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The Structure of Polyfulvenes[*,**]

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Cationic polymerisation of 6,6-disubstituted pentafulvenes yields highly unsaturated, reactive macromolecules of high molecular weight. The mechanistic pathways leading to the polymers are discussed, and the structure XIV of the polymers has been elucidated by a combination of spectroscopic methods as well as by comparison with model compounds. In contrast to reports in the literature, the main process in thermal oligomerisation of simple pentafulvenes at 20 °C is a Diels-Alder reaction giving products of type XXI. Anionic polymerisation of pentafulvenes is initiated by traces of sodium cyclopentadienide or phenylsodium respectively. The reaction products consist of a mixture of oligomers of the series (fulvene)$_n$. This surprising result can be explained by structure elucidation of the fulvene dimers, which gives formula XX. The mechanistic aspects of the reaction are discussed.

INTRODUCTION

Fulvenes are cyclic cross-conjugated molecules with an odd number of C-atoms in the ring. According to the size of the ring skeleton they are named triafulvenes I, pentafulvenes II, heptafulvenes III and nonafulvenes IV. Spectroscopic investigations show that the parent compounds of this family are characterized by the lack of diamagnetic ring current, strongly alternating bond lengths and a comparably low dipole moment. For instance the chemical shifts of the ring protons of pentafulvene[2,3], heptafulvene[4,5,6] and nonafulvene[7] are very similar to those of cyclopentadiene, cycloheptatriene and cyclononatetraene, and the vicinal ^1H, ^1H-coupling constants of pentafulvene alternate in a typical way ($J_{1,2} = J_{3,4} = 5.10$ Hz; $J_{2,3} = 1.95$ Hz)[3]. Furthermore microwave spectroscopy shows that the dipole moments of pentafulvene ($\mu = 0.44$ D)[8] as well as of heptafulvene ($\mu\ 0.477$ D)[9] are rather small.

Because of these facts, fulvenes have to be classified as typical non-aromatic compounds with rather olefinic behaviour. In fact, the thermal stability of the parent fulvenes is extremely low: While triafulvene I has not been isolated so far despite various attempts[10,11,12], pentafulvene II[13,14] oligomerises at 20 °C with a half-life of about 3 hours. Heptafulvene III is even more reactive and in pure form polymerises within a few minutes at 20 °C[6], and

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Scheme 1

nonafulvene undergoes a disrotative valence isomerisation to dihydrobenzo-fulvene with a half-life of 12 minutes at 10 °C in CDCl$_3$[7].

Fortunately these unstable parent compounds may be stabilised by the introduction of appropriate substituents at the exocyclic C-atom, namely tria-fulvenes and heptafulvenes by electron accepting groups (e. g. cyano groups), whereas pentafulvenes as well as nonafulvenes are stabilised by electron donating groups (e. g. dimethylamino groups). The following general rule is very important for preparative purposes: »Fulvenes are stabilised by substituents at the exocyclic C-atom which favour a Hückel-type electron configuration in the ring«. In consequence, 4,4-dicyano-triafulvenes[15,16] are quite stable compounds, whereas 6,6-bis(dimethylamino)pentafulvene[17,18] as well as 8,8-dicyanoheptafulvene[19,20] may be stored for years at room temperature. Similarly valence isomerisation of 10,10-bis(dimethylamino)nonafulvene proceeds only slowly at 20 °C[21].

There exist a considerable number of fulvene syntheses[22,23]. In most cases one starts with the corresponding nonbenzenoid cations V → I or VII → III, as well as with the corresponding anions VI → II or VIII → IV. During the last decade, a very general synthesis of penta-, hepta- and nonafulvenes as well as of the »mixed fulvalenes« has been developed[24,25]. With the aid of this synthesis (proceeding at low temperatures) the parent pentafulvene[2], hepta-fulvene[6] and nonafulvene[7] have been prepared and isolated in spectroscopically pure form.
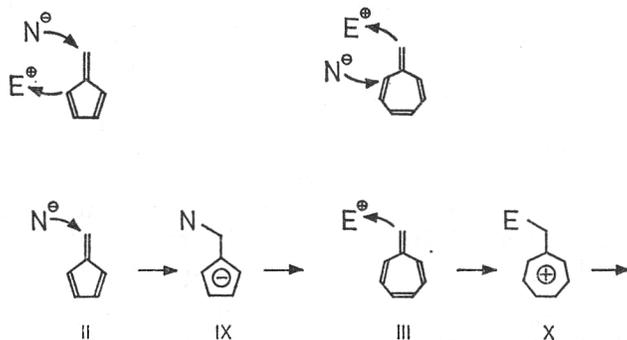
Scheme 2

