed with sat. Na$_2$S$_2$O$_3$-sol. (10 ml) and water (10 ml). The organic layer was dried with anhyd. MgSO$_4$ and the solvent was removed in vacuo. Chromatography of the residue on silica gel with hexanes/CHCl$_3$ (2 : 1) gave 105 mg (50 %) of 113 as colorless crystals.

$^1$H-NMR: $\delta = 3.03$ (s, 4H), 4.54 (s, 4H), 6.49 (s, 8H).

Dimethylene[2.2]paracyclophane (4)$^{47}$

A 10 ml flask was charged with a mixture of 113 (105 mg, 0.27 mmoles), activated zinc powder$^{88}$ (40 mg, 61 mmoles) and dry p- dioxane (5 ml). The flask was immersed in an ultrasound bath for 2
hrs and the temp. was kept at 25 - 30° C. Et₂O (5 ml) was then added and the excess of zinc was removed by filtration. The filtrate was washed with sat. NH₄Cl-sol. (10 ml) and water (10 ml). After drying the solvent was removed in vacuo and the residue was chromatographed on silica gel using hexanes. Compound 4 was obtained as colorless, fluffy powder.

Yield: 40 mg (64 %).

¹H-NMR: δ = 3.05 (s, 4H), 5.27 (d, 2H), 5.66 (d, 2H), 6.49 (m, 8H).

1,1,9,9- and 1,1,10,10-Tetrabromo[2.2]paracyclophane (117)⁵²

A solution of bromine (10 ml) in CCl₄ (20 ml) was added to a solution of [2.2]paracyclophane (92) (10 g, 48 mmoles) in CCl₄ (600 ml) while irradiating with a 500 Watt halogen sunlight-lamp. After the addition was completed the irradiation was continued for another hr. The solvent was then removed in vacuo and the residue was stirred with Et₂O (50 ml) for 1 hr. The slurry was filtered and the crude product was washed with cold Et₂O (2 x 10 ml) and dried in vacuo.

Yield: 19.17 g (76 %) brown crystals that were used without further purification for the synthesis of 118 and 121. A spectroscopic characterization of the material was not performed.
1,9- and 1,10-Dicyano[2.2]paracyclophane-1,9-diene (118)\textsuperscript{52}

The mixture of the tetrabromophanes 117 (7.50 g, 14.3 mmoles) was added in small amounts to a stirred solution of copper cyanide (6.40 g, 71.5 mmol) in N-methylpyrrolidone (34 ml). The temp. was hereby kept between 140\textdegree C and 150\textdegree C. The mixture was stirred at 140\textdegree C for an additional hour and then cooled to room temperature and poured into a 5 % NaCN solution (340 ml). The precipitated product was collected by vacuum filtration and dissolved in CHCl\textsubscript{3} (300 ml). After drying over anhyd. MgSO\textsubscript{4} the solvent was removed in vacuo and the brown oily residue was chromatographed on silica gel with CH\textsubscript{2}Cl\textsubscript{2} yielding yellow crystals (681 mg, 19 \%) of 118.

1,9- and 1,10 -Diformyl[2.2]paracyclophane-1,9-diene (119) and (120)\textsuperscript{52}

A solution of 1.5 M DIBAH in toluene (6.5 ml, 9.8 mmoles) was added via syringe to a stirred suspension of 118 (681 mg, 2.68 mmoles) in benzene (70 ml) at 5\textdegree C. After the addition was completed the mixture was warmed to room temperature over 1 hour and was then stirred for 2 additional hrs. The mixture was hydrolysed with water (6 ml) and acidified with several drops of dil. HCl. The organic layer was separated and the aq. layer was extracted 3x with CH\textsubscript{2}Cl\textsubscript{2} (10 ml). The combined organic layers were dried and the solvent was
removed in vacuo. The crude material was chromatographed on silica
gel. Isomer 119 eluted first with CH₂Cl₂ (yellow crystals) followed
by 120 (yellow crystals) that eluted with CH₂Cl₂/5 % MeOH.
Yield: 119 90 mg (12 %), 120 30 mg (4 %)
¹H-NMR of 119: δ = 6.58 (s, 8H), 8.10 (s, 2H), 9.90 (s, 2H).
¹H-NMR of 120: δ = 6.55 (s,4H), 6.61 (s, 4H), 8.10 (s, 2H), 9.90 (s,2H).

