89. Synthetic Attempts towards Polymers with Pentafulvene Structural Units[1])

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Synthetic attempts towards fully conjugated polymers **9** with pentafulvene-diyl structural units are described. Cationic polymerization of pentafulvenes **1a** (R = X = Me) and **1b** (R = X = MeS) nearly quantitatively gives polymers **8a** and **8b** with typical M_n and M_w values of 38800 and 53750, respectively, for **8a**, and 12000 and 35900, respectively, for **8b**. Key step of the conversion **8a** → **9a** (*Scheme 6*) is a quantitative bromination **8a** → **32a**, the structure of **32a** being confirmed by analytical data as well as by spectroscopic comparison with model compound **23**. Best results in view of two-fold the HBr elimination **32a** → **9a** are obtained with Et_3N, but so far elimination has not been complete. Synthetic sequences are optimized with model compound **21** (*Scheme 4*). Here again, bromination **21** → **23** is quantitative, while two-fold HBr elimination **23** → **22** with Et_3N proceeds in 51% yield. Dibromide **23** easily undergoes HBr elimination followed by a Br shift to give bromide **29**. Contrary to cationic polymerization, anionic polymerization of simple pentafulvenes **1** to **2** (which would be attractive in view of the conjugated polymers **3**) is not successful: For pentafulvene **1b** (R = X = MeS), the main reaction is *Diels-Alder*-type dimerization **1b** → **15b** (*Scheme 2*), even under anionic conditions.

1. Introduction.

– Pentafulvenes (= 5-methylidenecyclopenta-1,3-dienes) **1** are cyclic cross-conjugated molecules with a five-membered ring whose electronic properties are strongly varying with exocyclic substituents [4–6] influencing the extent of π-delocalization as well as the HOMO-LUMO gap. If these substituent effects would be operative in polymers containing pentafulvene-diyl structural units as well, then polymers with considerably varying electronic properties could in principle be available. In fact, semiempirical calculations [7] predict that some types of long-chain polyenes with fulvene-diyl or fulvalene-diyl structural units should be characterized by a relatively small energy difference between the HOMO and the LUMO. Therefore, they are very attractive in view of polymers with unique electrical and optical properties. Furthermore, polymers of this type or their dihydro precursors (see *Scheme 1*) should be of interest in view of the synthesis of 'nonclassical non-alternant polymers' [8].

Some synthetic pathways to polymers with pentafulvene- and pentafulvalene-(5-(cyclopenta-2,4-dien-1-ylidene)cyclopenta-1,3-diene)-derived structural units are summarized in *Scheme 1*. Considering the fact that pentafulvenes **1** are easily attacked by nucleophiles at C(6) to give substituted cyclopentadienides and, after protonation, substituted cyclopentadienes (for examples, see [9–11]), anionic polymerization of pentafulvenes **1** to **2** followed by HX elimination (→ **3**; *Route A*) should be an attractive procedure. On the other hand, intramolecular oxidative coupling of bi(cyclopentadienyl)diide **4** [12] [13]

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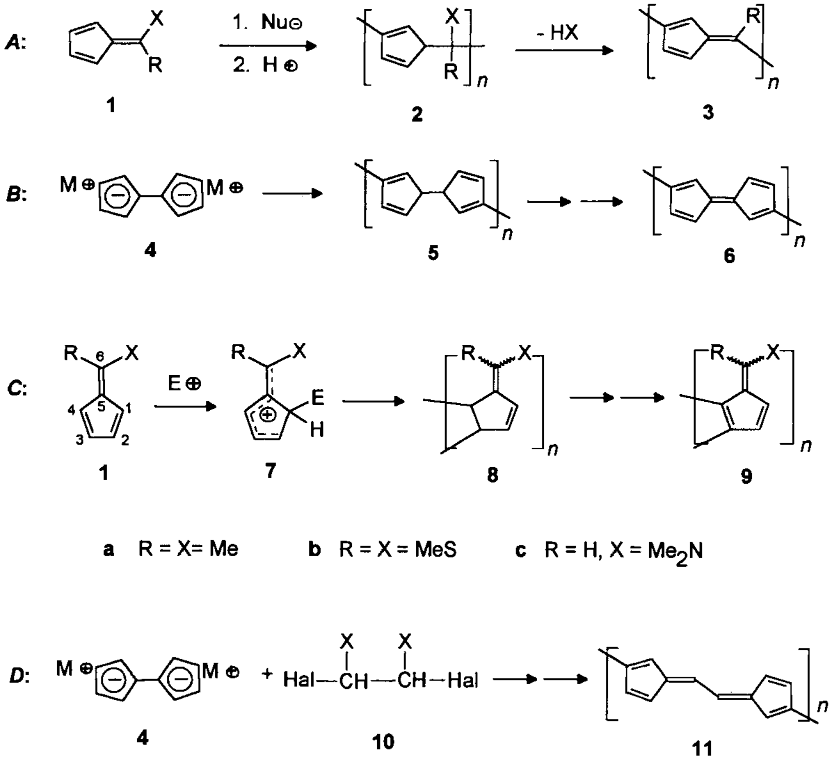
[1]) Fulvenes and Fulvalenes, Part 69; Part 68: [1]; short communication: [2].

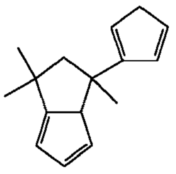
[2]) Part of the dissertation [3].

Scheme 1. *Pathways to Polymers with Pentafulvene-diyl and Pentafulvalene-diyl Structural Units*



should give polymers **5** with dihydrofulvalene-diyl structural units, which, by two-fold deprotonation and subsequent oxidative treatment, could possibly be transformed into polymers **6** with pentafulvalene-diyl structural units (*Route B*). Furthermore, taking into account that pentafulvenes are easily attacked at C(1)/C(4) to give delocalized pentadienyl cations **7** according to MNDO calculations [14], cationic polymerization of **1** (→**8**) could be possible, and subsequent dehydrogenation would lead to polymers **9** (*Route C*). Finally, polymers of type **11** could in principle be formed by a substitution-elimination sequence between dianion **4** and an appropriately functionalized 1,2-dichloro- or 1,2-dibromoethane **10** (*Route D*).

So far, polymers with fulvene-diyl of fulvalene-diyl structural elements are unknown, but attempts towards polymers of type **2**, **5**, and **8** were made. In fact, anionic polymerization of 6,6-dimethylpentafulvene (**1a**; *Route A*) was already attempted 15 years ago [15]. Quite surprisingly, even relatively weak bases like cyclopentadienide induced deprotonation of **1a**, and the main reaction product of the complex sequence was 3-(cyclopenta-1,4-diene)-1,2,3,3a-tetrahydro-1,1,3-trimethylpentalene (**12**) [15]. The conclusion is that proton-bearing substituents at C(6) of pentafulvenes **1** have to be avoided. Intermolecular oxidative coupling of bi(cyclopentadienyl)diide **4** (*Route B*) failed as well, since treatment of **4** with I_2, $CuCl_2$, or other oxidants mainly yielded reactive pentafulvalene (**13**) even at high concentrations of **4** [12] [13]. If the cyclopentadienide moieties of **4** were separated by two or more CH_2 units, then polymers of type **14** were in fact produced in high yields [16]. *Route C* seems to be an attractive pathway to fully conjugated polymers **9**, since cationic polymerization of 6,6-dimethylpentafulvene (**1a**) gave high-molecular-weight polymers **8a** in a nearly quantitative yield [17] whose structure were spectroscopically proved [18]. Attempts to transform **8** to fully conjugated polymers **9** are unknown so far. *Route D* is clearly the most problematic of the four pathways shown in *Scheme 1*, although polyfunctional ethanes of type **10** with two pairs of different nucleofugicity are known and were even used in reactions with cyclopentadienide to give pentafulvenes [19] [20]. The main problem is that HX elimination from **10** started before two-fold substitution of the halogen atoms was completed. Even if cyclopentadienide was reacted with bromomethyl acetates or chloromethyl acetates, best yields of pentafulvenes were only *ca.* 65% [21], and in reactions of tetrasubstituted ethanes **10** with cyclopentadienide, yields of 6,6′-bi(pentafulvenes) were much smaller [19] [20]. These facts definitely exclude *Route D* as a versatile method for the synthesis of conjugated polymers of type **11**.