Reactions of fulvenes and fulvalenes have been intensively investigated during the last 2 decades. With respect to polar reactions, the most important experimental results (assisted by theoretical calculations) are briefly summarised in Scheme 2. It is well known that pentafulvenes are attacked by nucleophiles at the exocyclic C-atom, a reaction by which substituted cyclopentadienides IX are formed as intermediates — while electrophiles attack the five-membered ring. On the other hand, heptafulvenes react with electrophiles at the exocyclic C-atom to give substituted tropylium ions X as primary products, and with nucleophiles at the seven-membered ring. These reactions have been realised in most cases with thermally relatively stable fulvenes; for instance with 6-dimethylaminofulvene mainly by Hafner et al.[26,27], and in the case of 8-cyanoheptafulvene mainly by Kitahara and Oda[28].

2. CATIONIC POLYMERISATION OF PENTAFULVENES

2.1. General remarks

Although it is well known that many simple pentafulvenes[29,30] as well as heptafulvenes[4] are extremely sensitive to traces of acid, nobody really knew until now what happens in cationic polymerisation of pentafulvenes. Similarly very little information was available about anionic[31] and thermal polymerisation of fulvenes[32].

At the beginning of our work we were interested in polymers containing substituted cyclopentadienes as structural units. Macromolecules of this type would easily be converted to poly-cyclopentadienides so that easy functionalisation by reaction with numerous electrophiles would be possible. For instance reaction with Fe^{II}-salts could give polymeric ferrocenes with interesting properties. Furthermore, some speculation about the structure of fulvene polymers[32] seemed to be rather unlikely and had to be corrected. Since 6,6-dimethyl--pentafulvene* is easily available on a technical scale by simple base-catalysed condensation of cyclopentadiene with acetone, we decided to use this fulvene for polymerisation.

2.2. Experimental results

In fact, DMF is polymerised in CH_2Cl_2 in the presence of traces of acids like CCl_3COOH and $ClSO_3H$, or of Lewis-acids like $SnCl_4$ or $TiCl_4$ within 5—60 minutes to give soluble reactive macromolecules of high molecular weight[33]. One of the products which was investigated under strict exclusion of air had an intrinsic viscosity η of 50 cm³/g (25 °C, THF) and a molecular weight of 136 000 (ultracentrifuge). After addition of alcohol a colourless amorphous powder of poly-DMF precipitates in almost quantitative yield**.

If the polymers are stored under strict exclusion of oxygen, they are quite stable and soluble in organic solvents of medium polarity. Figure 1 shows however that dry poly-DMF-powder is extremely sensitive to oxygen and

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* In the following text the name fulvene is normally used for pentafulvenes. DMF means 6,6-dimethylfulvene, poly-DMF means poly-6,6-dimethylfulvene.

