123. Synthetic Attempts towards 'Aromatic' Nonafulvenes[1])

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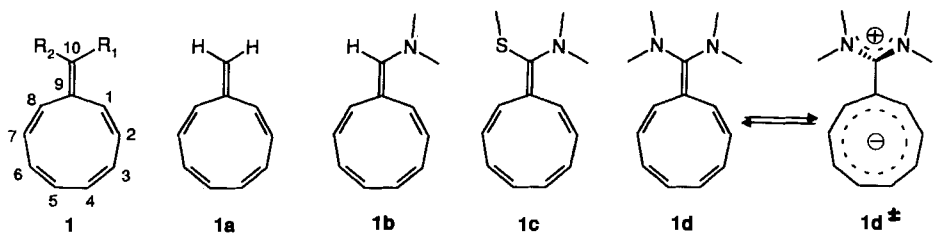
According to their spectroscopic behavior, four classes of nonafulvenes may be distinguished, but, so far, only three classes have been identified. *Type-A* nonafulvenes (including parent **1a**) are typically olefinic molecules with strongly alternating bond lengths and a nonplanar nine-membered ring. *Type-B* nonafulvenes are characterized by four pairs of equivalent ring H-atoms and ring C-atoms. Spectra of both *Type-A* and *Type-B* nonafulvenes are not dependent on temperature and solvent polarity. However, spectra of *Type-C* nonafulvenes (including prototype **1d** with $R^1 = R^2 = NMe_2$) are strongly influenced by temperature and solvent polarity due to an equilibrium $\mathbf{1} \rightleftarrows \mathbf{1}^{\pm}$ between the nonpolar olefinic **1** and dipolar planarized $\mathbf{1}^{\pm}$. So far, *Type-D* nonafulvenes occurring exclusively in the dipolar form $\mathbf{1}^{\pm}$ were unknown. Synthetic attempts towards nonafulvenes of *Type D* are described and problems encountered in nonafulvene syntheses are discussed. Several new cyclononatetraenes and four new nonafulvenes (or nonafulvalenes) **3l**, **1n**, **3**, and **5** have been synthesized. Spectroscopic evidence shows that 11,12-bis(diethylamino)nonatriafulvalene **5** is the first *Type-D* nonafulvene.

1. Introduction. – Since the first synthesis of a non-annelated nonafulvene 25 years ago [2] these cross-conjugated nonbenzenoid molecules have fascinated chemists[2]). Most nonafulvenes prepared so far, including parent **1a** [5], are typically olefinic molecules with strongly alternating bond lengths and a non-planar nine-membered ring. Due to an easy switch of the exocyclic C=C bond, pairs of ring H-atoms and of ring C-atoms are NMR-spectroscopically equivalent for **1** with $R^1 = R^2$, but not equivalent for $R^1 \neq R^2$[3]) (*Type A*). However, with increasing electron-donating capacity of substituents R^1, R^2 (*e.g.* **1c**), only four ^{1}H-NMR signals and (besides C(9)) four ^{13}C-NMR signals are seen in the olefinic range of NMR spectra as soon as rotation around the exocyclic C=C bond becomes fast enough (*Type B*). For both *Types A* and *B* of nonafulvenes, all the NMR parameters are not influenced by changes of temperature or solvents.



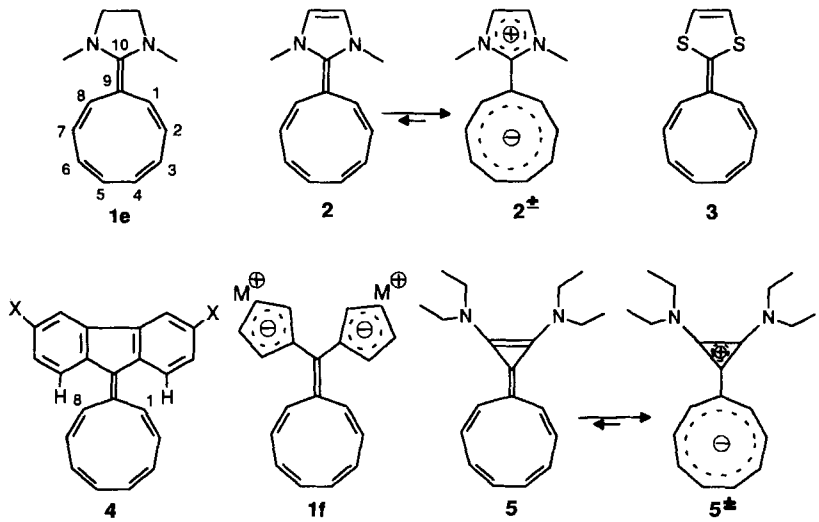
[1]) Fulvenes, Fulvalenes, Part 67; Part 66: [1].

[2]) Surveys see [3] [4].

[3]) A typical example is 10-(dimethylamino)nonafulvene (**1b**) whose 400-MHz ^{1}H-NMR has been completely analyzed [6].

The most spectacular NMR-spectroscopic behavior is shown by *Type-C* nonafulvene **1d** [2] [7]: at room temperature and in apolar solvents, **1d** displays features typical for olefinic nonafulvenes of *Type A* or *B*. However, lowering temperature from room temperature to −80° (or going to polar solvents) induces a low-field shift of H-atoms to the aromatic range, a substantial increase of ^3J values and a high-field shift of C(1)–C(8). This surprising behavior has been explained with an equilibrium **1d** ⇄ **1d**$^{\pm}$ [8]: If **1d**$^{\pm}$ and **1d** possess a similar energy content, then solvent or temperature effects might favor either **1d** or **1d**$^{\pm}$.

Finally, nonafulvenes whose dipolar aromatic form **1**$^{\pm}$ would be considerably lower than that of olefinic **1** should display all the characteristics of a dipolar compound with a planarized ring, but all the NMR parameters should be no more influenced by temperature effects or solvents (*Type D*). Nonafulvenes of that type are unknown so far.



We planned to test several promising concepts for the synthesis of *Type-D* nonafulvenes [9] including bridging of electron-releasing exocyclic substituents (see **1e**); introducing $+M$ substituents into an aromatic 6π-system (see **2**, **3**); combining electronic effects with steric effects[4]) (see **4**); introducing stronger $+M$ substituents (see **1f**); attaching electron-donating groups to a π-system being supposed to increase the electronic effect (see **5**).

The synthetic concepts of nonafulvenes are well-known and have been reviewed [4] [10]. Main problems are the low nucleophilicity of CNT anions **6**, the thermal instability of intermediate cyclononatetraenes, and severe problems encountered in the final HX elimination from intermediate cyclononatetraenes (see *Discussion*).

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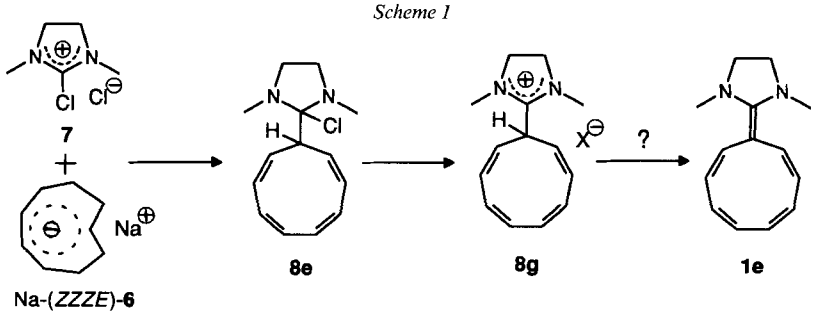
[4]) For X = Me_2N, **4** would have exocyclic electron-releasing substituents. Furthermore, aromatic H-atoms would sterically interfere with H–C(1) and H–C(8) and favor an out-of plane arrangement of the two ring systems. (An out-of plane arrangement is assumed to be correct for **1d**$^{\pm}$ [8].)

2. Synthesis of Novel Nonafulvenes. – 2.1. *Nonafulvenes with Bridged Electron-Releasing Exocyclic Substituents.* It is well-known from pentafulvenes [11] that the electron-donating capacity of exocyclic N, O, or S substituents is somewhat increased, if the heteroatoms are arranged within a five-membered ring; the reason is a maximum π-overlap of appropriate lone-pairs of heteroatoms with the π-system of the exocyclic C=C bond. If one takes into account that for **1d** both the apolar (**1d**) and the polar form (**1d**$^{\pm}$) are nearly of the same energy, exocyclic bridging, to give **1e**, could already be sufficient in order to favor the dipolar form **1e**$^{\pm}$.

Completing earlier attempts [12][5]), we observed that reaction of Na-(*ZZZE*)-**6** with 1-chloro-2,3-dimethylimidazolium chloride (**7**) at −50° in CH_2Cl_2/THF gave cyclononatetraene **8e** according to its ^{1}H- and ^{13}C-NMR data, while **8g** had been obtained earlier (*Scheme 1*)[5]). Transformation **8e** → **8g** could be easily and nearly quantitatively realized with *Lewis* acids like BF_3. However, the attempted HX elimination of **8g** to give nonafulvene **1e** failed.