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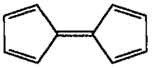

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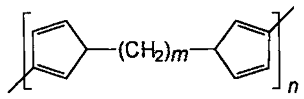

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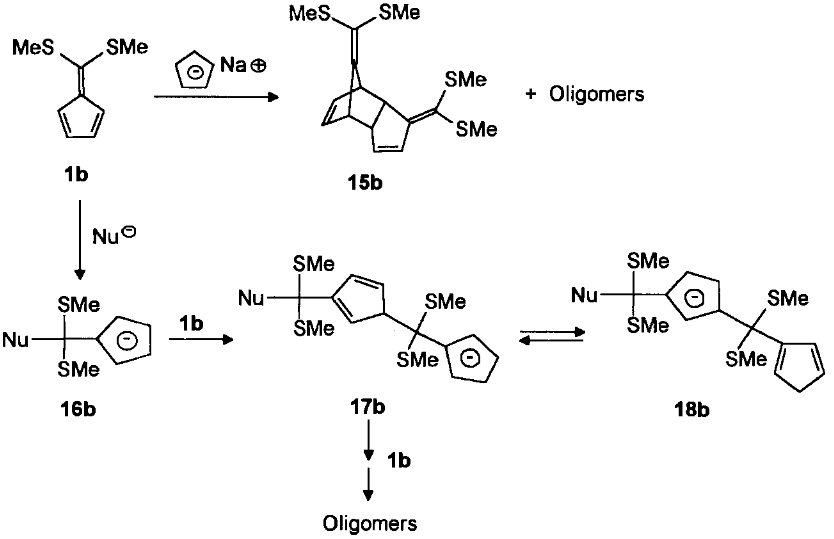
Thus, according to the literature results, *Route C* seems to be the only promising access to polymers with fully conjugated pentafulvene-diyl units, while *Route A* still has to be explored for non-acidic substituents R.

2. Attempted Anionic Polymerization of 1b and 1c. – In principle, 6,6-bis(methylthio)pentafulvene (**1b**) should be a good candidate in view of an anionic polymerization to **2b** (*Scheme 1, Route A*): contrary to 6,6-dimethylpentafulvene (**1a**), the Me groups of **1b** are no more acidic enough to be deprotonated in the presence of cyclopentadienide. Furthermore, electronic stabilization of the fulvene π-system by MeS groups is only moderate so that the reactivity of **1b** towards nucleophiles is expected to be quite close to that of **1a**. Various experiments showed, however, that **1b** reacted under anionic conditions (in the presence of 1.5 mol-% of cyclopentadienide) to give the *Diels-Alder* product **15** besides small amounts of low-molecular-weight oligomers, possibly of structure **2b** (*Scheme 2*). This result obviously means that dimerization **1b** → **15b** is faster than nucleophilic addition **1b** → **16b** and propagation **16b** → **17b**. Furthermore, in rare cases where nucleophilic addition works and propagation is possible, the active chain end may be easily protonated by H^+ transfer (**17b** → **18b**) due to the similar acidity of the different cyclopentadiene unit.

Similar experiments with electronically stabilized 6-(dimethylamino)pentafulvene (**1c**) failed under various conditions. Even after reacting **1c** in THF with 1.5 mol-% of cyclopentadienide at 30° for 5 days, **1c** was the only compound detected by NMR spectroscopy.

These results clearly show that anionic polymerization of pentafulvenes is not suited for the synthesis of high-molecular-weight polymers of type **2**.

Scheme 2



3. Cationic Polymerization of Pentafulvenes 1a–1c. – We observed that, in agreement with earlier findings [17], 6,6-dimethylpentafulvene (**1a**) easily reacted with various acids and *Lewis* acids to give, after precipitation with MeOH and drying under high vacuum, white polymer powders in nearly quantitative yield. Thus, polymerization of 0.5 ml of **1a** by means of 0.5 mol-% of CCl_3COOH in 10 ml of CH_2Cl_2 at 0° gave soluble (but O_2-sensitive) polymer **8a** with M_n 38800 and M_w 53750 and the spectral data typical for structure **8a** [17] [18].

Cationic polymerization of 6,6-bis(methylthio)pentafulvene (**1b**) was very slow under similar conditions with CCl_3COOH, but fast enough with 1 mol-% of $SnCl_4$ in 10 vol-% CH_2Cl_2 solution at 0°. After precipitation with MeOH and drying, a slightly yellowish polymer powder was isolated in nearly quantitative yield which was soluble in usual organic solvents but underwent easily cross-linking in the presence of O_2. GPC Measurements showed a molecular-weight distribution similar to that of **8a**, but with smaller M_n and M_w (12600 and 35900, resp.). All the spectroscopic data (briefly discussed in [2]) are consistent with structure **8b**[3]). Thus, pentafulvenes with weakly electron-donating substituents like **1b** are easily polymerized in the presence of *Lewis* acids like $SnCl_4$, but acids like CCl_3COOH are no more active enough to ensure a fast polymerization (*cf.* **1a** → **8a** [18]).

According to *Table 1*, polymerization of pentafulvenes like **1c** with strong electron-donating groups fails even in the presence of strong *Lewis* acids, although one would expect [4–6] that the ease of attack of electrophiles increases within the series **1a** < **1b** < **1c**. One major reason for the failure of **1c** to polymerize to **8c** is the energy of the pentadienyl cation **7** resulting from electrophilic attack at pentafulvenes **1** (see above,

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[3]) For reproductions of the complete set of spectra of all the isolated compounds and tables of spectroscopic data, see [3].

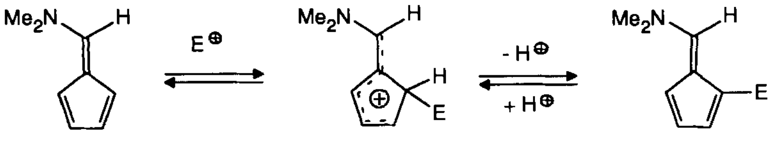
Table 1. *Cationic Polymerization of Pentafulvenes* **1a–1c** *with $SnCl_4$ in CH_2Cl_2 at 0°*

	c_M[a]) [vol.-%]	c_I[b]) [mol-%]	t[c]) [min]	η_{red}[d]) [ml/g]	Yield [%] of polymer **8** after precipitation
1a	2.5	1	10	42	98.5
1b	10	1	60	18.6	97
1c	10	1	60	0	–

[a]) Concentration of monomer **1**. [b]) Concentration of initiator ($SnCl_4$) relative to monomer **1**. [c]) Reaction time. [d]) Reduced viscosity.

Scheme 1). MNDO Calculations [14] show that the energy of the cation decreases in the series **7a** > **7b** > **7c**. Thus, highly delocalized pentadienyl cation **7c** has a comparably long lifetime and is prone to proton-transfer reactions of type **7c** → **19c** (which are facilitated by the basic Me_2N groups) and which can easily restore the fulvene structure according to *Scheme 3*. In fact, pentafulvenes with amino groups at C(6) easily undergo electrophilic substitution instead of addition reactions [22].

Scheme 3



1c **7c** **19c**

4. Bromination/Elimination Experiments with a Model Compound. – Low-molecular-weight model compounds are ideal for optimizing sequences to be applied to polymer synthesis (so-called 'polymer-analogous reactions') as well as for spectroscopic structure elucidation of polymers. We already selected 5-isopropylidenetricyclo[5.2.1.$0^{2,6}$]dec-3-ene (**21**) as a model compound for the structure elucidation of cationic poly(6,6-dimethylpentafulvene) (**8a**) by spectroscopic methods [23]. Tricyclodecene **21** was quite easily available by [4 + 2]cycloaddition between cyclopentadiene and **1a** (→**20**) [24], followed by selective hydrogenation of the strained C=C bond of **20** (*Scheme 4*). Of course, model compound **21** is also ideal for optimizing the sequence **21** → **22**, analogous to the conversion **8a** →→ **9a** (*Scheme 1, Route C*).