1,9-Divinyl[2.2]paracyclophane-1,9-diene (7)

Butyllithium solution (2 M) in hexanes (0.9 ml, 1.8 mmoles) was
added to a suspension of methyltriphenylphosphonium bromide (635
mg, 1.778 mmoles) in dry THF (25 ml). The orange solution was
stirred for another 3 hrs at room temperature. The solution of the
ylide was then added via a double-tipped needle to a stirred
suspension of 119 (11mg, 0.45 mmoles) in THF (20 ml) at 100°C. The
mixture was stirred for another hour at room temperature and the
solvent was removed in vacuo. The residue was dissolved in CH₂Cl₂
and filtered over silica gel. The crude product was then further
purified by column chromatography with hexanes on silica gel. Yield:
57 mg (48%), colorless crystals.
¹H-NMR: δ = 5.40 (m, 4H), 6.51 (m, 8H), 6.79 (dd, 2H, Jₑ₁=10 Hz, Jᵣₑ₂
=17.5 Hz), 7.09 (s, 2H).
1,9- and 1,10-Dibromo[2.2]paracyclophane-1,9-diene (121)\textsuperscript{57}

Potassium \textit{t}-butoxide (9.84 g, 87.7 mmole) was added to a suspension of the tetrabromides 120 (19.17 g, 36.6 mmole) in methyl \textit{t}-butyl ether (288 ml). The mixture was stirred at room temperature for 7 hrs and then filtered. The filtrate was washed with sat. NH\textsubscript{4}Cl-sol. (100 ml), water (100 ml) and the organic layer was dried over anhyd. MgSO\textsubscript{4}. After removal of the solvent in vacuo yellow crystals of the desired product 121 were obtained. These were used for the synthesis of 122 without further purification. Yield: 9.617 g (73 \%) 

1,1,2,9,9,10- and 1,1,2,9,10,10-Hexabromo[2.2]paracyclophane (122)\textsuperscript{4,6}

A solution of 122 (9.617 g, 26.56 mmole) in CHCl\textsubscript{3} (90 ml) was heated to reflux while a solution of bromine (8.50 g, 53.2 mmole) in CHCl\textsubscript{3} (50 ml) was added slowly until the brown color persisted. A colorless precipitate formed that was removed by vacuum filtration. The filtrate was concentrated in vacuo to a volume of 15 ml and hexanes (50 ml) was added. The precipitate that formed was filtered and washed with hexanes. Both fractions were combined, dried in vacuo and used for the preparation of 123.

Yield: 10.68 g (59 \%); \textsuperscript{1}H-NMR: \( \delta = 5.97 \) (s, 2H), 7.03 (m, 8H).
1,2,9,10-Tetabromo[2.2]paracyclophane-1,9-diene (123)\(^{46}\)

Potassium \(t\)-butoxide (3.420 g, 30.48 mmols) was added to a suspension of the bromide 122 (5.478 g, 8.03 mmols) in dry MTBE. The mixture was stirred for 12 hrs at room temperature. After removal of the solvent in vacuo the residue was extracted for 7 days with CHCl\(_3\) in a Soxhlet-apparatus. The yellow crystals of 123 obtained were collected by vacuum filtration and dried in vacuo.

Yield: 2.400 g (58 %)

\(^1\)H-NMR: \(\delta = 6.76\) (s, 8H).

1,2,9,10-Tetramethyl[2.2]paracyclophane-1,9-diene (124)\(^{47}\)

A mixture of copper iodide (1.490 g, 7.82 mmols) and the tetrabromide 123 (1.030 g, 1.98 mmols) was suspended in dry THF (62 ml) and cooled to -78\(^\circ\)C. A 3.1 M solution of MeMgBr in Et\(_2\)O (7.8 ml, 24.18 mmols) was then added with stirring. The suspension was then warmed to room temperature and sonicated for 16 hrs. For workup it was filtered, the filtrate was diluted with CH\(_2\)Cl\(_2\) (200 ml) and washed 3x with water (100 ml). The organic layer was dried with anhyd. MgSO\(_4\). The solvent was removed in vacuo and the yellow residue was chromatographed on silica gel with hexanes yielding fine colorless crystals.