Scheme 1



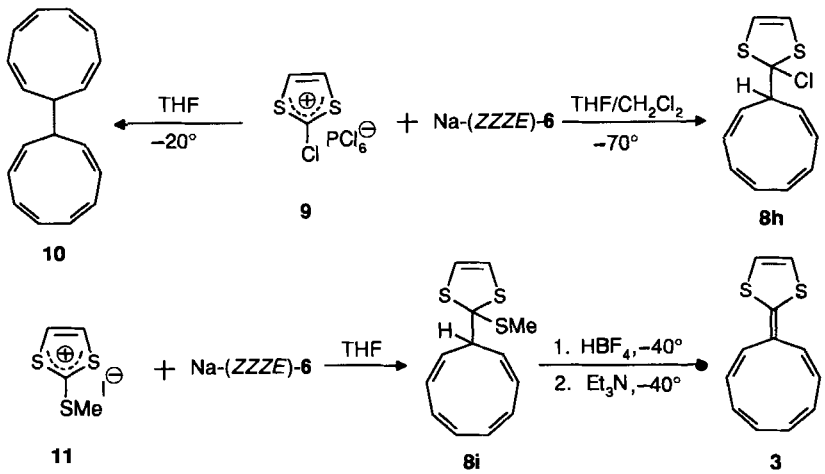
2.2. *Nonafulvenes Including* +M *Substituents into an Aromatic 6π-System.* 1,4-Diazanonapentafulvalenes of type **2** are very attractive candidates in view of the envisaged *Type-D* nonafulvenes, because the dipolar form **2**$^{\pm}$ should be strongly stabilized by the 6π system of the five-membered ring. Similarly, 1,4-dithianonapentafulvalenes **3** are electronically interesting as well, although it is well-known that the electron-releasing properties of heteroatoms are strongly decreasing in the series N > O > S.

Due to the attraction of **2**, we once more repeated earlier experiments of *Otter* [13]. However, reaction of 2-chloro-1,3-dimethylimidazolium chloride with Na-(*ZZZE*)-CNT **6** failed to give **2** under various conditions [9].

1,4-Dithianonapentafulvalene (**3**) should, in principle, be available by reaction of 1,3-dithiolium salts (bearing a potential leaving group at C(1)) with cyclononatetraenide followed by HX elimination out of the corresponding cyclononatetraene intermediate **8** (*Scheme 2*, see **8h**, **8i**). We knew, however, from earlier experiments [14] that 1,3-dithi-

[5]) Ten years ago, *Otter* [13] had reacted Na-(*ZZZE*)-**6** with **7** to give **8g** [12] [13], ^{1}H-NMR of which showed signals of vinylic H-atoms between 6.2 and 5.6, H–C(9) at 5.34, NCH_2 at 4.19 and NCH_3 at 3.22 ppm. This time [9], the same reaction under similar conditions [9] undoubtedly gave **8e** according to the ^{1}H-NMR (300 MHz, $CDCl_3$), with vinylic H-atoms between 6.2 and 5.2, H–C(9) at 4.68, NCH_2 at 2.61 and CH_3 at 2.01 ppm. **8g** is supposed to be the intermediate in the attempted elimination **8e** → → **1e**.

Scheme 2



olium salt **9** reacted with Na-(*ZZZE*)-**6** at −20° in THF under oxidative coupling[6]) to give 1,1′-bi(cyclononatetraenyl) **10** in a 74% yield[7]). Repeating these experiments, we realized that the reaction **9** + **6** → **10** may be suppressed, if Na-(*ZZZE*)-**6** is very slowly added to a stirred suspension of dithiolium salt **9** in THF/CH_2Cl_2 at −70°; it is surprising to see that in this case the envisaged cyclononatetraene **8h** is formed in a yield of 78%! Unfortunately, base-catalyzed HCl eliminations using a variety of bases as well as *Lewis*-acid-induced eliminations failed to give the target fulvalene **3**.

This failure brought us back to an alternative approach (*Scheme 2*, lower part) which we already had attempted several years ago starting with cyclononatetraene **8i** [12]: We considered acid-induced E_1 eliminations to be very promising and reacted cyclononatetraene **8i** first with 1.1 equiv. of HBF_4 in CH_2Cl_2 before treating the mixture at −40° with Et_3N. In fact, in this case $HSCH_3$ elimination is possible, although in moderate yield (30%), and yellow dithio-nonapentafulvalene **3** is isolated after low-temperature chromatography. All the spectroscopic data are consistent with structure **3**. They convincingly show that **3** belongs to the *Type A*[8]).

2.3. *Synthetic Attempts towards Sterically Shielded Nonafulvenes.* According to HMO calculations as well as to the experimental results available now, it is well established that π delocalization as well as charge separation of nonafulvenes is increased by electron-donating substituents at the exocyclic C(10). For the dipolar form $\mathbf{1}^{\pm}$ (see $\mathbf{1d}^{\pm}$ or $\mathbf{2}^{\pm}$), charge separation is complete, the exocyclic substituents (or the exocyclic π system, see $\mathbf{2}^{\pm}$ or $\mathbf{5}^{\pm}$) are fully delocalizing the positive charge of C(10), and the length of the C(9)–C(10) bond approaches that of a single bond. The consequences are that for dipolar forms $\mathbf{1}^{\pm}$, $\mathbf{2}^{\pm}$ *etc.* the exocyclic π system does not have to be coplanar to the planarized nine-membered ring. In fact, for $\mathbf{1d}^{\pm}$ an out-of-plane arrangement of the formamidinium unit has been

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[6]) Obviously, **9** is the oxidant.

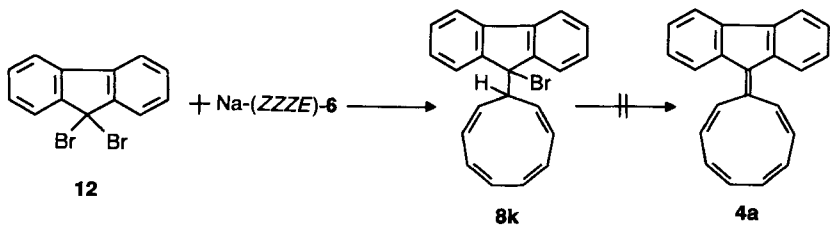
[7]) First synthesis of **10**: [15]; a nearly quantitative coupling takes place, if **6** is reacted with $AgBF_4$ [16].

[8]) NMR Spectra of nonafulvenes and nonafulvalenes will be extensively discussed elsewhere.

assumed [8][9]). On the other hand, steric effects between H–C(1)/H–C(8) of the nonafulvene and substituents could be deliberately increased, in order to favor an out-of-plane arrangement of the substituents. In a model compound of type **4** (X = NMe_2), steric and electronic effects could be combined in order to favor **4**$^{\pm}$.

We were carrying out first experiments in order to evaluate whether it would be possible to attach the fluorene unit to the cyclononatetraene unit. Reactions of that type (*Scheme 3*) are not trivial due to the low nucleophilicity of cyclononatetraenides **6**. In fact, direct nucleophilic substitution of 9,9-dibromofluorene (**12**) either with (*ZZZZ*)-**6** or with (*ZZZE*)-**6** failed. On the other hand, S_N1 substitution of **12** may be enhanced by activating **12** with *Lewis* acids. In fact, reaction of **12** with 1.1 mol-equiv. of $BF_3 \cdot Et_2O$ at $-70°$, followed by addition of Na-(*ZZZE*)-**6** gave yellow crystals of cyclononatetraene **8k** in a surprisingly high yield (81%).

Scheme 3



12 **8k** **4a**

Even more problems have to be expected for the elimination step **8k** → **4a** [4]. First of all, the acidity of cyclononatetraenes is comparably small. In addition, H–C(9) is sterically shielded by the non-planar nine-membered ring. Finally, if the fluorene and the cyclononatetraene rings of **8k** are nearly perpendicular to each other in the favored conformation, then the dihedral angle between H–C(9)–C(10)–Br will be unfavorable for a base-induced HBr elimination. In fact, all elimination experiments with various bases failed [9]. We hoped to overcome problems encountered in the final step **8k** → **4a** by activating **8k** with *Lewis* acids, however, these attempts failed as well [9].

2.4. *Attempted Synthesis of Nonafulvenes with Anionic Substituents.* It is well-known from pentafulvenes that nucleophiles easily attack at the exocyclic C(6) even at low temperature; if C(6) bears a potential leaving group, then addition-elimination takes place to give a new pentafulvene[10]). The so far unknown 10,10-dibromononafulvene (**11**) is an attractive target in view of an application in this synthetic sequence to nonafulvenes: so, nucleophilic displacement of bromide by an excess of cyclopentadienide could, in principle, give nonafulvene **1f** bearing two anionic exocyclic substituents. Further bridging of these substituents would result in an additional planarization of the exocyclic π system.

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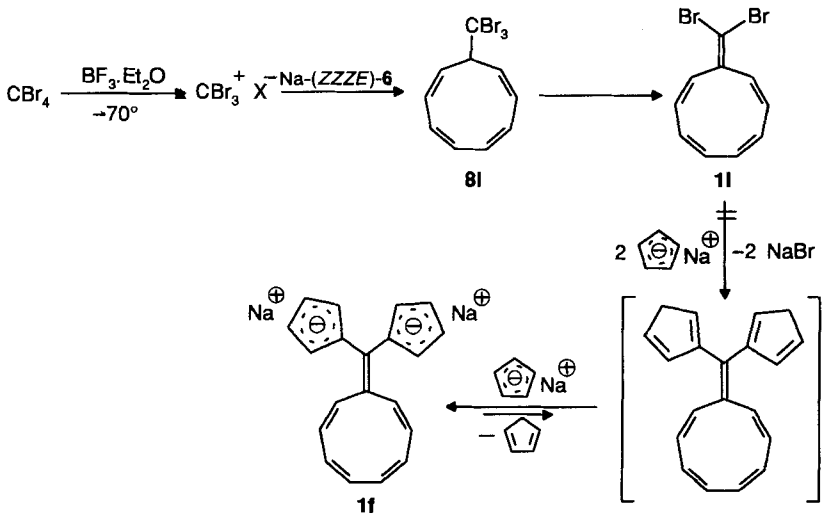
[9]) Unfortunately, no X-ray analysis of **1d**$^{\pm}$ is available so far. Indirect spectroscopic evidence for the out-of-plane arrangement of the formamidinium unit of **1d**$^{\pm}$ stems from ^{13}C-NMR data: going from **1d** to **1d**$^{\pm}$ by lowering temperature, C(9) is surprisingly shifted to higher frequency. This shift is easily explained if the formamidinium system is out-of-plane of the CNT unit ('steric release').