** Similarly 6-alkyl-, 6-aryl-, other 6,6-dialkyl as well as 6,6-diaryl-fulvenes are polymerised nearly quantitatively. In most cases however, the molecular weight of the polyfulvenes is somewhat lower than that of poly-DMF.
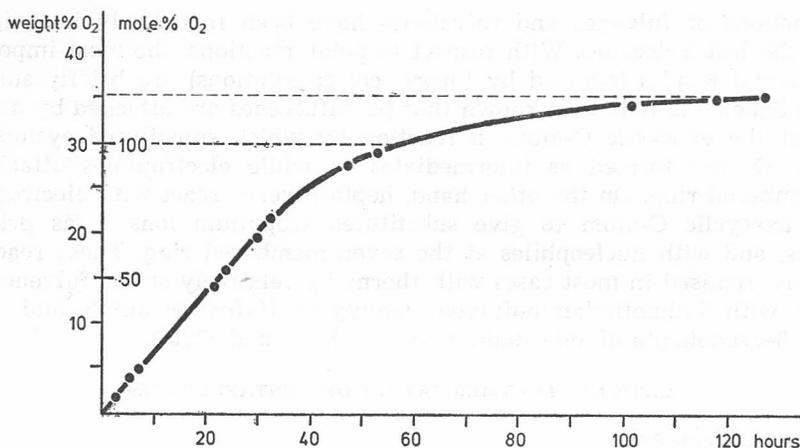
Figure 1. Weight of cationic poly-6,6-dimethylfulvene in function of time (dry polymer powder exposed to air).

consumes somewhat more than 1 mole-equivalent of oxygen within 3 days. This reaction causes cross-linking of the polymer chains.

2.3. Mechanistic possibilities

According to the calculated electron densities one might expect that DMF would be protonated at C(1). In this case a delocalised pentadienyl-cation
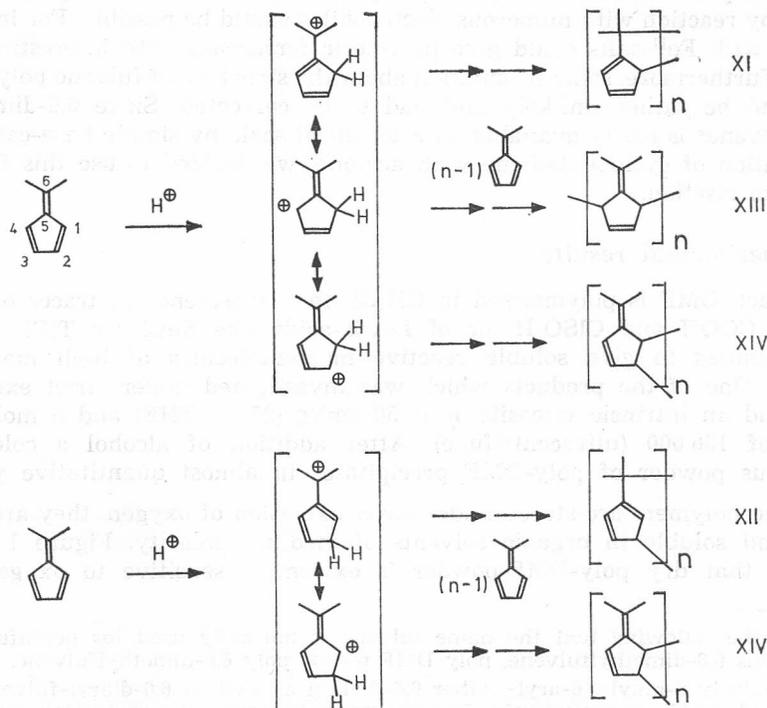
Scheme 3

should arise which has 3 electrophilic centers (represented in Scheme 3 by their mesomeric forms). Consecutive, rapid addition of monomeric DMF gives 3 structural alternatives, namely the target polymer XI with cyclopentadiene rings in its structural unit, as well as 1,4-linked polyfulvene XIII and a 1,2--linked polyfulvene XIV. If against theoretical predictions protonation at C(2) is taken into account, then an additional polymer XII with 1,3-linked cyclo-pentadiene moieties is possible.
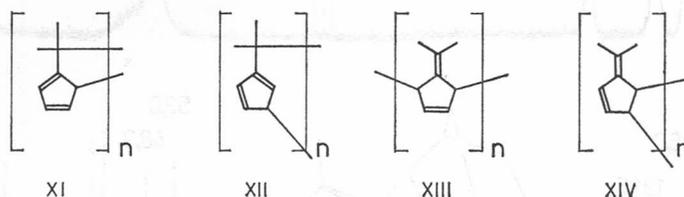
XI   XII   XIII   XIV

Scheme 4

Summarising cationic polymerisation of DMF may lead to 4 different homopolymers XI, XII, XIII and XIV. Naturally the situation could be complicated by the fact that copolymers containing different structural units in the chain are possible. Furthermore disubstituted cyclopentadienes (as present in XI and XII) normally are tautomeric mixtures because of rapid thermal 1,5-H-shift.