Yield: 187 mg (36 %); \(^1\)H-NMR: \(\delta = 2.22\) (s, 12H), 6.43 (s, 8H).
1,2,9,10-Tetra(bromomethyl)[2.2]paracyclophane-1,9-diene (125)\textsuperscript{47}

14.9 ml (5.9 mmoles) of a solution of bromine in CH\textsubscript{2}Cl\textsubscript{2} (1 : 50, v/v) were slowly added to a solution of 124 (365 mg, 1.40 mmoles) in CH\textsubscript{2}Cl\textsubscript{2} (24 ml) whereby the temp. was kept exactly at -15°C. After the addition was completed a colorless precipitate formed. The mixture was then stirred at -15°C for another 2 hrs and the precipitate was collected by vacuum filtration, washed with hexanes (10 ml) and dried in vacuo. The product obtained in this way was used for the synthesis of 8 without further purification.

Yield: 265 mg (33 %)

\textsuperscript{1}H-NMR: \( \delta = 4.55 \) (s, 8H), 6.64 (s, 8H).

1,2,9,10-Tetramethylene[2.2]paracyclophane (8)\textsuperscript{47}

Compound 125 (265 mg, 0.44 mmoles) was added to a solution of sodium iodide (2.650 g, 17.68 mmoles) in acetone (20 ml). The mixture was sonicated at room temperature for 3 hrs whereby it turned deep brown. The solvent was then removed in vacuo and CH\textsubscript{2}Cl\textsubscript{2} (50 ml) was added to the residue. The insoluble salts were removed by filtration and the filtrate was washed with sat. Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}-sol. (20 ml) and water (20 ml). After drying with anhyd. MgSO\textsubscript{4} the solvent was removed in vacuo and the brown residue was chromatographed on silica gel with hexanes. Compound 8 was
obtained as fluffy colorless powder. The product is air-sensitive, but can be stored under argon in the freezer for several weeks.
Yield: 59 mg (52 %)
$^1$H-NMR: $\delta = 5.40$ (d, $J=1.72$ Hz, 4H), 6.56 (s, 8H), 5.71 (d, $J=1.72$ Hz, 4H).

General procedure for the Diels-Alder addition of the dienes and tetraenes to 1-bromo-2-chlorocyclopropene (44):

A solution of each of the following ones (3, 4, 7, 8) in 1 ml of THF was added via syringe to a stirred solution of 1-bromo-2-chlorocyclopropene (44) (prepared as outlined on page 65 ) in THF at -78°C. The solution was slowly warmed up to -20°C and kept in the freezer at this temperature for two days. The mixture was then warmed up to 0°C and kept in the refrigerator (ca 0°C) for another 2 days. Finally the mixture was immersed in an ice bath and warmed up to room temperature overnight. After removal of the solvent in vacuo the residue was chromatographed on a silica gel column (18 x 1.5 cm) with chloroform/hexanes (1 : 3): Unreacted starting material eluted first followed by the Diels-Alder product. The product was chromatographed again for further purification. Small amounts of product (< 20 mg) were favorably chromatographed on an analytical silica gel plate using the same solvent.
Compound 105: 1-Bromo-2-chlorocyclopropene (44) was prepared from 47 (1.26 g, 4.8 mmoles) and n-Bu₄NF (2.27 g, 7.2 mmoles) in THF (5 ml) and purified by bulb-to-bulb distillation. Reaction of 57 mg (0.25 mmol) 3 with the cyclopropene 44 obtained this way gave 7 mg (9%) of the product 105 as colorless crystals, m.p. 196-200°C.
- IR (KBr): ν = 3050 cm⁻¹, 2950, 2925, 2850, 1620, 1525, 1430, 1110, 980. - ¹H-NMR: δ = 1.70 (d, 2J=7.5 Hz, 1 H, cyclopropane CH₂), 2.30 (d, 2J=7.5 Hz, 1 H, cyclopropane CH₂), 3.03 -3.15 (m, 6 H, -CH₂-CH₂-, allyl CH₂), 4.33 (m, 1 H, CH), 5.78 (m, 1 H, C=CH), 6.35-6.72 (m, 8 H, ArH). - ¹³C-NMR: δ = 24.35 (cyclopropane CH₂), 24.42 (cyclopropane CH₂), 34.80 (-CH₂-CH₂-), 34.83 (-CH₂-CH₂-), 34.97, 37.03, 37.35, 43.83, 45.28, 50.62, 55.25, 56.92, 119.25, 119.45, 131.47, 131.79, 131.81, 131.97, 132.09, 132.46, 132.55, 132.57, 133.62, 133.72, 133.77, 133.79, 134.67, 139.28, 139.33, 139.34, 139.98, 140.12, 140.17, 140.79, 144.32, 144.68. - MS: m/z (%) = 388 (9) [M⁺], 386 (41) [M⁺], 384 (31) [M⁺], 271 (17), 270 (14), 256 (10), 239 (14), 235 (60), 233 (57), 189 (100), 115 (44), 89 (8). - C₂₁H₁₈⁷⁹Br₃⁵Cl: calcd. 384.0280; found 384.0279 (MS).