[10]) Survey: [4]; for typical examples, see [17].

Scheme 4



Despite the expected high reactivity of 10,10-dibromononafulvene (**1l**), the synthesis turned out to be surprisingly simple (*Scheme 4*). If CBr_4 was activated by $BF_3 \cdot Et_2O$, then subsequent reaction of the intermediarily formed tribromocarbenium ion with Na-(*ZZZE*)-**6** smoothly proceeded at −60° in THF to give, after workup and recrystallization, 41% of pale-yellow crystals of 1-(tribromomethyl)cyclonona-2,4,6,8-tetraene (**8l**). Furthermore, dehydrobromination readily took place, if **8l** was reacted with *t*-BuOK in the presence of 18-crown-6 in THF at −60°. After workup and recrystallization, yellow crystals of **1l** were isolated in a 59% yield.

Compound **1l** is the first nonafulvene bearing two σ acceptors at C(10). Corresponding to that substitution pattern, **1l** is expected to be a highly olefinic molecule. In fact, the half lifetime of the valence isomerization of **1l** is even shorter than that of parent nonafulvene **1a** itself [5] (see later). It may be expected that the thermal instability of **1l** hampers the envisaged nucleophilic displacement reactions. In fact, the attempted displacement of bromide by an excess of cyclopentadienide (**1l** → **1f**) failed under various conditions. Displacement of Br by amides did not occur either. Surprisingly, **1l** did not react, even in the presence of LDA!

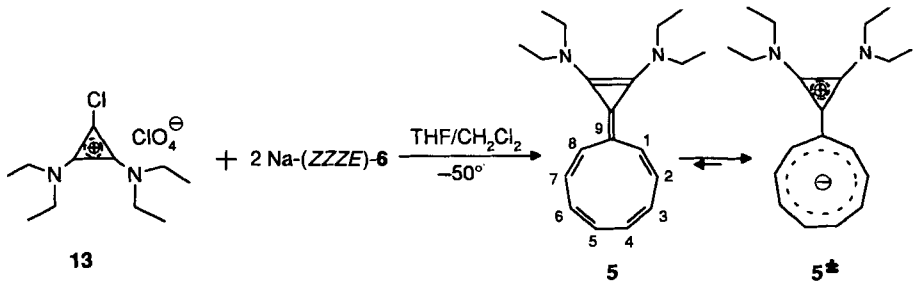
In our opinion the missing reactivity of **1l** towards nucleophiles (compared with 6,6-dihalo-pentafulvenes) is not only due to the enhanced 6π valence isomerization, but a result of the non-planar nine-membered ring of **1l** which strongly increases the activation energy of any nucleophilic attack at C(10)[11]).

2.5. *Synthesis of Nonatriafulvalenes.* Another promising concept for *Type-D* nonafulvenes consists in attaching strongly electron-donating substituents to a carbocyclic π

[11]) The first step of a nucleophilic displacement of Br by NEt_2 is the nucleophilic attack of $HNEt_2$ at C(10) of **1l**, giving a 1-{[dibromo(diethyl)ammonium]methyl}cyclononatetraenide as an intermediate: Thus formation of this intermediate affords a planarization of the ring which strongly increases the activation energy of a nucleophilic attack.

system placed at C(10) which is able to support or even increase the electron-releasing capacity of the substituents. It is well-known from calicenes (= pentatriafulvalenes) that the three- as well as the five-membered rings are stabilizing each other electronically[12]). Furthermore, if bond-length alternation of 6,6-bis(dimethylamino)pentafulvene is compared with that of 7,8-bis(dimethylamino)calicene, the result is that the three-membered ring even increases the capacity of electron-releasing substituents [22] [23]. Finally, since substituent effects are supposed to be effective in the same direction for nonafulvenes (and nonatriafulvalenes) as well as for pentafulvenes (and calicenes, respectively) [4], we expected that 11,12-bis(diethylamino)nonatriafulvalene (**5**) would be a perfect candidate for a *Type-D* nonafulvene (*Scheme 5*).

Scheme 5



Unsuccessful attempts towards **5** had been undertaken as early as 1978; however, they did not result in the isolation of the target molecule **5** [22][13]). Our experiments show that, if 2 mol-equiv. of Na-(*ZZZE*)-**6** are added dropwise to a stirred CH_2Cl_2 solution of the chloro-cyclopropenylium perchlorate **13**, an orange color develops. After centrifugation of salts and low-temperature crystallization, pale-yellow cubic crystals of **5** are isolated in a yield of 54%. Contrary to most nonafulvenes, crystals and solutions of **5**, when kept under Ar, are stable over days at room temperature and several hours at +50° and do not show any tendency of valence isomerization being typical for olefinic nonafulvenes. However, **5** polymerizes rapidly in the presence of O_2.

Of considerable importance concerning the structure of **5** and the position of the equilibrium **5** $\rightleftarrows$ $\mathbf{5}^{\pm}$ are the spectroscopic results, which will only be briefly discussed here[8]). The 600-MHz ^{1}H-NMR spectrum of **5** (*Fig. 1*) clearly shows that all the H-atoms of the ring are absorbing in the 'aromatic range' between 7.3 and 7.0 ppm. Additionally, the chemical shifts of NCH_2 (3.68 ppm) and NCH_2CH_3 (1.39 ppm) are nearly identical to those of positively charged **13** (3.50 and 1.32 ppm). This means that, according to

[12]) The dipole moments of pentafulvene and triafulvene are experimentally found to be 0.424 D [18] and 1.90 D [19], respectively. Both values match reasonably with the results of *ab initio* calculations [20], and the two systems are, as expected, polarized in the opposite direction. However, a significantly increased dipole moment of 4.3 D is calculated for planar calicene [21]!

[13]) *Araki* [22] reacted **13** together with 2 equiv. of the less nucleophilic Li-(*ZZZZ*)-**6** in THF at 0° and reported the identification of a valence-isomerization product of protonated **5** as a perchlorate. Compound **5** was not observed [22], and the data of the valence isomerization product strongly differ from those of **5**. We were not able to reproduce *Araki*'s sequence.

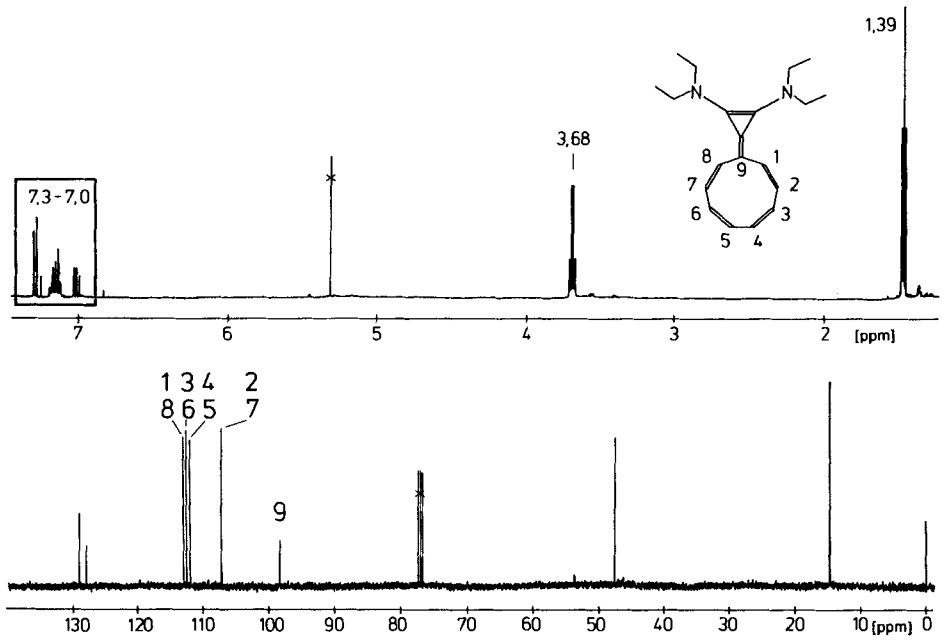
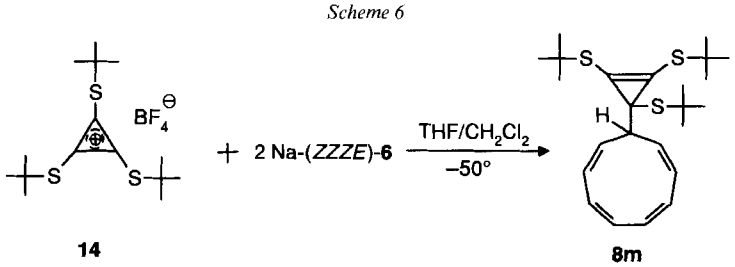


Fig. 1. *^{1}H-NMR* (600 MHz, $CDCl_3$, 25°) *and ^{13}C-NMR spectrum of* **5** (100 MHz, $CDCl_3$, −30°, below)

^{1}H-NMR shifts, the structure of the compound is best represented by $\mathbf{5}^{\pm}$. Furthermore, as expected for $\mathbf{5}^{\pm}$, the ^{13}C-NMR resonances of the C-atoms of the nine-membered ring are centered around 110 ppm (*Fig. 1*), which is in agreement with a negatively charged nine-membered ring, while the signals of C(11) and C(12) as well as those of NCH_2 and NCH_2CH_3 appear in the same region as those of **13**. These findings are in agreement with a positively charged three-membered ring. Finally, all the NMR parameters (including the nearly equally large ^3J(H,H) coupling constants) are not influenced in the temperature range of −50 to +50° nor by solvent polarity. That means that the equilibrium $\mathbf{5} \rightleftarrows \mathbf{5}^+$ is completely shifted towards $\mathbf{5}^{\pm}$ independently of solvent and temperature, *i.e.*, **5** is *the first nonafulvene of* Type D.