2.4. Structure of cationic poly-dimethylfulvene

It is obvious that the elucidation of the structure of polymers by a combination of spectroscopic methods is much more complicated than in the case of small organic molecules. The ^{1}H-NMR-spectrum is characterised by extremely broad lines and shows only that vinylic as well as alkyl protons are present. In the ultraviolet spectrum, the band of longest wavelength absorbs at 252 nm. This value correlates perfectly with the expected value of 255 nm for disub-stituted cyclopentadienes. However, if the structure of cationic polyfulvenes is of the cyclopentadiene-type XI or XII, then aromatic substituents at the exocyclic C-atom should not markedly influence the π—π*-band of the diene. This is exactly what happens in the case of poly-6,6-diphenylfulvene which shows an intense absorption at 298 nm. In consequence polyfulvenes of structure XI or XII have to be ruled out, supposing that both fulvenes are polymerising according to the same mechanism.

Decisive information concerning the structure of cationic polyfulvenes is deduced from the ^{13}C-NMR-spectra. The proton-noise-decoupled spectrum (Figure 2, above) immediately shows that the polymer chains are regularly built up of the same structure units. The spectrum contains 4 relatively broad signals in the vinylic part, one broad signal with shoulder at about 50 ppm as well as the signal of the methyl groups at 22 ppm. Of special interest for structure elucidation is the vinylic section of the spectrum in which 4 C-atoms are absorbing: Proton-off-resonance-decoupling proves that the 2 medium absorptions belong to tertiary C-atoms, while the signals at highest and lowest frequency are due to quarternary C-atoms. The considerable shift-difference of 23 ppm between the quarternary C-atoms is only compatible with the 1,2-
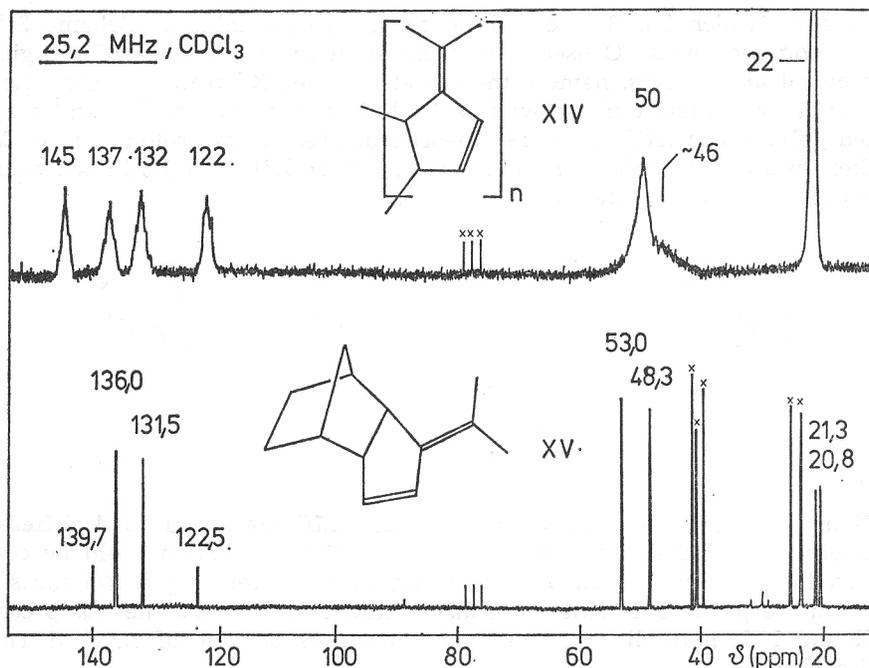
Figure 2. ¹³C-NMR-spectra of cationic poly-6,6-dimethylfulvene XIV (above) as well as of model XV (below). (x = lines of solvent and aliphatic rest of XV).

and 1,4-dihydrofulvene structures XIII and XIV, while structures of type XI and XII (that means tautomers with 2 quarternary C-atoms) are excluded. Finally the existence of 2 lines of non-equivalent tertiary vinylic C-atoms definitively shows that structural units of cationic poly-DMF are built up by 1,2-dihydrofulvene moieties of structure XIV[34].