Compound 114: Cyclopropene 44 was prepared from the cyclopropane 47 (2.10 g, 8.0 mmoles) and n-Bu₄NF (3.78 g, 12.0 mmoles) in THF (10 ml). Reaction of 95 mg (0.41 mmol) 4 with 44 yielded 47 mg (30%) of 114. Colorless crystals, m.p. 185°C. - IR: ν = 3060 cm⁻¹, 3000, 2920, 2840, 1575, 1480, 1425, 1400, 1075, 1025, 930, 800, 725, 625. - ¹H-NMR: δ = 1.65 (d, 2J=7.5 Hz, 1 H, cyclopropane
CH₂), 1.95 (d, ²J=7.5 Hz, 1 H, cyclopropane CH₂), 3.01 (s, 4 H, -CH₂-CH₂-), 3.45-3.67 (m, 4 H, allyl CH₂), 6.22-6.48 (m, 8 H, ArH). - ¹³C-NMR: δ = 25.9 (cyclopropane CH₂), 34.6 (-CH₂-CH₂), 39.6, 38.1, 41.9, 46.1, 130.6, 131.5, 132.2, 132.3, 137.7, 137.9, 139.1, 139.8, 139.9. - MS: m/z (%) = 388 (26) [M⁺], 386 (100) [M⁺], 384 (74) [M⁺], 270 (14), 239 (13), 202 (18), 165 (10), 127 (7), 115 (12), 91 (6), 65 (5). - C₂₁H₁₈Br₃Cl: calcld. 386.0261; found 386.0263 (MS).

Compound 125: The cyclopropene 44 was synthesized from from 47 (1.15 g, 4.4 mmoles) and n-Bu₄NF (2.08 g, 6.7 mmoles) in THF. (5 ml). Reaction with 57 mg (0.22 mmol) 7 yielded 7 mg (8%) 125 as colorless crystals, m.p. 172-173°C. - IR: ν = 3100 cm⁻¹, 3010, 2925, 2875, 2840, 1610, 1590, 1490, 1400, 1060, 1000, 925, 850, 700, 650. - ¹H-NMR: δ = 1.70 (d, ²J=7.5 Hz, 1 H, cyclopropane CH₂), 2.27 (d, ²J=7.5 Hz, 1 H, cyclopropane CH₂), 3.23 (m, 2 H, allyl CH₂), 4.28 (m, 1 H, CH) 5.41 (m, 2 H, H₂C=CH⁻), 5.82 (m, 1 H, C=CH-C=CH₂⁻), 6.31 (m, 3 H, ArH), 6.52-6.67 (m, 4 H, ArH), 6.79 (dd, ³J_{cis}=12.5 Hz, ³J_{trans}=17.5 Hz, 1 H, HC=C=CH=CH₂), 6.88 (m, 1 H, ArH), 7.12 (s, 1 H, HC=C=CH=CH₂) - ¹³C-NMR: δ = 24.29 (cyclopropane CH₂), 24.37 (cyclopropane CH₂), 34.86, 37.02, 37.24, 43.82, 45.26, 50.71, 54.69, 56.34, 118.97, 119.73, 129.22, 129.25, 130.67, 130.69, 131.11, 131.21, 132.75, 132.77, 132.84, 133.82, 133.85, 134.13, 137.18, 137.23, 138.60, 139.37, 139.57, 140.40, 141.00, 143.31, 143.66, 150.84. - MS: m/z (%) = 412 (29) [M⁺], 410 (100) [M⁺], 408 (80) [M⁺], 329 (59), 294 (20), 289 (12), 277 (25), 265 (25), 239 (22), 202 (16), 189 (13),
139 (23), 115 (30). - C\textsubscript{23}H\textsubscript{18}\textsuperscript{81}Br\textsuperscript{35}Cl: calcd. 410.0260; found 410.0260