Finally, although the electron-releasing capacity of alkylthio substituents is considerably reduced as compared to R_2N groups, we made some experiments towards the synthesis of 11,12-bis(*tert*-butylthio)nonatriafulvalene starting from **14** and were able to

Scheme 6



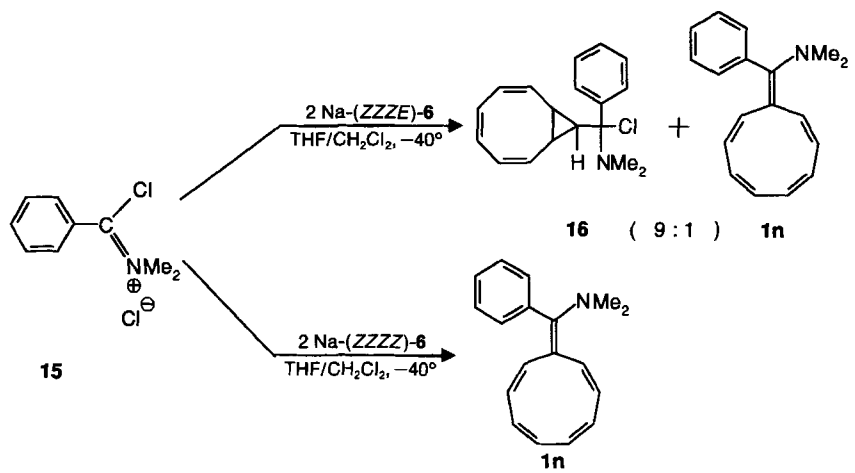
14 **8m**

isolate the key-intermediate **8m** (*Scheme 6*). However, so far the attempted elimination of (*t*-Bu)SH (both *via E*2- and *E*1-type mechanisms) failed [9].

2.6. *Synthesis of a Spectroscopically Interesting Model Compound.* 10-(Dimethylamino)-10-phenylnonafulvene (**1n**) is spectroscopically interesting for several reasons: First of all, **1n** is assumed to be a *Type-A* nonafulvene bearing eight nonequivalent ring H-atoms and nine nonequivalent ring C-atoms. It is also supposed that **1n** takes an intermediate position between **1a** and **1d** as far as the electron-releasing capacity of substituents is concerned. Finally, it is sterically more similar to **1d** than 10-(dimethylamino)nonafulvene (**1b**) so that ^{13}C-chemical shifts of ring C-atoms of **1d** and **1n** should be comparable, free of steric effects of the substituents.

If chloro(dimethylamino)benzylium chloride (**15**) is reacted with 2 equiv. of Na-(*ZZZE*)-**6** (*Scheme 7*, upper part), then the reaction mixture obtained, after chromatographic workup, consists of a 9:1 mixture of bicyclic **16** together with nonafulvene **1n**. It

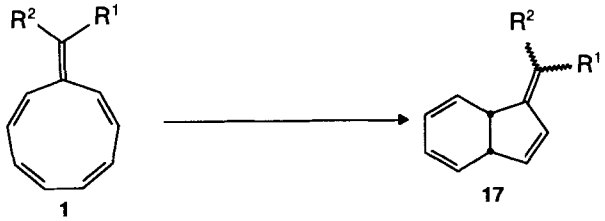
Scheme 7



is well-known that (*ZZZE*)-**6** has several nucleophilic centres [24]: nucleophilic attack with C(1) leads to cyclononatetraenes **8**, while attack with C(4) to C(7) gives, after rearrangement, bicyclo[6.1.0]nonatrienes of type **16**. In most cases, especially in reactions with delocalized carbenium ions, (*ZZZE*)-**6** reacts with C(1) [25] and is, therefore, preferred, due to its higher nucleophilicity compared with (*ZZZZ*)-**6**. In reactions of (*ZZZE*)-**6** with bulky electrophiles, however, bicyclo[6.1.0]nonatrienes **16** are the main products. The observed reaction (*Scheme 7*, upper part) is surprising in so far that carbenium ion **15** is involved. The formation of **16** can easily be avoided by using Na-(*ZZZZ*)-**6** as a nucleophile (and a base as well). In this case, yellow crystals of **1n** can be isolated in a yield of 61%.

3. Valence Isomerization of Nonafulvenes and Nonafulvalenes. – Thermal stability of most cyclononatetraenes **8** and nonafulvenes **1** (as well as of nonafulvalenes of type **3**) is essentially limited by the well-known disrotatory ring closure to give *cis*-3a,7a-dihydroindenes (from **8**) and *cis*-3a,7a-dihydrobenzofulvenes **17** (from **1**; *Scheme 8*). There is a

Scheme 8



thumb rule [26] [12] stating that thermal stability[14]) of nonafulvenes **1** qualitatively increases with increasing electron-releasing capacity of substituents R^1 and R^2. In fact, corresponding to the highly olefinic nature of parent **1a**, the half lifetime of the process **1a** → **17a** is only 12 min at 0° in $CDCl_3$ [5], while $\tau_{½}$ of **1b** → **17b** increases to 36 min in $CDCl_3$ at 40° [26]; **1d** is still much more stable with $\tau_{½}$ of 3 days at room temperature in $CDCl_3$ [7].

All the nonafulvenes and nonafulvalenes prepared in the frame of this work are behaving according to the rule given above: 10,10-dibromononafulvene (**1l**) with two $-I$ substituents is even more reactive than **1a**: $\tau_{½}$ of the cyclization **1l** → **17l** could only roughly be estimated to be less than 10 min in $CDCl_3$ at −10° [9]. Due to the considerable stabilization by electron-releasing substituents, the $\tau_{½}$ of cyclization of nonafulvene **1n** as well as of nonafulvalene **3** were easily determined by ^{1}H-NMR spectroscopy and turned out to be 96 min for **1n** and 63 min for **3**, both being measured in $CDCl_3$ at 37°.

On the other hand, 11,12-bis(diethylamino)nonatriafulvalene (**5**) does not undergo cyclization even when heated over hours at 50° in $CDCl_3$. This is in agreement with the conclusion that the equilibrium **5** ⇄ $\mathbf{5}^{\pm}$ completely on the side of $\mathbf{5}^{\pm}$, *i.e.* the chemical evidence of $\mathbf{5}^{\pm}$ is in agreement with the spectroscopic results.

4. Discussion. – In the work presented here, several concepts for the synthesis of *Type-D* nonafulvenes have been investigated, and besides novel 10,10-dibromononafulvene (**1l**) (needed as a synthetic intermediate) and 10-(dimethylamino)-10-phenylnonafulvene (**1n**; used for spectroscopic comparison) two so far unknown nonafulvalenes **3** and **5** have been prepared. While 1,4-dithianonapentafulvalene (**3**) behaves like a *Type-A* nonafulvene being characterized by a non-planar nine-membered ring, all the spectroscopic evidence[8]) clearly demonstrates that **5** is *the first* Type-D *nonafulvene* for which the dipolar structure $\mathbf{5}^{\pm}$ is predominant in the whole investigated temperature range and even in apolar solvents.

The considerable number of unsuccessful attempts once again shows that there are enormous preparative problems encountered in cyclononatetraene and nonafulvene synthesis. Some of these problems have already been discussed [12] [25]. They are substantially increased by the thermal instability of cyclononatetraenes **8** as well as of most nonafulvenes **1** which in many cases affords reactions – as well as workup procedures – at temperatures below 0°. As far as the synthesis of cyclononatetraenes is concerned, the low nucleophilicity of cyclononatetraenides is a major problem which makes reactive elec-

[14]) Thermal stability of nonafulvenes **1** is quite easily estimated by measuring $\tau_{1/2}$ of nonafulvenes in the first-order reaction **1** → **17**, *e.g.*, by ^{1}H-NMR spectroscopy.

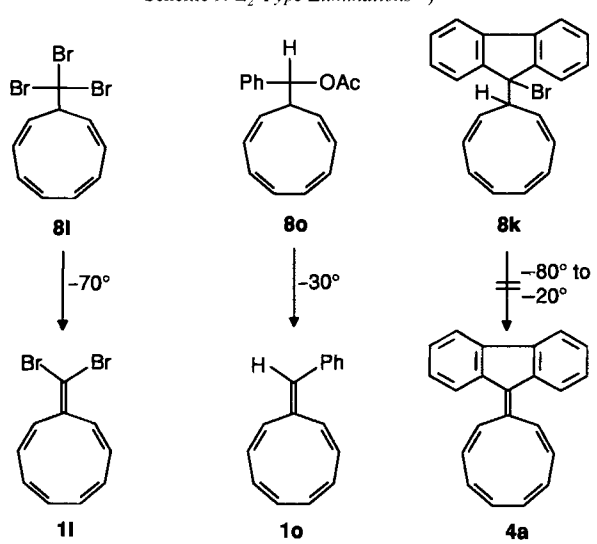
trophiles indispensable. Although Na-(*ZZZE*)-**6** is more nucleophilic than Na-(*ZZZZ*)-**6**, it cannot be used in every synthesis, because, in the case of bulky electrophiles, side-reactions may occur (see *Scheme 7*). However, the results presented here show that, if appropriate conditions are elaborated, cyclononatetraenes **8** are in many cases available in reasonable yields.