The most straightforward access to strained pentafulvene **22** seems to be a bromination/dehydrobromination sequence (*Scheme 4*). Direct bromination of **21** is expected to give a dibromide, possibly **23**, which should be convertible to **22** by two-fold HBr elimination. In fact, direct bromination of **21** with Br_2 in CCl_4 proceeded easily and quantitatively to give crystalline dibromide **23** which was quite unstable (loss of HBr, see below). The structure of **23** convincingly follows from spectroscopic data, especially from the ^{13}C- and ^{1}H-NMR spectra. A reasonable mechanism for this formal 1,4 addition **21** → **23** involves allylic cation **24** (*Scheme 4*[4])). It is interesting to note that diene **21** reacted exactly in the

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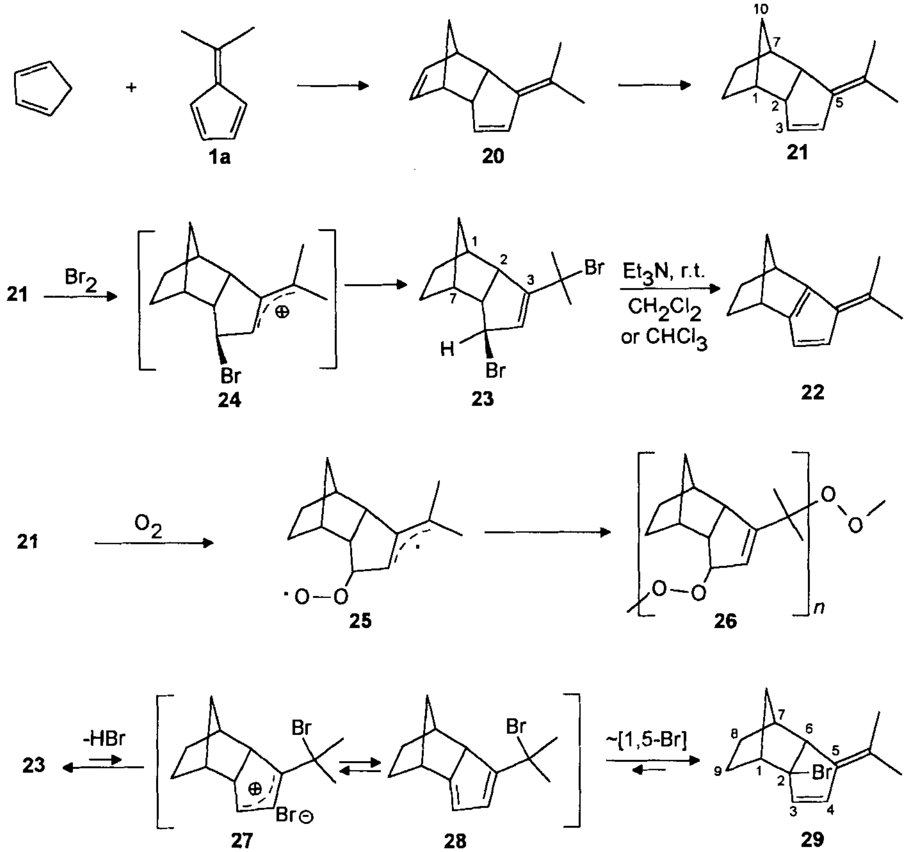
[4]) An alternative mechanism, which starts by an initial attack of $Br^{\oplus}$ at the exocyclic olefinic C-atom of **21** to give a cyclic allylic cation (see **27**), seems to be sterically less favorable but cannot be excluded.

Scheme 4



same way with O_2 – in this case, however, according to a radical-chain mechanism *via* diradical **25** – to give oligomers of type **26** [23].

In view of the planned conversion of dibromide **23** to the target compound **22**, we tested several bases like *t*-BuOK, DBU, and $AgBF_4/Et_3N$, but they did non produce the desired pentafulvene **22** in high yield. Quite surprisingly, the best yield of **22** (51%) was obtained by reacting **23** with an excess of Et_3N in CH_2Cl_2 or $CHCl_3$ at room temperature (*Scheme 4*).

All the analytical and spectroscopic data[3]), especially the ^{13}C- and ^{1}H-NMR data, are in agreement with structures **22** and **23**. In the ^{1}H-NMR spectrum of **23** (*Fig. 1*; assignment is confirmed by both selective decoupling experiments and 1D and 2D pulse sequences) vinylic H–C(4) produces a relatively broad signal at 5.90 ppm, while allylic H–C(3) at 5.06 ppm splits into a narrow *q*, because *J*(2,3), *J*(3,4), and *J*(3,6) are small and of about equal size (2.2 Hz). The small value of *J*(2,3) immediately places Br–C(3) in *exo*-position[5]). The broad *m*'s at 3.55 and

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[5]) For structurally similar 'dicyclopentadiene', bearing additional protons at C(3) and C(5) instead of the substituents of **23**, coupling constants (with the numbering of **23**, see *Fig. 1*), are: *J*(2,3*exo*) = 10.20 Hz and *J*(2,3*endo*) = 4.23 Hz [25]. Going from 'dicyclopentadiene' to **23** and its *endo*-isomer, both *J* values are expected to be somewhat reduced due to the electronegativity of Br–C(3). This means that *J*(2,3) = 2.2 Hz of **23** establishes the *exo*-position of Br–C(3) in **23**!

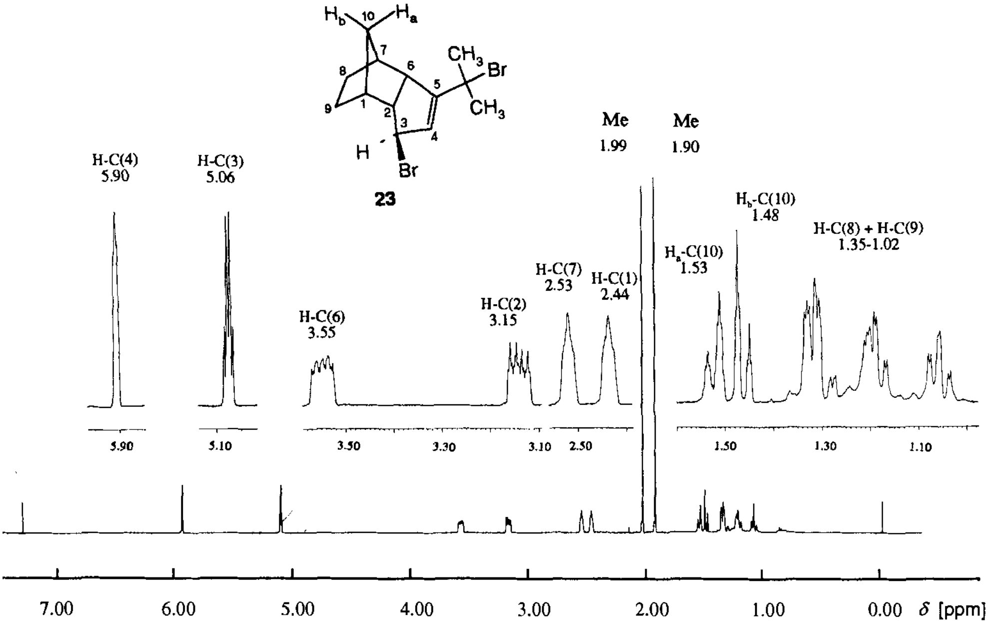


Fig. 1. *^{1}H-NMR Spectrum* (400 MHz, $CDCl_3$, −20°) *of dibromide* **23**[3])