Compound 126: The cyclopropene 44 was prepared from 47 (1.72 g, 6.6 mmoles) and n-Bu\textsubscript{4}NF (3.13 g, 9.8 mmoles) in THF (5 ml). Reaction of 85 mg (0.33 mmol) 8 with 44 gave 33 mg (24%) of colorless crystals, m.p. 175 \degree C. IR: \nu = 3080 cm\textsuperscript{-1}, 3020, 2900, 2825, 1725, 1655, 1580, 1430, 1405, 1075, 1025, 910, 830, 730, 615. - \textsuperscript{1}H-NMR: \delta = 1.65 (d, \textsuperscript{2}J=7.5 Hz, 1 H), 1.93 (d, \textsuperscript{2}J=7.5 Hz, 1 H, cyclopropane CH\textsubscript{2}), 3.45-3.70 (m, 2 H, allyl CH\textsubscript{2}), 5.32 (d, \textsuperscript{2}J=1.7 Hz, 2 H, C=CH\textsubscript{2}), 5.67 (d, \textsuperscript{2}J=1.7 Hz, 2 H, C=CH\textsubscript{2}), 6.30-6.61 (m, 8 H, ArH). - \textsuperscript{13}C-NMR: \delta = 25.8 (cyclopropane CH\textsubscript{2}), 37.8, 39.2, 41.4, 45.9, 109.9 (C=CH\textsubscript{2}), 130.22, 130.26, 131.0, 132.29, 132.31, 137.2, 137.3, 138.8, 139.0, 140.6, 152.4. - MS: m/z (%) = 412 (29) [M\textsuperscript{+}], 410 (100) [M\textsuperscript{+}], 408 (72) [M\textsuperscript{+}], 375 (5), 373 (5), 329 (28), 278 (22), 252 (12), 189 (10), 165 (18), 139 (16), 115 (11). - C\textsubscript{23}H\textsubscript{18}\textsuperscript{81}Br\textsuperscript{35}Cl: calcd. 410.0260; found: 410.0264 (MS).

General procedure for the preparation of the cyclopropenes 1, 2, 5 and 6.

A solution of each of the following addition products (105, 114, 125, 126) in 1 ml of dry THF was added quickly to a stirred suspension of potassium t-butoxide in 2 ml of THF under an argon
atmosphere at -50°C. The mixture was warmed to -20°C and stirred for an additional hour. The solvent was removed in vacuo and the residue was extracted with several ml of n-pentane. The combined n-pentane-extracts were filtered over a florisil-plug. Removal of the solvent in vacuo yielded the pure products 1, 2, 5 and 6.