Numerous failures show that the most problematic step of a nonafulvene synthesis is the elimination **8** → **1** + HX. First of all, cyclononatetraene is much less acidic than cyclopentadiene [27]. Combined with steric shielding of H–C(9) by the non-planar cyclononatetraene ring, deprotonation of substituted cyclononatetraenes is difficult, and [1,5]-sigmatropic H-shifts do not help as they are too slow at low temperature. Therefore, it can be assumed that *E*1*cb* elimination is not the predominant pathway in the synthesis of nonafulvenes from cyclononatetraenes.

However, in view of a smooth *E*2 elimination of HX, the proton as well as the leaving group X should assume a *trans*-diaxial-arrangement with a dihedral angle close to 180°. In the course of our present as well as of earlier experiments [12], we were often surprised to see that, in some cases, *E*2-type eliminations were proceeding quite easily at low temperature while they did not work in other cases under similar conditions.

For example, HBr elimination from **8l** to give **1l** proceeds easily at −70°, and even AcOH elimination from **8o** to give 10-phenylnonafulvene (**1o**) is possible at −30° [12], while several attempts to realize HBr elimination from **8k** failed to give nonafulvene **4a** under various conditions (*Scheme 9*)[15]). Of course, the substituent of **8k** is relatively bulky (although the fluorene π system is planar). However, inspection of stereomodels suggests that the main reason for the failure of the sequence **8k** → **4a** is not so much due to steric shielding H–C(1) of the cyclononatetraene, but to an out-of-plane arrangement of the

Scheme 9. E_2-*Type Eliminations*[15])



[15]) All the eliminations have been accomplished or attempted with *t*-BuOK/18-crown-6 in THF.

bromofluorene unit with respect to the cyclononatetraene unit in the favored conformation. If, additionally, rotation around the central C–C bond of **8k** would be frozen at low temperature, then *E*2 elimination of HBr (requiring a dihedral angle of *ca.* 180° between H and Br) would not be possible.

This idea is, in principle, confirmed by force-field calculations of **8k** (*Fig. 2*, right part) which shows a dihedral angle between H and Br of 90° for the energetically favored conformation. On the other hand, in the energetically favored conformation of **8l** (*Fig. 2*,

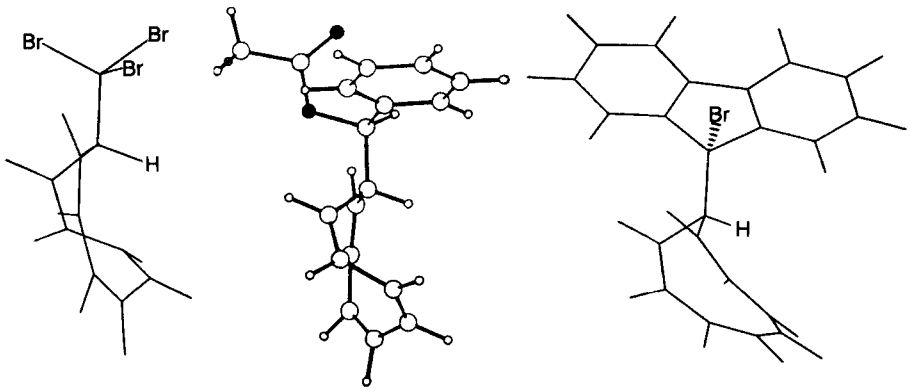
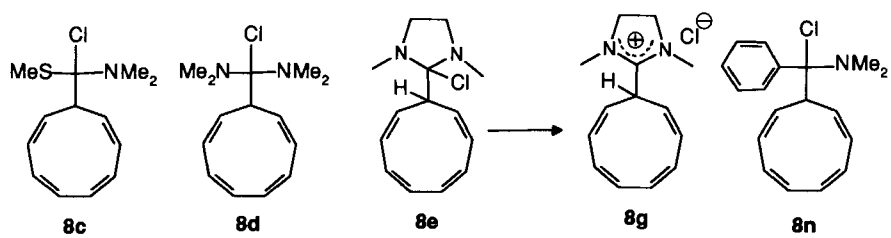


Fig. 2. *Conformations of cyclononatetraenes* **8l** (left) *and* **8k** (right) *according to MM2 force-field calculations and conformation of* **8o** (middle) *according to X-ray analysis* [28]

left part), H and Br are approximately in a *trans-diaxial*-arrangement. The same conformation of **8o** is even the favored one in the crystal (*Fig. 2*, middle part [28]). Therefore, we believe that many failures observed in *E*2-type elimination reactions of bulky cyclononatetraenes might be due to an unfavorable dihedral angle of H and X in the energetically favored conformation, combined with a strongly hindered or even frozen rotation around the central C–C bond.

Since *E*1*cb* eliminations are at least not easy in cyclononatetraenes, and *E*2 eliminations may fail for bulky compounds **8**, the question arises whether *E*1-type eliminations would be possible. Bearing in mind that eliminations of substituted cyclononatetraenes **8** are realized in solvents of comparably low polarity like THF and at low temperature, *E*1 eliminations seem to be problematic unless exocyclic substituents of **8** would be strongly stabilizing the hereby formed carbenium ion intermediate. This is the case for cyclononatetraenes of type **8e** (see *Scheme 1*) and similar cyclononatetraenes **8c**, **8d**, **8n**.



8c **8d** **8e** **8g** **8n**

In fact, *E*1 elimination **8e** → **8g** has been established by NMR spectroscopy [12], because subsequent deprotonation of **8g** is extremely slow[16]) established, while in all the other cases shown above deprotonation is so fast that nonafulvenes **1c**, **1d**, and **1n** are isolated instead of cyclononatetraenes **8c**, **8d**, and **8n**. A general rule says that there is a strong support for an *E*1-type elimination as soon as formal elimination **8** → **1** takes place in the presence of cyclononatetraenide **6**, which is normally known to be ineffective in *E*2 eliminations.

Furthermore, our experiments show that *E*1 eliminations sometimes may be successfully induced in cases where *E*2 eliminations **8** → **1** do not proceed, namely by reacting the cyclononatetraene **8** with 1 equiv. of HBF_4 or of $BF_3 \cdot Et_2O$ prior to elimination (see *Scheme 2*; **8i** → **3**). Even 'induced *E*1 eliminations' fail, however, for reactions **8g** → **1e** and **8k** → **4a** (*Scheme 3*) where the exocyclic substituents R^1 and R^2 are part of a very bulky ring system[16]).

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Experimental Part

General. Spectra were recorded with the following instruments: UV: *Philips PU 8740*. IR: *Perkin-Elmer 399b* and *782*. NMR: *Bruker AMX-600*, *AM-400*, *AC-300*; *Varian EM 360 L*. MS: *Varian MAT CH 7A*. HR-MS: *Varian MAT 311*. Syntheses of cyclononatetraenes and nonafulvenes were all run under Ar in a 50-ml three-necked round flask equipped with a thermometer, a magnetic stirring bar, and a pressure-equalizing dropping funnel with cooling jacket fitted with an Ar bubbler. Prior to the introduction of reagents, the reaction system was thoroughly flame-dried while flushed with Ar. Small amounts of sensitive liquid compounds or solns. were injected into the reaction vessel through the septum with a syringe. For long-term low-temp. reactions, a cooling machine (*Huber HS-80*) was employed. ^{1}H-NMR spectra were often used for controlling the reaction. Since most cyclononatetraenes and nonafulvenes are thermally unstable and quite sensitive towards moisture and O_2, most normal workups could not be applied in these cases. All manipulations had to be performed under inert gas and at low temp.

Special Manipulations. Centrifugation. If the reaction mixture was a suspension, a certain amount of cold pentane/Et_2O 1:1 was added to complete precipitation. The suspension was then transferred through a cooled *Teflon* tube into a 70-ml centrifugation tube by applying a slight pressure of Ar or N_2, and subsequent centrifugation took place in a minicentrifugator (*Minifuge Heraeus Christ*) at −30° with 4000 U/min for 10–15 min. After transferring the resulting soln. under Ar through a *Teflon* tube into a cooled flask, the residue was washed twice with the same solvent, once more centrifugated and the resulting solns. were combined with the original soln.

Filtration. For filtering off inorg. salts, a long (*ca.* 40 cm) chromatography column with a cooling jacket was employed and cooled to the appropriate temp. with a cooling machine. The column was filled with 35 g of Alox (basic I) or with 30 g of deactivated silica gel, topped with 10 g of seasand and cooled to −40°. The mixture was then transferred to the column with a cold *Teflon* tube under slight pressure of inert gas and eluted with precooled pentane/Et_2O 1:1. The filtrate was collected in a cooled flask under a static of pressure of inert gas.

Chromatography. Further purification of cyclononatetraenes and nonafulvenes was normally performed by low-temp. chromatography. For that purpose, a column with a cooling jacket was filled with deactivated silica gel at −40° to −60° under inert gas. First, the column was eluted with precooled pentane to remove unpolar impurities, then the polarity of the eluent was increased according to the TLC, until elution of the desired compounds took place. All the eluents were kept under Ar and stored at −78° in a CO_2/i-PrOH bath during the operation.

Deactivating Silica Gel. Deactivated silica gel was prepared by drying the silica gel (*C560 Uetikon*, 60–200 μm) at 120°/0.01 mbar. After cooling, pentane was added to give a slurry to which 5 weight-% of Et_3N (corr. to the silica gel) was dropped. The mixture was first rotated in a rotatory evaporator (*Fig. 3*) for two h, then unreacted Et_3N

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[16]) We assume that deprotonation is so slow because, due to a nearly perpendicular arrangement of the two rings (and due to a frozen rotation around the exocylic C–C bond), the CNT proton does not overlap with the p orbital of the carbenium ion.

was removed by washing with pentane/Et_2O 3:1. Finally, the mixture was dried in a rotatory evaporator (*Fig. 3*) at 100°/0.1 mbar.