This result is supported by independent synthesis and spectroscopic comparison of appropriate models[1]. For instance the ¹³C-NMR-spectrum of poly--DMF (Figure 2, above) fits surprisingly well with the ¹³C-NMR-spectrum of the model compound XV (Figure 2, below), prepared according to Houk and Luskus[35] by cycloaddition of cyclopentadiene to 6,6-dimethylfulvene.
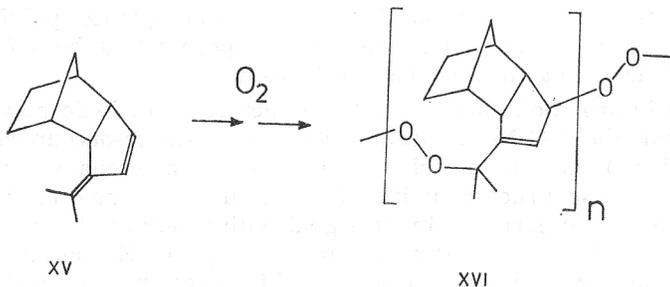
Scheme 5

Model compound XV not only shows similar spectroscopic properties to cationic poly-DMF, but also the same sensitivity towards oxygen (Scheme 5).

Reaction with air gives an exact 1:1-copolymer XVI, the structure of which has been proved by spectroscopic methods.

3. ANIONIC POLYMERISATION OF 6,6-DIMETHYLFULVENE

It is well known that fulvenes II react with nucleophiles at the exocyclic C-atom, thus forming a substituted cyclopentadienide. After protonation, substituted cyclopentadienes are isolated in high yield[22,23]. We suppose that, because of this well defined reaction, the anionic homopolymerisation of fulvenes has never been attempted so far. Only very recently, DMF has been attached to a living polybutadiene[31].
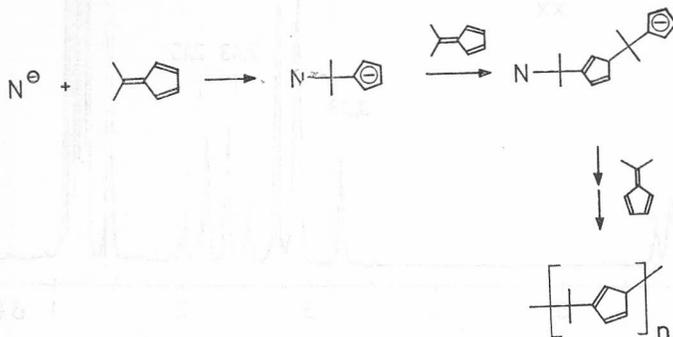
Scheme 6. Planned synthesis of polymer cyclopentadienes by means of anionic catalysts.

If cyclopentadienide is able to attack ot C(6) of fulvenes, then anionic polymerisation should take place, thus producing polymers containing cyclopentadiene rings in their structural unit.

In fact yellow DMF (20 vol.-% in THF) reacts in the presence of 1 mol-% of sodium cyclopentadienide to give $> 95\%$ conversion of the fulvene after 20 hours at 20 °C. The reaction is considerably accelerated by traces of crown ether[36]. After evaporation of the solvent a pale-brown oil results. Very surprisingly the mass-spectrum of the mixture shows oligomers of the type $(C_8H_{10})_n$. This means that cyclopentadiene has not been incorporated. The result is confirmed by gel-chromatography which shows that the mixture mainly consists of dimers, trimes and tetramers.

Dimeric 6,6-dimethylfulvene (DMF-dimer) of the formula $C_{16}H_{20}$ is easily separated by simple vacuum distillation. The ultraviolet spectrum shows that DMF-dimer is not fulvenic, since there is no band at 350 nm. The intense absorption at 253 nm is normally characteristic for cyclopentadines.