3.15 ppm are easily assigned to H–C(6) and H–C(2), respectively; the main splittings of both signals result from $J(2,6) = 9.4$ Hz as well as from $J(6,7) = 5.0$ and $J(1,2) = 5.0$ Hz. Both *m*'s are complicated by further small couplings. H–C(7) and H–C(1) produce broad signals at 2.53 and 2.44 ppm, respectively, which are assigned by selective decoupling experiments [3]. As expected, the *AB* system of the $CH_2(10)$ bridge at 1.53 and 1.48 ppm is additionally split by small vicinal couplings with H–C(1) and H–C(7). Furthermore, H_a–C(10) shows long-range couplings with the axial protons at C(9) and C(8). The splitting pattern of $CH_2(9)$ and $CH_2(8)$, absorbing between 1.4 and 1.0 ppm, is very complex and cannot be analyzed. Finally, the signals of the exocyclic Me groups appear as narrow *s*'s at 1.99 and 1.90 ppm. The ^{1}H-NMR assignments of **23** are confirmed by a series of selective decoupling experiments. Thus, on irradiating H–C(3) at 5.06 ppm, the small vicinal coupling $J(2,3)$ and $J(3,4)$ as well as the small homoallylic coupling $J(3,6)$ disappear so that the signal of H–C(4) at 5.90 ppm narrows, while the signals of H–C(6) at 3.55 ppm as well as of H–C(2) at 3.15 ppm are simplified to *dd*'s. Irradiation of H–C(6) sharpens the signal of H–C(4) at 5.90 ppm, strongly affects H–C(2) at 3.15 ppm and allows the assignment of H–C(7) to the signal at 2.53 ppm. Similar effects are observed by irradiation of H–C(2), so that H–C(1) can be unambiguously assigned to the signal at 2.44 ppm.

In the HR-MS of **22**, the molecular ion supports the formula $C_{13}H_{16}$. In the UV (hexane), the intense absorption at 266 nm (ε 21730) as well as the weak and broad absorption at 350 nm (ε 440) are very typical for pentafulvenes [4–6]. The ^{1}H-NMR spectrum of **22** (*Fig. 2*; assignments confirmed by both selective decouplings, and 1D and 2D experiments) displays the *AB* system of the two vinylic protons with a typical $J(3,4) = 5.2$ Hz at 6.35 and 6.30 ppm. Compared with the spectrum of dibromide **23** (*Fig. 1*), the complex *m*'s of H–C(2) and H–C(6) are missing, and the signals of the bridgehead protons H–C(1) and H–C(7) are shifted towards higher frequencies by 0.7 and 0.9 ppm due to the adjacent C=C bond. Otherwise, besides the fact that the splitting pattern of $CH_2(9)$ and $CH_2(8)$ is approaching that of *AA'XX'YZ* spectrum (because pairs of protons are nearly equivalent), all the features of the alkyl range of the spectrum of **22** are very similar to those of dibromide **23**.

As mentioned above, dibromide **23** very easily rearranged in $CDCl_3$ or CH_2Cl_2 solution by simultaneous elimination of 1 equiv. of HBr to give impure allylic bromide **29** in *ca.* 60% yield, presumably *via* acid-catalyzed elimination of bromide (→ **27**) followed by deprotonation (→ **28**) and final [1,5-Br] shift (*Scheme 4*). The structure of **29** easily

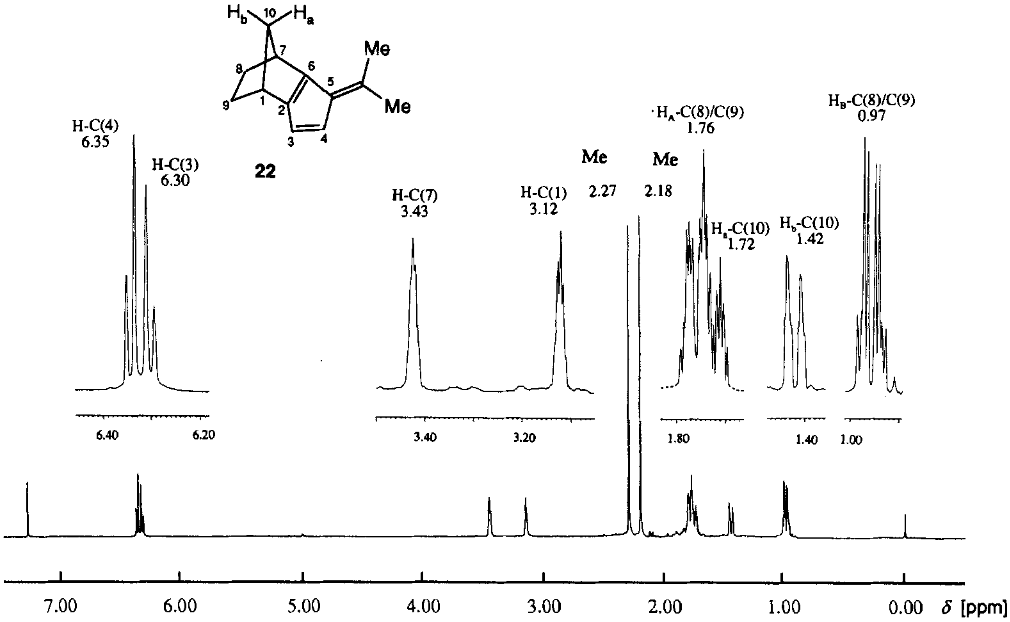
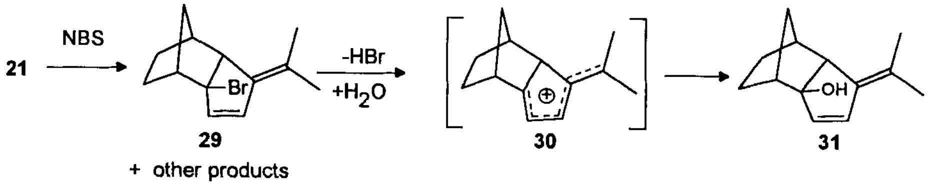


Fig. 2. *^{1}H-NMR Spectrum* (300 MHz, $CDCl_3$) *of* **22**3)

follows from the analytical and spectroscopic data3). In the 300-MHz ^{1}H-NMR spectrum of **29** the most remarkable feature besides the Me *s*'s at 1.84 and 1.72 ppm is the clean *AB* system of vinylic protons H–C(4) at 6.35 and H–C(3) at 6.03 ppm with the characteristic *J*(3,4) of 5.52 Hz.

Allylic *N*-bromosuccinimide (NBS) bromination of tricyclic diene **21** was supposed to give a bromide, possibly **29**, which could in principle be transformed to **22** (see above) as well. However, refluxing **21** with NBS in CCl_4 under N_2 gave a very complex mixture which, according to the analytical GC, showed three main products (16, 27, and 21%) besides some starting material (6.5%). After chromatography (silica gel), crystalline **31** was isolated in 12% yield, most likely formed from **29** *via* **30** (*Scheme 5*). Thus, allylic bromination of **21** is not suited for a high-yield conversion to **29**. The structure of **31** is established by analytical and spectroscopic data.

Scheme 5



In the MS of **31**, the M^+ at *m/z* 190 is consistent with the absence of a Br-atom in the structure. The main fragments are $[M-15]^+$, $[M-15-18]^+$, and $[M-15-18-15]^+$. The ^{1}H-NMR spectrum of **31** (*Fig. 3*) is very similar to that of **29**, besides different chemical shifts for H–C(6) and H–C(1) adjacent to the OH group. Very typical for the diene moiety of **31** are the Me groups at 1.79 and 1.70 ppm as well as the clean *AB* system of H–C(4) at 6.36 and H–C(3) at 5.75 ppm, with $J(3,4) = 5.60$ Hz. As expected, the signal of H–C(3) is somewhat broadened by small long-range couplings with the Me groups. Further characteristic features are the typical splitting patterns of the signals of H–C(6), H–C(7), H–C(1), and $CH_2(10)$ (*Fig. 3*).