Low-Temperature Rotating Evaporation. Evaporation of solvents at low temp. was carried out in the apparatus shown in *Fig. 3*. The evaporator was run at −40°/0.1 mbar to get rid of solvents with low boiling point such as pentane, Et_2O, and CH_2Cl_2. THF and $CHCl_3$ could be removed by adding Et_2O and by 2–3-fold repeated evaporation.

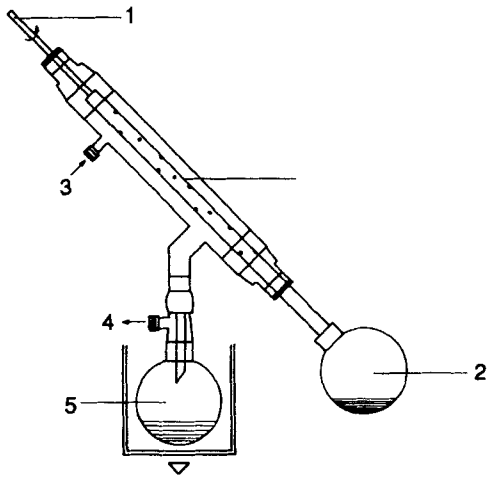

Fig. 3. *Low-temperature rotatory evaporator* (*1*: motor; *2*: perforated glass-tube connected with motor; *3*: N_2 inlet; *4*: vacuum inlet; *5*: condensed solvent cooled by liquid N_2; *6*: reaction mixture)

1. Synthesis of Cyclononatetraenides 6. – Slightly modified and optimized procedures according to [27] [29] [30], which are extensively described in [25].

Isomerization of Sodium (2Z,4Z,6Z,8E)-Cyclonona-2,4,6,8-tetraenide (Na-(*ZZZE*)-**6**) *to Sodium (2Z,4Z,6Z,8Z)-Cyclonona-2,4,6,8-tetraenide* (Na-(*ZZZZ*)-**6**). A soln. of 150 to 170 ml of 0.3–0.4M Na-(*ZZZE*)-**6** in THF, kept under N_2 or Ar, is transferred to the photolysis apparatus (*Fig. 4*). The THF soln. is cooled with H_2O and irradiated during 12 to 16 h with a 125-W high-pressure Hg lamp (*Hanau 125*) under stirring. Every few h, the isomeric ratio is controlled by ^{1}H-NMR. After 14–16 h, a ratio of 9:1 for Na-(*ZZZZ*)-**6**/Na-(*ZZZE*)-**6** is observed.

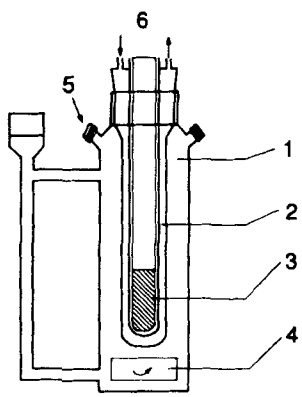

Fig. 4. *Photolysis apparatus* (*1*: reaction flask; *2*: cooling jacket; *3*: Hg lamp; *4*: *Teflon* magnetic stirring bar; *5*: N_2 inlet; *6*: H_2O inlet and outlet)

2. Attempted Synthesis of 10,10-(*N,N'*-Dimethylethylendiamino)nonafulvene (= *2-(Cyclonona-2,4,6,8-tetraen-1-ylidene)-1,3-dimethylimidazolidine;* **1e**; *Scheme 1*). *2-Chloro-2-(cyclonona-2,4,6,8-tetraen-1-yl)-1,3-dimethylimidazolidine* (**8e**). A 50-ml three-necked flask equipped with a magnetic stirring bar, a thermometer, a septum as well as an Ar bubbler was flame-dried while flushed with Ar. The flask was charged with 170 mg (1 mmol) of *(2-chloro-1,3-dimethylimidazolidinium chloride)* (**7**), 15 ml of CH_2Cl_2 and then cooled to −60°. At this temp., 2 ml (2 mmol) of Na-(*E,Z,Z,Z*)-**6** (1.001M in THF) were dropwise added under Ar with a syringe during 20 min. After the addition was complete, the orange suspension with yellow precipitate was stirred for 4 h at −40° to −50°, 20 ml of cooled pentane/Et_2O 1:1 were added, and the mixture was stirred at −78° for 10 min. Then, it was centrifugated for 10 min with 4000 U/min at −30° under Ar. The resulting soln. was concentrated at −40°/0.1 bar to give 122 mg of yellow, partly solid crude **8e**. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.12 (*m*, 2 H); 6.00 (*m*, 2 H); 5.84 (*m*, 2 H); 5.20 (*m*, 2 H); 4.68 (*m*, 1 H); 2.61 (*s*, 4 H); 2.01 (*s*, 6 H)[17]).

3. Synthesis of 11,14-Dithianonapentafulvalene (= *2-(Cyclonona-2,4,6,8-tetraen-1-ylidene)-1,3-dithiole;* **3**; *Scheme 2*). – 3.1. *2-Chloro-2-(cyclonona-2,4,6,8-tetraen-1-ylidene)-1,3-dithiole* (**8h**). A 50-ml three-necked flask equipped with a magnetic stirring bar, a septum, a thermometer, and a dropping funnel with cooling jacket fitted with an Ar bubbler was flame-dried while flushed with Ar. The flask was charged with 800 mg (2.3 mmol) of 2-chloro-1,3-dithiolium hexachlorophosphate (**9**) [31], 5 ml of CH_2Cl_2, and 10 ml of THF, and the hereby formed suspension was cooled to −70°. At this temp., 5 ml (4 mmol) of chilled (−20°) Na-(*Z,Z,Z,E*)-**6** (0.7895M in THF) were slowly added during 30 min. After stirring at −40° to −60° for 3 h, 15 ml of cold pentane/Et_2O 1:1 were added to the yellow mixture to give a dark-brown precipitate, which was centrifugated for 10 min with 4000 U/min at −30°; the resulting soln. was transferred under Ar over a precooled *Teflon* tube to a cooled (−40°) column containing 30 g of deactivated silica gel and eluted with pentane/Et_2O 2:1. The orange eluate (*ca.* 80 ml) was concentrated at −30°/0.1 mbar to give a yellow-orange solid. Recrystallization from 4 ml pentane/Et_2O 1:1 at −70° gave 456 mg (77.9%) yellow crystals of **8h**. R_f (pentane/Et_2O 20:1): 0.62. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.88–5.52 (*m*, 10 H); 4.92 (*t*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 131.1 (*d*); 130.9 (*d*); 128.2 (*d*); 117.6 (*d*); 117.2 (*d*); 50.2 (*d*). MS: 255 (1, M^+), 234 (18), 220 (17), 219 (100), 218 (13), 217 (9), 185 (113), 166 (7), 164 (8), 157 (5), 154 (11), 153 (16), 152 (13), 151 (15), 149 (20), 139 (11), 138 (90), 136 (27), 134 (31), 116 (7), 114 (21), 113 (13), 112 (36), 108 (8), 107 (9), 90 (30), 89 (18), 79 (6), 78 (13), 77 (15), 74 (14), 72 (21), 71 (19), 65 (16), 63 (8), 59 (16), 57 (8), 51 (8), 45 (10), 43 (21), 42 (33), 41 (22), 39 (16), 31 (15), 31 (9), 27 (8)[17]).

3.2. *1,1-Bi(cyclonona-2,4,6,8-tetraenyl)* (**10**) *by Reaction of Na-*(ZZZE)-**6** *and* **9**: [14].

3.3. *2-(Methylthio)-2-(cyclonona-2,4,6,8-tetraen-1-yl)-1,3-dithiole* (**8i**): [25].

3.4. *Compound* **3**. A 50-ml three-necked flask equipped with a magnetic stirring bar, a thermometer, a septum, and an Ar bubbler was flame-dried while flushed with Ar. The flask was charged with 266 mg (1 mmol) of **8i** and 10 ml of CH_2Cl_2 and then cooled to −60°. At this temp., 97 mg (1.1 mmol) of HBF_4 were added during 10 min to give a pink suspension containing a white precipitate. The mixture was allowed to be stirred for 20 min and to warm up to −40°. Then, 2 ml (2 mmol) of NEt_3 were dropwise added over 20 min. After the addition was complete, stirring was continued for 4 h at −30° to −50°. The orange soln. was filtered under Ar over a cooled (−40°) column containing 30 g of deactivated silica gel with pentane/Et_2O 5:1. The resulting filtrate (60 ml) was concentrated at −30°/0.1 mbar to give an orange oil. Chromatography over 50 g of deactivated silica gel, at first with pentane, then with pentane/Et_2O 5:1 at −40° under Ar, followed by concentration at −30°/0.1 mbar, gave 66 mg (30.2%) of a yellow oil of **3**. R_f (pentane/Et_2O 10:1): 0.52. UV (hexane): 352 (25700). IR (KBr): 3040*w–m*, 2850*w–m*, 1598*m*, 1415*w*, 1075*w*, 1018*w*, 970*w–m*, 800*m–s*, 790*m–s*, 750*m*, 690*m–s*, 640*m–s*, 615*m*. ^{1}H-NMR (400 MHz, CD_2Cl_2): 6.42 (*s*, 2 H); 6.02 (*m*, 2 H); 5.85 (*m*, 2 H); 5.79 (*m*, 2 H); 5.65 (*m*, 2 H). ^{13}C-NMR (100 MHz, CD_2Cl_2): 141.4 (*s*); 128.2 (*d*); 127.5 (*d*); 127.3 (*d*); 125.5 (*d*); 119.3 (*d*); 118.2 (*s*). MS: 220 (11), 219 (31), 218 (100, M^+), 217 (99), 216 (17), 192 (7), 191 (6), 186 (6), 185 (25), 184 (56), 159 (10), 158 (14), 152 (8), 147 (5), 141 (5), 129 (8), 128 (21), 127 (38), 118 (6), 117 (20), 116 (53), 115 (85), 114 (11), 108 (7), 103 (33), 102 (7), 101 (23), 100 (8), 91 (14), 89 (13), 87 (9), 86 (82), 77 (6), 68 (8), 58 (33), 56 (6), 44 (8), 42 (6), 30 (13). HR-MS: 218.0221 ($C_{12}H_{10}S$, M^+; calc. 218.0223)[17]).