Compound 1: Reaction of 11 mg (0.03 mmol) of 22 with 28 mg (0.25 mmol) t-BuOK yielded 4 mg (50%) 4 as fine colorless powder, dec. > 200°C. - IR: \( \nu = 2925 \text{ cm}^{-1} \), 2850, 1740, 1450, 1400, 1260, 825, 730 - UV (hexane): \( \lambda_{\text{max}} (\log \epsilon) = 200 \text{ nm} (4.52), 222 (4.46), 276 (3.27) \) - \(^1\)H-NMR: \( \delta = 3.13 \) (s, 4 H, -CH\(_2\)-CH\(_2\)-), 3.42 (s, 2 H, CH\(_2\)), 6.56 (s, 4 H, p-ArH), 7.28 (d, \( ^3\)J=7.5 Hz, 1 H, o-ArH), 7.49 (d, \( ^3\)J=7.5 Hz, 1 H, o-ArH). - \(^1^3\)C-NMR: \( \delta = 19.7, 34.8, 34.9, 113.3, 121.3, 124.9, 126.8, 132.30, 132.34, 132.49, 132.53, 137.8, 139.3, 139.6, 140.6, 147.5. - MS: m/z (%) = 292 (100) [M\(^+\)], 291 (8), 289 (12), 276 (13), 263 (11), 146 (5) - C\(_{21}\)H\(_{16}\): calcd. 268.1252; found: 268.1250 (MS).

Compound 2: Treatment of 20 mg (0.05 mmol) 114 with 56 mg (0.50 mmol) of t-BuOK gave 9 mg (67%) 2. Fine colorless crystals, dec. > 200°C. - IR: \( \nu = 2940 \text{ cm}^{-1} \), 2850, 1660, 1410, 960, 725, 625. - UV (hexane): \( \lambda_{\text{max}} (\log \epsilon) = 200 \text{ nm} (4.46), 224 (4.33), 280 (3.66) \) - \(^1\)H-NMR: \( \delta = 3.10 \) (s, 4 H, -CH\(_2\)-CH\(_2\)-), 3.42 (s, 2 H, CH\(_2\)), 6.54 (s, 8 H, p-ArH), 7.51 (s, 2 H, o-ArH). - \(^1^3\)C-NMR: \( \delta = 20.1 \) (-CH\(_2\)-), 34.8 (-CH\(_2\)-CH\(_2\)-), 113.5, 124.8, 132.2, 132.8, 139.2, 140.7, 139.2, 140.7, 146.9. - MS: m/z (%) = 268 (100) [M\(^+\)], 267 (9), 265 (9), 253 (7), 252 (21), 239 (7), 126 (5). - C\(_{21}\)H\(_{16}\): calcd. 268.1252; found: 268.1249 (MS).
Compound 5: Reaction of 15 mg (0.04 mmol) 125 with 45 mg (0.4 mmol) t-BuOK yielded 7 mg (61 %) 5 as fluffy, colorless powder, dec. > 170°C. - IR: ν = 2990 cm⁻¹, 2950, 1675, 1600, 1550, 1490, 1440, 1000, 925, 840, 730, 650. - UV (hexane): λ_max (lg ε) = 202 nm (4.45), 220 (4.47), 276 (3.24) - ¹H-NMR: δ = 3.42 (s, 2 H, cyclopropene CH₂), 5.44 (m, 2 H, H₂C=CH⁻), 6.53-6.71 (m, 8 H, p-ArH), 6.82 (dd, 3J_cis=10 Hz, 3J_trans=17 Hz, 1 H, H=CH=CH=CH₂), 7.15 (s, 1 H, H=CH=CH=CH₂), 7.30 (d, 3J=7.5 Hz, 1 H, o-ArH), 7.51 (d, 3J=7.5 Hz, 1 H, o-ArH). - ¹³C-NMR: δ = 19.7 (-CH₂⁻), 113.4, 118.8, 121.3, 125.0, 126.6, 130.5, 131.0, 131.65, 131.67, 131.8, 134.2, 137.4, 137.7, 139.0, 140.3, 146.5, 150.6. - MS: m/z (%) = 292 (100) [M⁺], 289 (24), 276 (23), 263 (17), 138 (8), 132 (7). - C₂₃H₁₆: calcd. 292.1252; found: 292.1250 (MS).