At 60 MHz, the ^{1}H-NMR-spectrum of anionic DMF-dimer (Figure 3, above) shows a very complex pattern of the vinylic protons (5, 3 H), then 3 multiplets in the range of cyclopentadiene-CH_2-groups (3.23, 2.89, 2.74 ppm, 3.7 H). Furthermore, complex multiplets absorb between 2.6 and 1.9 ppm (2 H), and the methyl-range contains a signal at 1.45 ppm (3 H) as well as a series of singlets between 1.3 and 1.0 ppm (6 H). The important point is a correct interpretation of this complex spectrum. For instance it is decisive that the multiplets at 2.43 and 2.15 ppm seem to show an AB splitting. In this case we have an integral ratio of 2 : 3 : 6 for the multiplets at (2.3—1.9)/1.45/(1.3—1.0) ppm. This means that in anionic dimerisation of dimethylfulvene a methyl
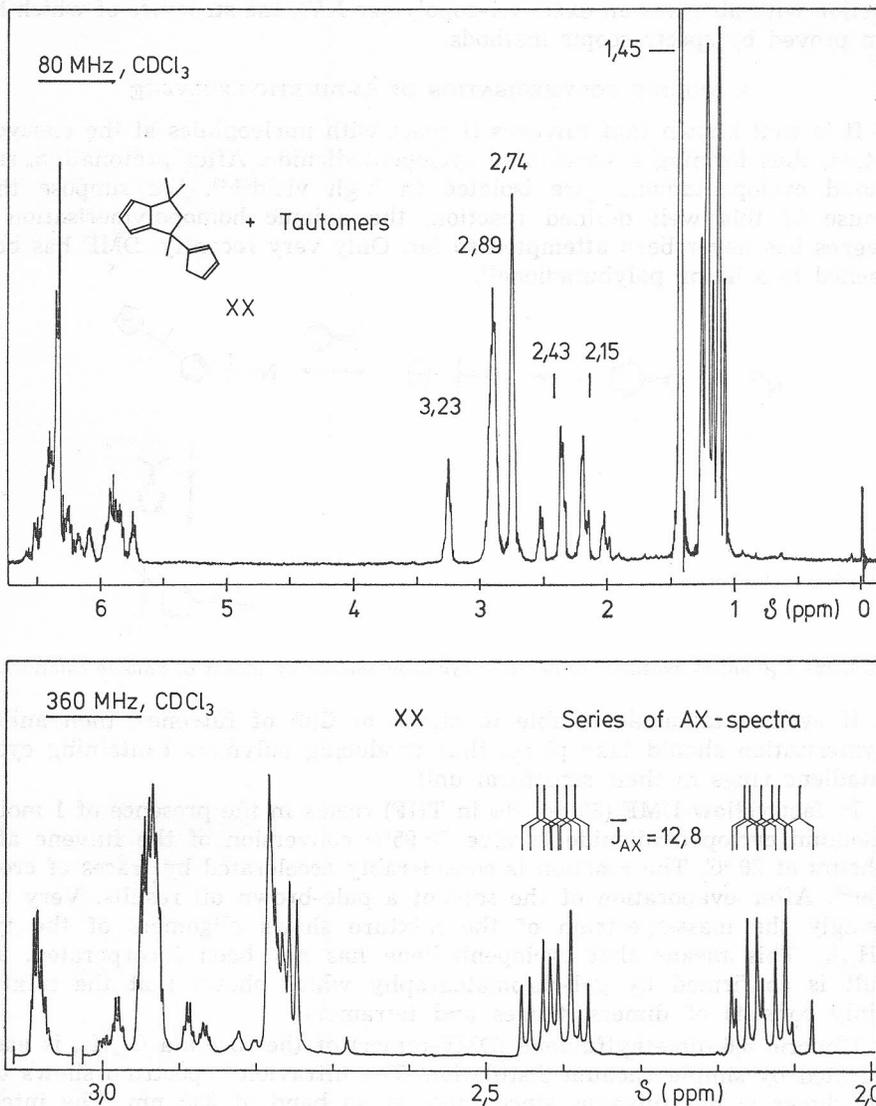
Figure 3. ¹H-NMR-spectrum of anionic DMF-dimer XX; above: 80 MHz, CDCl₃; below: 360 MHz, CDCl₃, alkylmethylene and -methine-region.

group is replaced by a methylene group, the protons of which are diastereotopic. This is confirmed at 360 MHz, where at least 6 AX-multiplets with $\bar{J} = 12.8$ Hz can be identified (Figure 3, below).