4. Attempted Synthesis of 11,12:13,14-Dibenzononapentafulvalene (= *9-(Cyclonona-2,4,6,8-tetraen-1-ylidene)fluorene*; **4**, X=H; *Scheme 3*). – *9-Bromo-9-(cyclonona-2,4,6,8-tetraen-1-yl)-fluorene* (**8k**). A 50-ml three-necked flask fitted with a magnetic stirring bar, a septum, a thermometer, and an Ar bubbler was flame-dried while flushed with Ar. The flask was charged with 648 mg (2 mmol) of 9,9-dibromofluorene (**12**) [32] in 4 ml of abs. THF and cooled to −70°. At this temp., 310 mg (2.2 mmol) of $BF_3 \cdot Et_2O$ were dropwise added during 20 min by means of a syringe. After stirring for 30 min at this temp., 2.2 ml (2.2 mmol) of Na-(*Z,Z,Z,E*)-**6** (1.001M in THF) were

[17]) For more spectroscopic data and illustrations of spectra, see [9].

dropwise added with a syringe at −68° to −70° over 20 min. The brown mixture was allowed to stir at −50° for 2 h. Inorg. salts were filtered off by transferring the resulting mixture under Ar (−40°) through a precooled *Teflon* tube to a cooled column containing 35 g of Alox (basic I) and eluted with pentane/Et_2O 5:1. The orange filtrate (80 ml) was concentrated at −30°/0.1 mbar to give an orange oil. Recrystallization from 4 ml of pentane/Et_2O 1:1 at −70° yielded 588 mg (81.4%) of **8k** as yellow crystals. ^{1}H-NMR (400 MHz, (D_6)acetone): 7.68–7.31 (*m*, 8 H); 5.81–5.52 (*m*, 8 H); 5.68 (*t*, 1 H). ^{13}C-NMR (100 MHz, (D_6)acetone): 148.3 (*s*); 138.7 (*s*); 131.5 (*d*); 129.3 (*d*); 129.1 (*d*); 128.8 (*d*); 128.2 (*d*); 127.6 (*d*); 124.9 (*d*); 120.1 (*d*); 67.1 (*s*); 49.6 (*d*). MS: 363 (6), 362 (24, $M^{+\cdot}$), 361 (6), 360 (23), 282 (30), 281 (93), 280 (110), 279 (93), 278 (46), 277 (46), 276 (47), 275 (9), 274 (11), 267 (8), 266 (35), 265 (42), 264 (12), 263 (15), 253 (14), 252 (22), 250 (8), 245 (10), 243 (9), 239 (8), 204 (18), 203 (74), 202 (69), 201 (23), 200 (18), 189 (12), 178 (11), 176 (8), 166 (28), 165 (90), 164 (10), 163 (8), 140 (9), 139 (8), 138 (11), 132 (7), 126 (9), 117 (77), 116 (13), 115 (22), 105 (6), 91 (7), 82 (15), 80 (14). HR-MS: 360.0512 ($C_{22}H_{17}Br$, $M^{+\cdot}$; calc. 360.0513)[17]).

5. Attempted Synthesis of Nonafulvenes with Anionic Substituents: Synthesis of *10,10*-Dibromononafulvene (= *9-(Dibromomethylidene)cyclonona-1,3,5,7-tetraene*; **11**; *Scheme 4*). – 5.1. *9-(Tribromomethyl)cyclonona-1,3,5,7-tetraene* (**8l**). A 50-ml three-necked flask fitted with a magnetic stirring bar, a septum, a thermometer, and an Ar bubbler was flame-dried while flushed with Ar. The flask was charged with 663 mg (2 mmol) of CBr_4 in 2 ml of Et_2O and cooled to −70°; 310 mg (2.2 mmol) of $BF_3 \cdot Et_2O$ were dropwise added during 20 min at −70° to −68° with a syringe. After stirring for 30 min at this temp., 4 ml (4 mmol, 1.001M in THF) of Na-(*Z,Z,Z,E*)-**6** were dropwise added over 20 min at −70° with a syringe. After addition was complete, stirring was continued for 4 h at −60° to give a brown soln. Inorg. salts were filtered off by transferring the resulting mixture under Ar over a precooled *Teflon* tube to a cooled column (−50°) containing 35 g of Alox (basic I) and eluted with pentane/Et_2O 5:1. The resulting yellow filtrate (60 ml) was concentrated at −50°/0.05 mbar to give a yellow oil. Recrystallization from 4 ml of pentane/Et_2O 5:1 at −70° gave 304 mg (41.2%) of pale yellow crystals of **8l**. R_f (pentane/Et_2O 10:1): 0.70. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.09–5.57 (*m*, 9 H). MS: 367 (2), 366 (1, $M^{+\cdot}$), 235 (8), 234 (38), 233 (6), 219 (6), 206 (6), 205 (10), 203 (7), 193 (9), 191 (8), 180 (10), 179 (9), 168 (13), 167 (14), 165 (12), 156 (21), 155 (29), 154 (17), 153 (20), 152 (16), 144 (16), 143 (56), 142 (32), 141 (34), 131 (9), 130 (45), 129 (50), 128 (62), 127 (33), 120 (9), 119 (47), 118 (54), 117 (100), 116 (71), 115 (82), 114 (23), 113 (22), 105 (7), 104 (14), 103 (12), 102 (12), 92 (20), 91 (56), 89 (11), 79 (7), 78 (17), 77 (23), 65 (20), 51 (7), 39 (10). HR-MS: 365.8258 ($C_{10}H_9Br$, $M^{+\cdot}$; calc. 365.8254)[17]).

5.2. *Compound* **11**. A 50 ml two-necked flask fitted with a magnetic stirring bar, a thermometer, a septum, and an Ar bubbler was flame-dired while flushed with Ar. The flask was charged with 304 mg (0.82 mmol) of **8l** dissolved in 5 ml of THF and cooled to −70°. At this temp., 180 mg (1.6 mmol) of *t*-BuOK and 423 mg (1.6 mmol) of 18-crownether-6 were added in small portions, while the soln. was continuously stirred for 40 min under a constant stream of Ar. The mixture was allowed to stir for additional 4 h at −60° to −70° to give a dark brown suspension. Inorg. salts were filtered off by transferring the suspension under Ar over a precooled *Teflon* tube into a cooled colum (−50°) containing 35 g of deactivated silica gel and eluted with pentane/Et_2O 5:1. The resulting *ca.* 60 ml of yellow filtrate were concentrated at −50°/0.05 mbar to give a yellow solid. Recrystallization from 2 ml of pentane/Et_2O 5:1 at −70° yielded 140 mg (59.2%) of **11** as pale yellow crystals. R_f (pentane/Et_2O 10:1): 0.71. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.06 (*d*, 2 H); 5.97–5.90 (*m*, 4 H); 5.65 (*dd*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 139.9 (*s*); 129.1 (*d*); 128.5 (*d*); 128.2 (*d*); 127.6 (*d*); 96.0 (*s*)[17]).

6. Synthesis of Nonatriafulvalenes (*Schemes 5* and *6*). – 6.1. *9-[2,3-Bis(diethylamino)cycloprop-2-en-1-ylidene]cyclonona-1,3,5,7-tetraene;* **5**). A 50 ml three-necked flask equipped with a magnetic stirring bar, a thermometer, a septum as well as an Ar bubbler was flame-dried while flushed with Ar. The flask was charged with 315 mg (1 mmol) of *1,2-bis(diethylamino)-3-chlorocyclopropenylium perchlorate* (**13**) [33], 8 ml of CH_2Cl_2, and 5 ml of THF and then cooled to −60°. At this temp., 2 ml (2 mmol) of Na-(*ZZZE*)-**6** (1.001M in THF) were dropwise added under Ar with a syringe during 20 min. After the addition was complete, the orange mixture was stirred for 4 h at −40° to −50°, 20 ml of cooled CH_2Cl_2/pentane 1:1 were added, and the mixture was stirred at −78° for 10 min. Then it was centrifugated for 10 min with 4000 U/min at −30° under Ar. The resulting soln. was concentrated at −40°/0.1 mbar to give yellow crystals. Recrystallization from 6 ml of CH_2Cl_2/Et_2O 2:1 under Ar at −70° gave 161 mg (54.3%) pale yellow cubic crystals[18]) of **5**. UV ($CHCl_3$): 407 (8650), 290 (12900), 255 (8590). IR (KBr): 2970*m–s*, 2930*m*, 2870*w*, 1915*m*, 1538*s*, 1485*w*, 1435*w–m*, 1415*m–s*, 1380*m–s*, 1360*m–s*, 1345*m–s*, 1300*m–s*, 1215*w–m*, 1190*m*, 1075*w*, 870*w*, 685*w*, 615*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.29 (*m*, 2 H); 7.17 (*m*, 2 H); 7.12 (*m*, 2 H); 7.00 (*m*, 2 H); 3.68 (*q*, 8 H); 1.39 (*t*, 12 H). ^{13}C-NMR (100 MHz, $CDCl_3$, 0°): 128.9 (*s*); 128.7 (*s*); 113.5 (*d*); 113.2 (*d*); 112.4 (*d*); 107.4 (*d*); 97.8 (*s*); 47.4 (*t*); 14.7 (*q*). MS: 297 (9), 296 (47, $M^{+\cdot}$), 295 (100), 267 (6), 224 (10), 223 (6), 211

[18]) Crystals as well as solns. of **5** are stable at r.t. under Ar. Solns. of **5** do not show any valence isomerization over at +50°. However, **5** polymerizes easily in the presence of O_2.