Compound 6: Dehydrohalogenation of 24 mg (0.06 mmol) 126 with 67 mg (0.60 mmol) t-BuOK gave 10 mg (57 %) 6 as fine, colorless powder, dec. > 150°C. - IR: ν = 2950 cm⁻¹, 2850, 1660, 1590, 1500, 1450, 905, 840, 740, 625 - UV (hexane): λ_max (lg ε) = 202 nm (4.58), 226 (4.31), 280 (3.85) - ¹H-NMR: δ = 3.42 (s, 2 H, cyclopropene CH₂), 5.39 (d, 2J=1.5 Hz, 2 H, C=CH₂), 5.72 (d, 2J=1.5 Hz, 2 H, C=CH₂), 6.63 (m, 8 H, p-ArH), 7.55 (s, 2 H, o-ArH). ¹³C-NMR: δ = 19.9 (-CH₂⁻), 109.8, 113.5, 125.0, 132.27, 132.27, 139.6, 140.6, 145.9, 152.8. - MS: m/z (%) = 292 (100) [M⁺], 289 (13), 276 (13), 263 (11), 146 (5). - C₂₃H₁₆: calcd. 292.1252; found: 292.1251 (MS).
Synthesis of the Diels-Alder adduct 153

44 was prepared from 47 (3.75 g, 14.3 mmol) and n-Bu₄NF (7.50 g, 23.8 mmol) in THF (10 ml) and purified by bulb-to-bulb distillation as described above. A solution of the tetraene 152 (226 mg, 1.43 mmol) in THF (2 ml) was then added via syringe and the mixture was warmed up to -20°C followed by the addition of BF₃·Et₂O (0.1 ml). The mixture was stored for 8 days in the freezer at -20°C. For workup the solvent was removed in vacuo and the residue was purified on silica gel with CHCl₃/hexanes (3:1) giving 153 as colorless crystals.
Yield: 428 mg (64 %)
¹H-NMR: δ = 1.10-1.45 (m, 8 H), 2.80-3.15 (m, 10 H)

Dicyclopropyrene 1084

A solution of 153 (228 mg, 0.49 mmol) in dry THF (5 ml) was added to a stirred solution of potassium t-butoxide (570 mg, 5.08 mmol) in THF (8 ml) at -50°C. The solution was warmed to -20°C and stirred at this temp. for 90 min. After removal of the solvent in vacuo the residue was extracted with pentane (5 x 5 ml) and the combined extracts were filtered over a layer of florisil (2 cm). The filtrate was evaporated to dryness in vacuo giving the product 10 as white, fluffy powder.
Yield: 95 mg (84 %).

$^1$H-NMR: δ = 1.75 (s, 4H), 3.15 (d, 2H, J=7.4 Hz), 3.30 (d, 2H, J=7.4 Hz), 4.49 (s, 2H), 7.21 (s, 4H).

General procedure for the synthesis of the polymers 11 and 12

A solution of the dicyclopentadiene 9 (10) in dry CDCl$_3$ (4 ml) was added to a catalytic amount of dry AgBF$_4$ under an Argon atmosphere. Formation of the polymer was visible after three hrs (12) and 12 hrs. (11). The polymerization was completed after 8 hrs (12) and 4 days (11). The polymers were collected by vacuum filtration, washed with CHCl$_3$ and dried in vacuo. The polymer flakes were ground to fine brown-yellow powders that were used for characterization.

Yield: 35 mg 9 gave 34 mg (97 %) polymer 11.

40 mg 10 gave 35 mg (88 %) polymer 12.

IR-spectra:

11: ν = 3025 cm$^{-1}$, 2925, 2850, 1690, 1620, 1500, 1425, 1075, 890, 840.

12: ν = 3000 cm$^{-1}$, 2940, 2860, 1700, 1470, 1140, 920.
Preparation of the dimers 150 and 151.

A solution of the dicyclopentene 9 (10) in dry CDCl₃ (4 ml) was added to a catalytic amount of dry AgBF₄ under an argon atmosphere. The formation of the dimers 150 and 151 was monitored by ¹H-NMR-spectroscopy. When the maximum concentrations of the dimers had built up (~ 2.5 - 3 hrs for 151, ~28 hrs for 150) the catalyst and polymeric material were removed by filtration over florisil. Dimer 151 was then separated from the monomer 10 by preparative TLC on a deactivated³¹ silica gel plate with CHCl₃/hexanes (1 : 3). Dimer 151 was obtained as third zone after the monomer and an unidentified impurity. Dimer 150 was isolated by chromatography on a small florisil column (6 x 0.4 cm). The monomer 9 eluted first with n-pentane, the product 150 was next using CHCl₃ as eluting solvent.