The final structure of anionic DMF-dimer is determined by a combination of spectroscopic data with mechanistic considerations (Scheme 7).

Obviously cyclopentadienide doesn't attack C(6) of the fulvene but abstracts a proton from DMF to give the delocalised anion XVII which has a relatively high electron density at the exocyclic C(7). Addition at C(6) of

Scheme 7
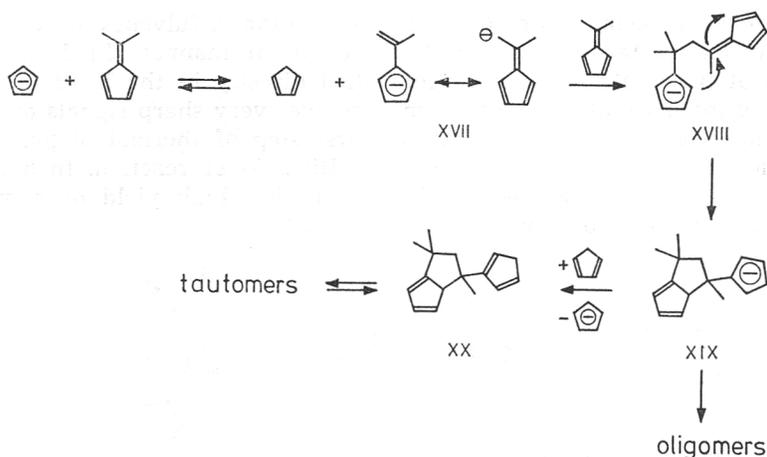
monomeric DMF gives the intermediate XVIII in which the cyclopentadienide and the fulvene moiety are in close proximity. This induces intramolecular cyclisation. Protonation of the bicyclic intermediate XIX followed by equilibration leads to a mixture of several tautomeric 4-cyclopentadienyl-4,6,6-trimethyl-tetrahydropentalenes XX.

This reaction sequence has been confirmed by identification of oligomers as well as of the protonation product of XVIII. An additional proof of the structure of DMF-dimer XX is obtained by deprotonation of the dimer with 2 equivalents of methyllithium[37]. As expected the ^{1}H-NMR-spectrum of the dianion of XX shows a very simple pattern, namely 3 singlets for the methyl groups, 1 AX-spectrum for the diastereotopic CH$_2$-group, and an AA'XX' as well as an AMX-spectrum for the cyclopentadienide protons. Summarising anionic polymerisation of DMF proceeds smoothly to give a mixture of oligomers of the type (fulvene)$_n$ with a high ratio of DMF-dimer XX.

4. THERMAL POLYMERISATION OF SIMPLE FULVENE

In 1956/58 Thiec and Wiemann prepared fulvene II as well as 6-methylfulvene for the first time. They observed that on standing at room temperature both fulvenes were transformed into a transparent gel[32]. As a result of UV- and IR-investigations different structures were proposed for the 2 polymers (Scheme 8).
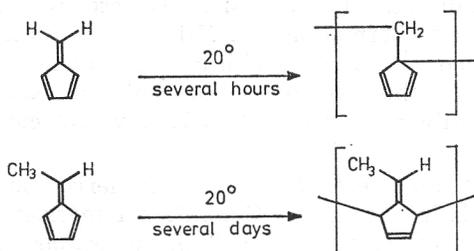
Scheme 8. Thermal polymerisation of fulvene and 6-methylfulvene according to Thiec and Wiemann[32].

However, it seemed to be quite improbable that 2 fulvenes of very similar structure should react in a completely different manner! In fact, thermal reaction of pure fulvenes can be controlled directly in the NMR-tube. With decreasing intensity of the fulvene one observes very sharp signals of definite compounds. Our results show that the first step of thermal oligomerisation of simple fulvenes is (at least at 20 °C) a Diels-Alder reaction. In both cases dimeric products are isolated in the remarkably high yield of about 60% besides oligomeric and/or polymeric products[38].