(7), 196 (8), 181 (6), 180 (6), 167 (6), 166 (5), 155 (5), 154 (15), 153 (9), 152 (6), 129 (5), 128 (7), 127 (7), 117 (8), 116 (7), 115 (11), 100 (8), 91 (5), 73 (5), 72 (11), 58 (9), 18 (5). HR-MS: 296.2257 ($C_{20}H_{28}N_2$, $M^{+\cdot}$; calc. 296.2253)[17].

6.2. *9-[1,2,3-Tris(*tert*-butylthio)cycloprop-2-en-1-yl]cyclonona-1,3,5,7-tetraene* (**8m**). A 50 ml three-necked flask fitted with a magnetic stirrer, a septum, a thermometer, and an Ar bubbler was flame-dried while flushed with Ar. The flask was charged with 379 mg (1 mmol) of *1,2,3-tris(*tert*-butylthio)cyclopropenylium fluoroborate* (**14**) [34] in 6 ml of CH_2Cl_2 and cooled to −60°. At this temp. 2 ml (2 mmol) of Na-(*ZZZE*)-**6** (1.001M in THF) were dropwise added by means of a syringe during 20 min. After stirring at −40° to −60° for 4 h, the yellow mixture was transferred with a precooled *Teflon* tube into a cooled (−40°) column containing 30 g of deactivated silica gel under Ar and eluted with pentane/Et_2O 5:1. The filtrate (60 ml) was concentrated at −30°/0.1 mbar. The resulting yellow oil was separated by chromatography over 50 g of deactivated silica gel at −40°, first with pentane to remove cyclononatetraene, then the yellow zone was eluted with pentane/Et_2O 5:1 to give 100 ml of a yellow eluate. After concentration at a −30°/0.1 mbar, 236 mg (45.6%) of a yellow oil of **8m** were obtained which could not be crystallized from solvents like pentane, pentane/Et_2O 5:1, and Et_2O at −70°. R_f (pentane/Et_2O 5:1): 0.83. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.76–5.51 (*m*, 8 H); 5.39 (*t*, 1 H); 1.48 (*s*, 18 H); 1.39 (*s*, 9 H). MS: 420 (7, $M^{+\cdot}$), 365 (7), 364 (13), 363 (38), 332 (7), 331 (24), 330 (10), 320 (6), 309 (7), 308 (14), 307 (36), 303 (10), 276 (6), 275 (23), 274 (13), 273 (9), 264 (6), 253 (18), 252 (30), 251 (65), 250 (10), 249 (11), 247 (14), 221 (7), 220 (13), 219 (47), 218 (47), 217 (54), 216 (13), 191 (20), 187 (6), 186 (16), 185 (38), 184 (42), 183 (18), 174 (9), 173 (10), 159 (6), 153 (11), 152 (21), 151 (10), 149 (6), 146 (10), 141 (11), 139 (8), 137 (7), 135 (23), 129 (8), 128 (10), 125 (7), 123 (6), 119 (34), 118 (72), 117 (100), 116 (4), 115 (70), 114 (12), 113 (18), 111 (11), 109 (8), 105 (8), 97 (13), 95 (8), 92 (16), 91 (53), 90 (13), 89 (19), 85 (10), 83 (10), 79 (9), 78 (21), 77 (22), 72 (20), 71 (32), 65 (21), 58 (13), 57 (39), 42 (21), 41 (22), 39 (19). HR-MS: 420.1978 ($C_{24}H_{36}S_3$, $M^{+\cdot}$; calc. 420.1979)[17].

7. Synthesis of 10-(Dimethylamino)-10-phenylnonafulvene (= *9-[(Dimethylamino)(phenyl)methylidene]-cyclonona-1,3,5,7-tetraene*; **1n**; *Scheme 7*). – 7.1. *9-[α-chloro-α-(Dimethylamino)benzyl]bicyclo[6.1.0]nona-2,4,6-triene* (**16**). A 50 ml three-necked flask equipped with a magnetic stirring bar, a thermometer, a septum, and an Ar bubbler was flame-dried while flushed with Ar. The flask was charged with 408 mg (2 mmol) of *α-chloro-α-(dimethylamino)benzyliumchloride* (**15**) [35], 5 ml of CH_2Cl_2, and 5 ml of THF and then cooled to −70°. At this temp., 4 ml (4 mmol) of Na-(*ZZZE*)-**6** (1.001M, in THF) was dropwise added with a syringe over 30 min. The mixture was allowed to be stirred for 4 h at −70° to −40° to give a brown soln. Inorg. salts were filtered off by transferring the brown mixture to a cooled (−40°) column filled with 35 g of Alox (basic I) and eluted with pentane/Et_2O 5:1. The orange filtrate (*ca.* 80 ml) was concentrated. The resulting orange oil was chromatographed over 50 g of deactivated silica gel at −40°, first with pentane to remove cyclononatetraene, then the orange zone was eluted with pentane/Et_2O 10:1 to give 80 ml yellow eluate. After concentrating at −30°/0.1 mbar, 128 mg (46.9%) of a yellow oil of **16** were isolated, which could not be crystallized[19]. R_f (pentane/Et_2O 10:1): 0.78. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.49–7.20 (*m*, 5 H); 5.90–5.40 (*m*, 6 H); 2.69 (*s*, 6 H); 1.34–1.24 (*m*, 2 H); 0.88 (*t*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 140.5 (*s*); 134.2 (*d*); 130.6 (*d*); 129.9 (*d*); 128.4 (*d*); 127.3 (*d*); 126.8 (*d*); 126.6 (*d*); 71.7 (*s*); 48.5 (*d*); 41.8 (*d*); 14.2 (*q*)[17].

7.2. *Compound* **1n**. A 50 ml two-necked flask equipped with a magnetic stirring bar, a thermometer, and a pressure equalizing dropping funnel with cooling jacket fitted with an Ar bubbler was flame-dried while flushed with Ar. The flask was charged with 612 mg (3 mmol) of **15** [35], 5 ml of THF, and 6 ml of CH_2Cl_2 and cooled to −50°. At this temp., 12 ml (6 mmol) of cold (−20°) Li-(*ZZZZ*)-**6** (0.501M in THF) were dropwise added during a period of 45 min. After stirring for 2 h at −40° to −30°, the orange mixture was transferred under Ar over a precooled *Teflon* tube into a cooled (−40°) column containing 30 g of deactivated silica gel and eluted with pentane/Et_2O 5:1. The orange filtrate (100 ml) was concentrated at −30°/0.1 mbar to give a red oil. Recrystallization from 5 ml of pentane/Et_2O 4:1 at −70° yielded 432 mg (60.9%) of yellow crystals of **1n**. R_f (pentane/Et_2O 10:1): 0.78. UV (hexane): 342 (2250). IR (neat): 3000*s*, 2924*s*, 2856*m*, 1642*w*, 1528*w*, 1430*w–m*, 1362*w*, 1068*w*, 778*m*, 756*m–s*, 748*m–s*, 700*m–s*, 650*m*. ^{1}H-NMR (400 MHz, (D_6)acetone, −25°): 7.36–7.16 (*m*, 5 H); 6.23 (*m*, 1 H); 6.14 (*m*, 1 H); 6.03 (*m*, 1 H); 5.87 (*m*, 1 H); 5.78 (*dd*, 1 H); 5.75 (*m*, 2 H); 5.24 (*dp*, 1 H); 2.61 (*s*, 6 H). ^{13}C-NMR (100 MHz, (D_6)acetone, −25°): 156.7 (*s*); 138.5 (*s*); 131.2 (*d*); 130.8 (*d*); 130.3 (*d*); 129.8 (*d*); 129.4 (*d*); 129.0 (*d*); 128.9 (*d*); 126.9 (*d*); 126.0 (*d*); 124.9 (*d*); 121.7 (*d*); 117.9 (*s*); 44.0 (*q*). MS: 249 (18, $M^{+\cdot}$), 248 (21), 205 (10), 203 (6), 178 (5), 158 (10), 141 (6), 129 (8), 128 (99), 119 (20), 118 (65), 117 (100), 116 (71), 115 (78), 114 (18), 113 (19), 106 (8), 105 (18), 104 (8), 103 (34), 102 (15), 92 (23), 91 (54), 90 (13), 89 (31), 84 (7), 79 (12), 78 (30), 77 (29), 76 (6), 71 (9), 66 (8), 65 (28), 64 (6), 63 (21), 57 (16), 53 (7), 52 (12), 51 (20), 50 (6), 43 (8), 41 (9), 39 (21), 27 (6). HR-MS: 249.1518 ($C_{18}H_{19}N$, $M^{+\cdot}$; calc. 249.1518)[17].

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[19]) In most cases, **16** contained traces of nonafulvene **1n**.

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