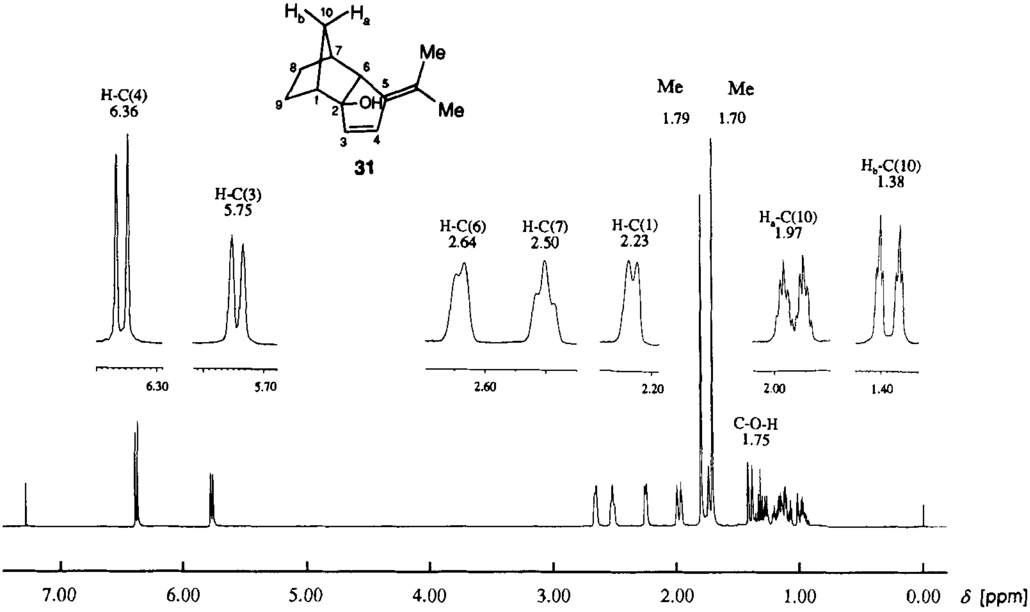


Fig. 3. *^{1}H-NMR Spectrum* (300 MHz, $CDCl_3$) *of* **31**[3]

5. Bromination/Elimination Experiments with Poly(6,6-dimethylpentafulvene) (8a). – Thus, our bromination experiments show that direct bromination of tricyclic diene **21** is the method of choice, giving crystalline dibromide **23** in quantitative yield, whereas more problems are encountered with the two-fold HBr elimination **23** → **22** (51 % yield), despite a broad variation of bases and reaction conditions. In view of the planned synthesis of fully conjugated polymers **8** → → **9**, the results of *Chapt. 4* suggest that a direct bromination of polyfulvenes of type **8** looks very promising, while the elimination step giving fully conjugated polymers could be problematic. Indeed, bromination of poly(6,6-dimethylfulvene) (**8a**) proceeded very easily in CCl_4 at room temperature (see *Exper. Part*). After filtration (under Ar) of the precipitated polymer and drying under high vacuum, a colorless powder with a satisfactory elemental analysis for $(C_8H_{10}Br_2)_n$ was collected in 87% yield. All the spectroscopic data of this brominated poly(6,6-dimethylpentafulvene)[3] are in agreement with the proposed structure **32** and fit to the spectroscopic characteristics of model compound **23**. Thus, the UV spectra (dioxane) of **32a** (λ_{max} 232 nm and ε 6600 per structural unit) as well as of **23** (λ_{max} 230 nm and ε 8800) are very similar. Furthermore, both ^{1}H- and ^{13}C-NMR spectra of **32a** show broad absorptions in exactly the ranges in which the corresponding H- and C-atoms of **23** are absorbing

Table 2. *Selected* ^1H- *and* ^{13}C-*NMR Spectral Data of Polymer* **32a**[a]) *and Model Compound* **23**[a])

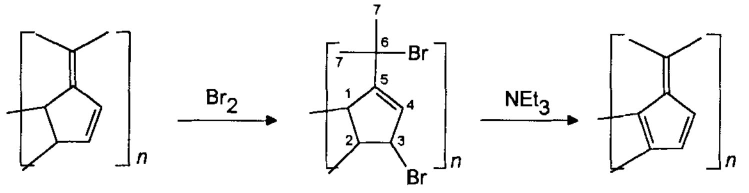
	32a		**23**	
	^{1}H-NMR	^{13}C-NMR[b])	^{1}H-NMR	^{13}C-NMR
H–C(1)	*ca.* 3.9 (br.)	50–60[c])	3.55	56.3
H–C(2)	*ca.* 3.0 (br.)	50–60[c])	3.15	52.9
H–C(3)	*ca.* 5.1 (br.)	50–60[c])	5.06	58.1
H–C(4)	*ca.* 6.1 (br.)	132 (br.)	5.90	129.1
C(5)	–	155 (br.)	–	154.3
C(6)	–	50–60[c])	–	56.3
Me(7)	*ca.* 1.9 (br.)	36 (br.)	1.99, 1.90	33.6

[a]) Identical arbitrary numbering of **32a** and **23**, see *Formula* **32a**.

[b]) Additional low-intensity absorptions at 146, 140, 125 ppm as well as a broad absorption around 20 ppm could be due to a partial HBr elimination during recording of the ^{13}C-NMR spectrum.

[c]) Broad absorptions between 45 and 65 ppm, with maxima in the range of 50–60 ppm, due to several overlapping ^{13}C-NMR signals.

Scheme 6



8a **32a** (arbitrary numbering) **9a**

(*Table 2*). The analytical data confirm that bromination of poly(6,6-dimethylpentafulvene) (**8a**) gives polymer **32a** (*Scheme 6*) in very high yields.

Polymer **32a** is very sensitive to heat, air, and moisture. It produced easily HBr either in solution or in pure form at room temperature and had to be stored at low temperature under Ar. Therefore, subsequent elimination experiments **32** → **9a** (see below) were best undertaken with freshly prepared **32a** (see below). GPC Measurements of **32a** (THF, *Ultrastyragel*) gave approximate M_n and M_w values of 71300 and 369500, respectively; these values are not very accurate since *ca.* 10% of the polymer with $M_w > 10^6$ were beyond the exclusion limit of the gel. Considering the fact that virtually each structural element of a sample of polyfulvene **8a** with M_n 38800 and M_w 53750 was brominated (see **8a** → **32a**), thus increasing in molecular weight from M 106 to M 266, the obtained (inaccurate) M_n of **32** is quite satisfactory in relation to a theoretical value of M_n 97300. The markedly increased M_w/M_n factor of 5.2 for brominated polymer **32a**, compared with M_w/M_n 1.39 for the starting material **8a**, hints at the conclusion that either a certain amount of chain fission took place during bromination or that the polymer **32a** lost some HBr during the GPC measurement.

Attempts towards a complete HBr elimination of polymer **32a** to give polymer **9a** with pentafulvene structural units are not yet completed and have to be continued. Similar to

HBr elimination of model compound **23** to **22**, HBr elimination of polymer **32a** to **9a** was at first tried with Et_3N in refluxing CH_2Cl_2 solution over 48 h (see *Exper. Part*). After 10 h, the polymer began to precipitate. However, elemental analysis of the precipitate as well as titration of inorganic salts showed that HBr elimination was not complete. The polymer was a dark-brown brittle solid, being insoluble (but swelling) in usual solvents. According to its UV spectrum (*Fig. 4a*), the polymer is supposed to contain segments with conjugated pentafulvene structural elements but no complete conjugation.