R = R' = H, CH₃ ; R = H, R' = CH₃   XXI
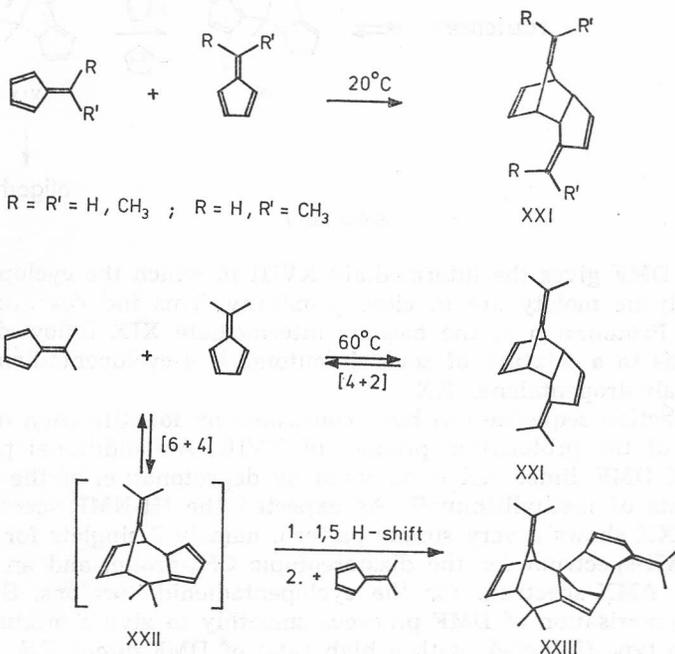
Scheme 9

A very interesting behaviour is shown by 6,6-dimethylfulvene (DMF): Under kinetic control again dimer XXI is formed at 20 °C, the reaction rate being very low (ca. 15% of XXI after 1 month). In this case however, dimer XXI (R=R'=CH₃) equilibrates at 60 °C with monomeric DMF, and a trimer is isolated from the reaction mixture with a 35% yield. The structure of trimer XXIII has been roughly assigned by NMR-spectroscopy[38] and definitively proved by X-ray analysis[39]. Formation of XXIII may be explained by a thermodynamically controlled [6 + 4] cycloaddition of 2 molecules of DMF. In this case a 1,5-H-shift in the cyclopentadiene unit of XXII and Diels-Alder addition of a third fulvene molecule to XXIII would complete the sequence DMF → XXIII.

The results presented here show that polymerisation of simple fulvenes proceeds in a very definite manner: Cationic polymerisation of pentafulvenes gives 1,2-linked polyfulvenes XIV of high molecular weight, which very often show a remarkable sensitivity to oxygen. Anionic as well as thermal initiation gives oligomeric mixtures with a high percentage of dimers and

(in the anionic case) quite surprising structure. In the case of thermal reactions of fulvene and 6-methylfulvene earlier speculations have been corrected, while DMF shows a remarkable trimerisation reaction at 60 °C.

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SAŽETAK

Struktura polifulvena

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i C. Rentsch

Struktura polimera pentafulvena nije do sada određena. Autori su našli da
kationska polimerizacija 6,6-disupstituiranih pentafulvena daje jako nezasićene, reak-
tivne makromolekule visoke molekulske težine. Razmotreni su mehanistički putevi
koji vode do polimera i predočen je spektroskopski dokaz za jednu od struktura.

Nasuprot indikacijama u literaturi, glavni proces u termičkoj oligomerizaciji
jednostavnih pentafulvena jest Diels-Alderova reakcija.

Anionska ploimerizacija pentafulvena može se inicirati tragovima natrij-ciklo-
pentadienida i fenilnatrija. Produkt je mješavina oligomera niza (fulven)$_n$. Određi-
vanje strukture fulven-dimera pomoglo je u objašnjenju toga iznenađujućeg rezultata.
Prodiskutirani su mehanistički aspekti reakcije.

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