Yield:  
50 mg 10 gave 4 mg (4 %) of dimer 151.

The yield of 150 was not determined. The product is very sensitive and best stored in solution.

¹H-NMR: 151: δ = 1.68 (s, 8 H, -CH₂-CH₂-), 3.11 (d, 2H, J = 2.5 Hz, cyclopropyl CH₂), 3.23 ( d, 2 H, J = 2.5 Hz, cyclopropyl CH₂ ), 3.80 (s, 4H, -CH₂-), 4.34(s, 4H, tert.-H), 7.16 (m, 8 H, ArH).

150: δ = 3.59 (s), 4.33 (s), 4.41 (s), 4.49 (s), 7.76-7.81 (m), 7.88 (d), 8.57 (s), 8.77 (d).
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88. 12g commercial zinc dust (Aldrich) were successively treated with 2 % HCl (30 ml), water (3 x 30 ml), anhydrous ethanol (2 x 30 ml) and anhydrous ether (30 ml) and dried in vacuo.
89. The silica gel plates were deactivated by dipping them into a solution of triethylamine (0.5 ml) in n-pentane (50 ml) and drying them on air.
Spectra

Figure 1: $^1H$-NMR of the Diels-Alder adduct 105

Figure 2: $^{13}C$-NMR of the Diels-Alder adduct 105
Figure 3: *IR of the Diels-Alder adduct 105*

![IR spectrum of Diels-Alder adduct](image)

Figure 4: *EIMS of The Diels-Alder adduct 105*

![EIMS spectrum of Diels-Alder adduct](image)
Figure 5: $^1$H-NMR of the Diels-Alder adduct 114

Figure 6: $^{13}$C-NMR of the Diels-Alder adduct 114
Figure 7: IR of the Diels-Alder adduct

Figure 8: EIMS of The Diels-Alder adduct
Figure 9: $^{1}H$-NMR of the monoadduct 125

Figure 10: $^{13}C$-NMR of the monoadduct 125
Figure 11: IR of the monoadduct 125

Figure 12: EIMS of the monoadduct 125
Figure 13: $^1$H-NMR of the monoadduct 126

Figure 14: $^{13}$C-NMR of the monoadduct 126
Figure 15:  IR of the monoadduct 126

Figure 16:  EIMS of the monoadduct 126
Figure 17: $^1$H-NMR of the cycloproparene 1

![Image of $^1$H-NMR spectrum]

Figure 18: $^{13}$C-NMR of the cycloproparene 1

![Image of $^{13}$C-NMR spectrum]
Figure 19: IR of the cyclopropene 1

Figure 20: EIMS of the cyclopropene 1
Figure 21: $^1$H-NMR of the cyclopropene 2

Figure 22: $^{13}$C-NMR of the cyclopropene 2
Figure 23:  **IR of the cyclopropene 2**

Figure 24:  **EIMS of the cyclopropene 2**
Figure 25: $^1$H-NMR of the cyclopropene 5

Figure 26: $^{13}$C-NMR of the cyclopropene 5
Figure 27: IR of the cyclopropene 5

Figure 28: EIMS of the cyclopropene 5
Figure 29: $^1$H-NMR of the cyclopropene 6

Figure 30: $^{13}$C-NMR of the cyclopropene 6
Figure 31: IR of the cyclopropene 6

Figure 32: EIMS of the cyclopropene 6
Figure 33: $^1$H-NMR of the dimer 150

Figure 34: CIMS of the dimer 150
Figure 35: $^1$H-NMR of the dimer 151

Figure 36: FABMS of the dimer 151
Figure 37: $SS^{13}C$-NMR (CP/TOSS) of polymer 11

Figure 38: IR of polymer 11
Figure 39:  IR of polymer 12

Figure 40:  TGA of polymer 11
Figure 41: TGA of polymer 12