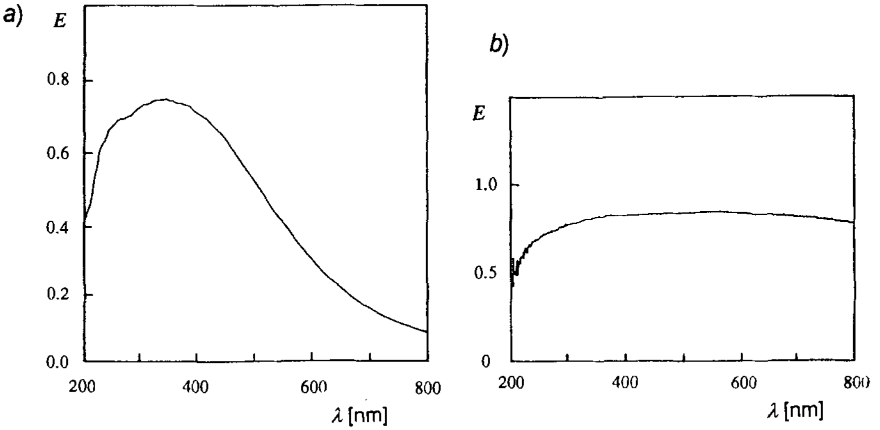
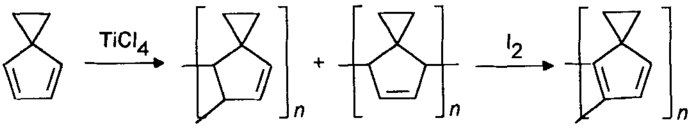


Fig. 4. *UV Spectra of polymer samples containing conjugated structural elements of the type* **9a**.
a) *Product after treatment of polymer* **32a** *with an excess of* Et_3N *in boiling* CH_2Cl_2. b) *Product after treatment of polymer* **32a** *with* I_2 *in* CCl_4

This unsatisfactory result prompted us to test a procedure by which a polymer containing structural elements **34A** and **34B** – being prepared by $TiCl_4$-induced polymerization of spiro[2.4]hepta-4,6-diene (**33**) [26] – had been partially transformed into conjugated segments **35** by treatment with I_2 [27] (*Scheme 7*). When I_2 was added to the solution of poly(6,6-dimethylpentafulvene) (**8a**) in CCl_4 at room temperature, the intense color of I_2 did not disappear, but a violet-black precipitate started to be formed after a short time. If the mixture was boiled under reflux for 24 h, more and more black polymer was precipitating. The polymer was collected by filtration (see *Exper. Part*), it had the appearance of charcoal and was insoluble in all the usual solvents. The result of the elemental analysis of 'I_2-treated poly(6,6-dimethylpentafulvene)' was fitting to the for-

Scheme 7



33 **34A** **34B** **35**

mula $C_8H_{9.2}I_{0.66}$, showing that a substantial amount of I_2 had been incorporated. So far, conductivity measurements failed, because it was not possible to prepare adequate sample pellets. The UV spectrum (*Fig. 4b*) of the polymer is very surprising in so far that the polymer has approximately the same absorption throughout the whole range from 200 to 800 nm, the absorption range obviously extending far beyond 800 nm. A more detailed investigation of this polymer is planned.

The author thanks *Ciba-Geigy AG*, Basel and Marly, for financial support.

Experimental Part

1. *General*[6]. Cyclopentadiene was prepared by monomerization of dicyclopentadiene [28]. Synthesis of pentafulvenes: **1a** (R = X = Me) [29] was kindly provided by *Ciba-Geigy*, Marly; **1b** (R = X = SMe) [30]; **1c** (R = H, X = Me_2N) [31]. Cationic polymerization **1a** → **8a**: [18]. All the reactions were run under Ar. Prior to the introduction of the reagents, the reaction vessel was thoroughly flame-dried while being flushed with Ar (or N_2). Gel-permeation chromatography (GPC): HPLC system (*Waters*); columns, *Ultrasyragel* 10^6, 10^5, 10^4, and 10^3 Å; standard, polystyrene; eluent, THF. GC: *Hewlett-Packard 5890* with integrator *HP 3390* and FID equipped with 20 m capillary columns (*SE-54*). Electrical conductivity measurements were kindly carried out by Dr. *J. Finter, Ciba-Geigy AG*, R-1060-202, CH-4002 Basel. Viscosity η_{red} of polymer solns. was measured with a *Ostwald* viscosimeter. For that purpose, polymer solns. were prepared by dissolving the polymer sample in THF containing 0.5 wt.-% of diphenylamine. Polymer concentration c_p was 8 mg/ml. UV Spectra: *Perkin-Elmer 554*. IR Spectra: *Perkin-Elmer 782*. NMR Spectra: *Bruker AC-300* and *Bruker AM-400*. MS: *Varian-Mat CH-7A*. HR-MS: *Varian-Mat 311*. Microanalyses were performed by Drs. *H.* and *K. Eder*, Institute of Pharmaceutical Chemistry, Service of Microchemistry, Quai Ernest-Ansermet 30, CH-1211 Genève.

2. *Polymerization of 6,6-Bis(methylthio)pentafulvene* (**1b**). 2.1. *Attempted Anionic Polymerization of* **1b**. Under Ar, 1.84 g of **1b** (10.8 mmol) were dissolved in 10 ml of freshly distilled abs. THF (→ red soln.). Then 0.1 ml of sodium cyclopentadienide (1.21 mmol) were added by syringe. After addition of the catalyst (→ dark-brown soln.), the mixture was stirred at r.t. for 24 h. Then polymerization was stopped by adding 3 ml of abs. MeOH. The mixture was dropwise added to 150 ml of pentane under Ar to precipitate the polymer, giving, after filtration under Ar, only a small amount (*ca.* 7 mg) of brownish powder. The filtrate (containing **1b** and dimer **15b** according to TLC and ^{1}H-NMR) was evaporated: 1.46 g of brownish oil. The oil was separated by flash chromatography (FC; deactivated silica gel, pentane/Et_2O 99:1 (*v*/*v*)): 0.78 g (42.4%) of **15b** and 0.32 g of **1b** (17.4%).

Data of 5,10-Bis[bis(methylthio)methylidene]tricyclo[5.2.1.0^{2,6}]deca-3,8-diene (**15b**): White crystals. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.64 (*d*, 1 H); 5.93 (*m*, 3 H); 4.18 (*m*, 1 H); 3.66 (*m*, 1 H); 3.33 (*m*, 2 H); 2.33 (*s*, 3 H); 2.23 (*s*, 3 H); 2.20 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 164.7 (*s*); 154.4 (*s*); 137.4 (*d*); 137.4 (*d*); 132.6 (*d*); 132.0 (*d*); 122.5 (*s*); 110.6 (*s*); 50.8 (*d*), 49.2 (*d*); 48.1 (*d*); 47.1 (*d*); 17.5 (*q*); 16.7 (*q*); 16.7 (*q*); 16.5 (*q*).

2.2. *Cationic Polymerization of* (**1b**)[6]. CH_2Cl_2 (9.0 ml) was distilled into a flask flushed with Ar and cooled to 0° (ice-bath). Then, 1 ml (7.2 mmol) of **1b** was added by syringe with stirring (→ red soln.). At 0°, 0.72 ml (0.072 mmol) of 1M $SnCl_4$ in CH_2Cl_2 were added by syringe to start polymerization. After 60 min, the soln. had turned to dark-green. Polymerization was terminated by adding 4 ml of 0.5 wt.-% of diphenylamine in THF. The soln. was added dropwise and slowly into 100 ml of abs. MeOH. The precipitated polymer was filtered off, washed 4 × with MeOH, and dried at 10^{-3} Torr: 1188 g (97%) of poly[6,6-bis(methylthio)pentafulvene] (**8b**). White powder. UV (dioxane): 306 (11620). IR (KBr)[7]: 2920*s*, 1432*m-s*, 1420*m-s*, 1310*m*, 968*m*, 890*m*, 790*m-s*, 770*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.7 (br., 1 H); 5.8 (br., 1 H); 2.9 (sh, 2 H); 2.2 (br., 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 156 (*s*); 141 (*d*); 133 (*d*); 122 (*s*); 54 (*d*); 50 (*d*); 17 (*q*). GPC-Measurements: M_n 12611, M_w 35904, M_w/M_n 2.8.

3. *Synthesis of and Experiments with Model Compound* **21**. 3.1. *5-Isopropylidenetricyclo[5.2.1.0^{2,6}]deca-3,8-diene* (**20**)[6]. To 17.9 g (87%, 0.147 mmol) of 6,6-dimethylpentafulvene (**1a**) under N_2, 60 g (0.91 mmol) of monomerized cyclopentadiene [28] were slowly added by distillation within 6 h while heating the mixture to 60°

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[6] For a more detailed description of general methods, procedures, and equipment as well as for reproduction of spectra, see [3].

[7] IR: Only typical absorptions. MS: Only $M^{+\cdot}$ and key fragments.

under stirring. After distillation of cyclopentadiene was complete, stirring was continued for another 2 h at 60° and the mixture separated by distillation. Unreacted **1a** and dicyclopentadiene formed during the reaction were removed by distillation at 31°/4 mbar, a 2nd fraction was obtained at 35°/4 mbar. The residue which contained **20** and polymers was treated with 100 ml of pentane. The insoluble polymers were filtered off. Evaporation of the filtrate gave 11 g (*ca.* 43%) of **20**. Slightly yellow oil. UV (hexane): 252 (13440). IR (neat)7): 3060*m*, 2963*s*, 2907*s*, 2865*s*, 1450*m-s*, 1371*m*, 1340*m*, 910*w-m*, 840*m*, 767*m-s*, 722*m-s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 6.18 (*dd*, 1 H); 5.80 (*m*, 2 H); 5.72 (*dd*, 1 H); 3.29 (*m*, 1 H); 3.15 (*m*, 2 H); 2.84 (*m*, 1 H); 1.81 (*s*, 3 H); 1.72 (*s*, 2 H); 1.50 (*d*, 1 H); 1.38 (*d*, 1 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 140.5 (*s*); 135.5 (*d*); 133.7 (*d*); 133.5 (*d*); 132.9 (*d*); 122.0 (*s*); 52.2 (*d*); 50.1 (*d*); 46.2 (*d*); 46.0 (*d*); 45.2 (*d*); 21.4 (*q*); 21.4 (*q*); 20.8 (*q*). MS7): 172 (22.5, $M^{+\cdot}$), 134 (22), 119 (55), 106 (100), 105 (36), 91 (70), 77 (12), 66 (10), 65 (13).

3.2. *5-Isopropylidenetricyclo[5.2.1.$0^{2,6}$]dec-3-ene* (**21**)6). To 540 mg of 5% Pd/C, a soln. of 10.8 g (62.8 mmol) of **20** in 70 ml of abs. MeOH was added very carefully thus avoiding to stir up the catalyst. The flask was evacuated (water pump) and subsequently filled with H_2. This operation was repeated at least 3 times. Then the soln. was stirred at r.t. When *ca.* 1 mol-equiv. of H_2 (*ca.* 1.5 l) was absorbed, the reaction was stopped. The catalyst was filtered off and the filtrate evaporated. The crude material (*ca.* 10.5 g) was purified by FC (pentane): 10.0 g (92%) of **21**. Colorless oil. UV (hexane): 246 (15090). IR (film7)): 2943*s*, 2905*s*, 2870*s*, 1453*m*, 1371*w-m*, 760*s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 6.33 (*dd*, 1 H); 5.75 (*dd*, 1 H); 3.1 (*m*, 1 H); 2.97 (*m*, 1 H); 2.42 (*m*, 1 H); 2.28 (*m*, 1 H); 1.79 (*s*, 3 H); 1.70 (*s*, 3 H); 1.53 (*d*, 1 H); 1.42 (*d*, 1 H); 1.25–1.15 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 139.8 (*s*); 136.2 (*d*); 131.6 (*d*); 122.7 (*s*); 53.0 (*d*); 48.3 (*d*); 41.2 (*t*); 40.8 (*d*); 39.7 (*d*); 25.3 (*t*); 23.5 (*t*); 21.2 (*q*); 20.8 (*q*). MS7): 174 (73, $M^{+\cdot}$), 159 (66), 133 (30), 131 (77), 119 (18), 117 (34), 108 (100), 107 (80), 106 (71), 105 (48), 93 (95), 91 (92), 79 (22), 77 (27), 67 (27).

3.3. *5-Bromo-3-(1-bromo-1-methylethyl)tricyclo[5.2.1.$0^{2,6}$]dec-3-ene* (**23**)6). To a soln. of 1.128 g (6.48 mmol) of **21** in 15 ml CCl_4 under N_2, a soln. of 1.042 g (6.5 mmol) of Br_2 in 3 ml of CCl_4 was dropwise added by syringe within 20 min at r.t. The color of Br_2 disappeared quickly during the addition. After the addition of Br_2 was complete, the solvent was evaporated at < 0°. The residue was dissolved in 5 ml of CH_2Cl_2 and after removing CH_2Cl_2 at −20°, white crystals of **23** (2.144 g, 99%) were obtained. Thereof, 2 g were dissolved in 3 ml of CH_2Cl_2 at −40° under N_2 and kept overnight at −60°: 1.14 g (57%) of white crystals. Storage at −60° under N_2. UV (hexane): 230 (8800). IR (CS_2/CCl_4)7)): 2960*s*, 2882*s*, 1550*m-s*, 1458*m-s*, 1370*m*, 1116*m-s*, 1100*m-s*, 857*s*, 710*m*, 650*m*, 620*m*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 5.90 (br., 1 H); 5.06 (*q*, 1 H); 3.55 (*m*, 1 H); 3.15 (*m*, 1 H); 2.53 (*m*, 1 H); 2.44 (*m*, 1 H); 1.99 (*s*, 3 H); 1.90 (*s*, 3 H); 1.53 (*d*, 1 H); 1.48 (*d*, 1 H); 1.38–1.08 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 154.3 (*s*); 129.1 (*d*); 62.7 (*s*); 58.1 (*d*); 56.3 (*d*); 52.9 (*d*); 41.5 (*t*); 40.8 (*d*); 39.2 (*d*); 33.6 (*q*); 24.2 (*t*); 22.6 (*t*). MS7): 336 (1.1, $[M + 2]^+$), 334 (2.5, $M^{+\cdot}$), 332 (1.3), 256 (54), 255 (92), 254 (59), 253 (100), 252 (23), 189 (31), 187 (34), 174 (53), 173 (83), 159 (35), 145 (30), 144 (16), 131 (42), 119 (28), 117 (29), 108 (27), 107 (53), 106 (30), 105 (34), 93 (23), 91 (37), 87 (16), 80 (29), 79 (34), 67 (34.5).

3.4. *2-Bromo-5-isopropylidenetricyclo[5.2.1.$0^{2,6}$]dec-3-ene* (**29**)6). A colorless 20% soln. of **23** in CH_2Cl_2 was kept under N_2 at r.t. for 2 h, giving a nearly black soln. which was added to pentane. After filtering off the black precipitate, evaporation of the filtrate gave a light green oil (*ca.* 60%), consisting mainly of **29**. *Data of* **29**: ^{1}H-NMR ($CDCl_3$, 300 MHz): 6.35 (*d*, 1 H); 6.03 (*d*, 1 H); 3.50 (*d*, 1 H); 2.78 (*d*, 1 H); 2.54 (*m*, 1 H); 2.23 (*d*, 1 H); 1.84 (*s*, 3 H); 1.72 (*s*, 3 H); 1.55 (*d*, 1 H); 1.4–1.0 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 136.6 (*d*); 136.0 (*s*); 131.6 (*d*); 128.2 (*s*); 85.0 (*s*); 61.2 (*d*); 50.7 (*d*); 42.3 (*d*); 40.1 (*t*); 27.8 (*t*); 21.5 (*t*); 21.5 (*q*); 20.7 (*q*).

3.5. *Attempted Allylic Bromination of* **21**: *2-Hydroxy-5-isopropylidenetricyclo[5.2.1.$0^{2,6}$]dec-3-ene* (**31**)6). A mixture of 556 mg (3.12 mmol) of NBS, 527 mg (3.03 mmol) of **21**, and 10 mg of AIBN (2,2′-azobis(isobutyronitrile)) in 8 ml of CCl_4 under N_2 was boiled under reflux for 14 h (→ brownish mixture). Insoluble material was filtered off (funnel) and the filtrate evaporated at r.t./12 Torr. The crude material was purified by FC (silica gel, pentane/Et_2O 7:3) at −5°: 68 mg (12%) of **31**. White crystals. UV (hexane): 246 (13278). IR (KBr)7): 3440*s*, 2945*s*, 2920*s*, 2903*s*, 2875*s*, 1450*m-s*, 1370*s*, 1317*m-s*, 1294*m-s*, 1058*s*, 999*s*, 950*m*, 789*m-s*, 775*m-s*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 6.36 (*d*, 1 H); 5.75 (*d*, 1 H); 2.64 (*m*, 1 H); 2.50 (*t*, 1 H); 2.23 (*m*, 1 H); 1.97 (*d*, 1 H); 1.79 (*s*, 3 H); 1.75 (*s*, 1 H); 1.70 (*s*, 3 H); 1.38 (*d*, 1 H); 1.4–0.9 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 300 MHz): 136.8 (*s*); 134.9 (*d*); 132.3 (*d*); 126.2 (*s*); 93.3 (*s*); 58.6 (*d*); 45.8 (*d*); 40.6 (*d*); 38.9 (*t*); 25.7 (*t*); 21.5 (*t*); 21,4 (*q*); 20.4 (*q*). MS7): 191, 190 (90, $M^{+\cdot}$), 175 (88), 147 (69), 123 (73), 122 (100), 109 (37), 108 (28), 107 (44), 91 (24), 79 (32), 67 (30). HR-MS: 190.1356 ($C_{13}H_{18}O^+$; calc. 190.1358).

3.6. *5-Isopropylidenetricyclo[5.2.1.$0^{2,6}$]deca-2(6),3-diene* (**22**)6). To 417 mg (4.13 mmol) of Et_3N in 5 ml of CH_2Cl_2 under N_2, a cooled soln. (−20°) of 536 mg (1.61 mmol) of **23** in 5 ml of CH_2Cl_2 was dropwise added at r.t. within 30 min (→ yellow soln.). After the addition of **23** was complete, stirring was continued for another 2 h. The crude product was filtered by column chromatography (pentane/Et_2O 95:5) at −30°: **22** (51.3%). Orange oil. The yield was determined by ^{1}H-NMR, pyrazine being used as an internal standard (δ 8.5). UV (hexane): 266 (21730), 350 (443). IR (film[7]): 2940*m*, 2920*m*, 2870*m*, 1648*m*, 1450*m*, 1370*w-m*, 1280*m*, 743*w-m*, 690*w*. ^{1}H-NMR (CDCl$_3$, 300 MHz): 6.35 (*d*, 1 H); 6.30 (*d*, 1 H); 3.43 (*m*, 1 H); 3.12 (*m*, 1 H); 2.27 (*s*, 3 H); 2,18 (*s*, 3 H); 1.76 (*m*, 2 H); 1.72 (*m*, 1 H); 1.42 (*d*, 1 H); 0.97 (*m*, 2 H). ^{13}C-NMR (CDCl$_3$, 75 MHz): 154.2 (*s*); 147.5 (*s*); 140.7 (*s*); 136.5 (*s*); 124.7 (*d*); 122.3 (*d*); 50.1 (*t*); 43.1 (*d*); 40.9 (*d*); 26.9 (*t*); 26.3 (*t*); 23.1 (*q*); 22.9 (*q*). MS[7]: 173 (30.5), 172 (99, $M^{+\cdot}$), 157 (46), 145 (57), 144 (100), 143 (32), 142 (35), 141 (46), 129 (84), 128 (65.5), 127 (43.5), 115 (63), 91 (28), 77 (16). HR-MS: 172.1253 ($C_8H_{16}^+$; calc. 172.1252).

4. *Bromination/Elimination of Poly(6,6-dimethylpentafulvene)* (**8a**). 4.1. *Reaction of* **8a** *with* Br_2[6]. To a soln. of 852 mg (8.0 mmol per monomer unit) of **8a** in 30 ml of CCl_4 under Ar, a soln. of 1286 mg (8.0 mmol) of Br_2 in 4 ml of CCl_4 was dropwise added at r.t. by syringe. The color of Br_2 disappeared during the addition, and the polymer began to precipitate nearly at the end of addition. After the addition was complete, the white precipitate was filtered (funnel) under Ar and washed with CCl_4 (3 ×), Et_2O (2 ×), and pentane (3 ×). The combined CCl_4 filtrates were dropwise added to 150 ml of pentane under Ar, and the white precipitate produced was filtered (funnel) and washed with Et_2O (2 ×) and pentane (3 ×). The combined precipitates were dried at $-20°/10^{-3}$ Torr: 1870 mg (87.5%) of *poly(3,6-dibromo-3,6-dihydro-6,6-dimethylpentafulvene)* (**32a**). White powder. UV (dioxane): 232 (6600). IR (KBr)[7]: 2980*s*, 2920*s*, 1445*m-s*, 1375*m-s*, 760*m*. ^{1}H-NMR (CDCl$_3$, 300 MHz): 6.1 (br., 1 H); 5.1 (br., 1 H); 3.9 (br., 1 H); 3.0 (sh, 1 H); 1.9 (br., 6 H). ^{13}C-NMR (CDCl$_3$, 300 MHz): 155 (*s*); 132 (*d*); 50–60; 36 (*q*). GPC Measurements: M_n 71320, M_w 369500, M_w/M_n 5.18. Anal. calc. for $(C_8H_{10}Br_2)_n$ (265.9754): C 36.28, H 3.87, Br 60.50; found: C 36.13, H 3.79, Br 60.08.

4.2. *Dehydrobromination of* **32a** *with* Et_3N[6]. To 456 mg of **32a** (1.7 mmol per monomer unit) in 15 ml CH_2Cl_2 under Ar, 440 mg (4.3 mmol) of Et_3N were added at r.t. The mixture was boiled under reflux for 48 h. The color of the soln. changed from yellow to yellow-brown, brown, and then red brown, and after 10 h, yellowish polymer started to precipitate. The amount of the precipitate increased, and the color turned to dark-brown as the reaction continued. After 48 h, the mixture was allowed to cool and the precipitate filtered under Ar. The precipitate was rinsed several times with CH_2Cl_2 (removal of inorg. salts produced during the elimination). The brownish solid was dried at r.t./10^{-3} Torr: 133 mg of partly dehydrobrominated product. Dark-brown solid. UV (solid sample): *ca.* 350, tail beyond 800 (*Fig. 4*). Conductivity measurements: $1.02 \cdot 10^{-4}$ S/cm. Anal. calc. for (C_8H_{10}): C 92.26, H 7.74; found: C 69.45, H 6.33, Br 24.22, fitting to $C_8H_{8.69}Br_{0.49}$.

5. *Treatment of* **8a** *with* I_2[6]. To a soln of. 262 mg of **8a** (2.6 mmol per monomer unit) in 10 ml of CCl_4 under Ar, a soln. of 658 mg (2.6 mmol) of I_2 in 30 ml of CCl_4 was dropwise added under stirring at r.t. A violet-black precipitate was formed after a short while within min. After the addition was complete, the mixture was boiled under reflux for 24 h. The mixture was then cooled and the precipitate filtered (funnel) under Ar. The precipitate was washed 3 times with 5 ml of CCl_4, then several times with CH_2Cl_2 to remove traces of I_2. After drying at 10^{-3} Torr, 253 mg of a black polymer powder were obtained. UV (solid sample): strong absorption between 200 and 800 and extending far beyond 800. Anal. calc. for (C_8H_{10}): C 92.26, H 7.74; found: C 50.36, H 4.88, I 43.73, fitting to $C_8H_{9.2}I_{0.66}$.

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