CYCLIC CROSS-CONJUGATED PI-SYSTEMS

α, ω-CYCLOADDITION REACTIONS

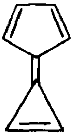
HORST PRINZBACH

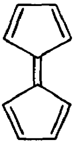
Chemisches Laboratorium der Universität Freiburg i.Br., Germany

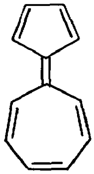
ABSTRACT

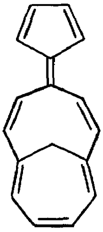
In five chapters (A–E) new results concerning the cyclic cross-conjugated π-systems calicene (**1**), pentafulvalene (**2**), sesquifulvalene (**3**), fidecene (**4**) and pentaphenafulvalene (**5**) are presented. These hydrocarbons, or simple yet sufficiently stable derivatives, have become of interest as participants in α, ω-cycloaddition reactions—opening up attractive new pathways towards the bridged annulene-type systems **6–10**. In preliminary experiments such additions with TCNE as a 'polyenophile' have been observed: [8 + 2] in the case of alkylated calicenes, [12 + 2] with the parent sesquifulvalene and several alkyl derivatives, and [16 + 2] with di-*t*-butyl-fidecene (see note on page 35). The same polyenes, however, add methylacetylenedicarboxylate in a formal [6 + 2] way. The isolation of two stereoisomers starting out from **C-10** (**C-27a**; **C-27b**) makes a two-step mechanism probable.

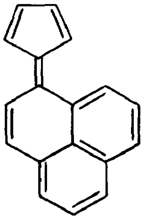
Over the last few years the interest of my research group in the area of the so-called 'non-benzenoid aromatic compounds' has been concerned mainly with the hydrocarbons **1**–**5** having 8, 10, 12, 16 and 18 π-electrons respectively. Although these hydrocarbons might be classified as fulvalenes, they are probably best known by their trivial names: calicene (**1**), pentafulvalene (**2**), sesquifulvalene (**3**), fidecene (**4**) and pentaphenafulvalene (**5**).


1


2

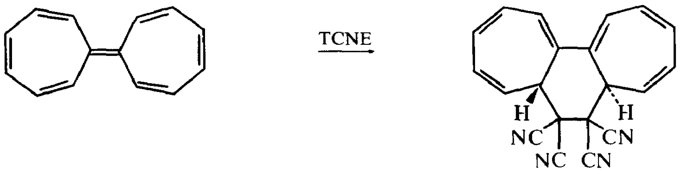

3


4


5

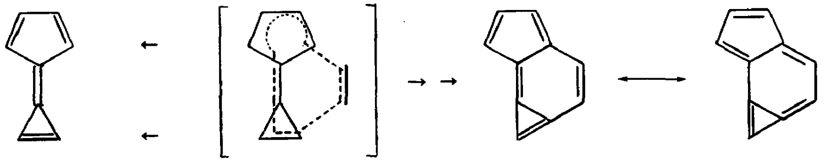
In the meantime, questions which were originally raised regarding the π-electron configuration, dipole moments, and 'aromaticity' of these and similar cross-conjugated π-electron systems, stimulated primarily by theoretical considerations, have been answered quite convincingly. The hydrocarbons **1**–**5** are in fact typical polyenes with rather strongly localized carbon–carbon double bonds.

Our interest in this field was especially renewed by the finding of Doering and Schröder that heptafulvalene, probably as a result of its particularly favourable geometry, undergoes a [π14 *a* + π2 *s*] addition with tetracyanoethylene.



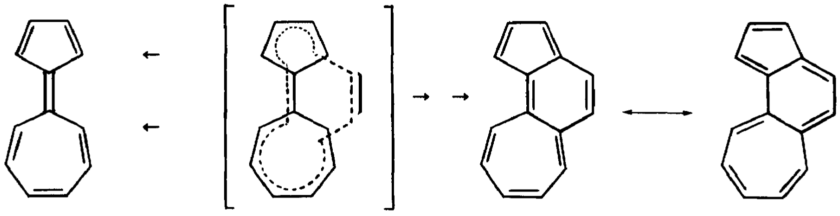
This suggested to us that analogous α,ω-cycloadditions to the polyenes 1–5 might open up an attractive and general synthesis for the systems **6–10** having two more π-electrons. The 'dehydroazulene' (**6**), the as-indacene (**7**), the products **8** from sesquifulvalene and (**9**) from fidecene can be considered as annulenes in which the two zero-bridges hold the perimeter in a rather rigid and, as much as possible, coplanar geometry. While one might hasten to view this programme with great expectation, I should caution you at the outset that our success has been quite limited so far. This is attributable mainly to the following two reasons:

1



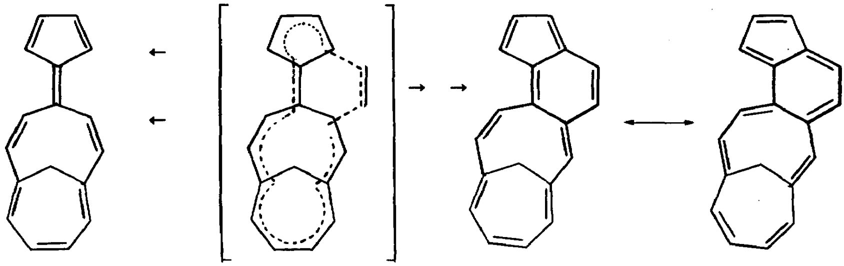
6

3



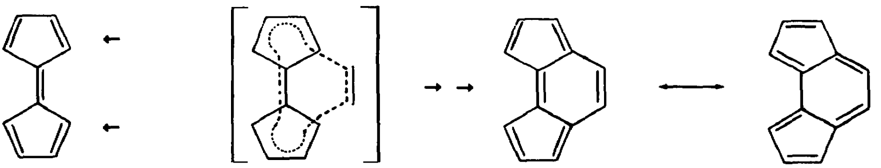
8

4



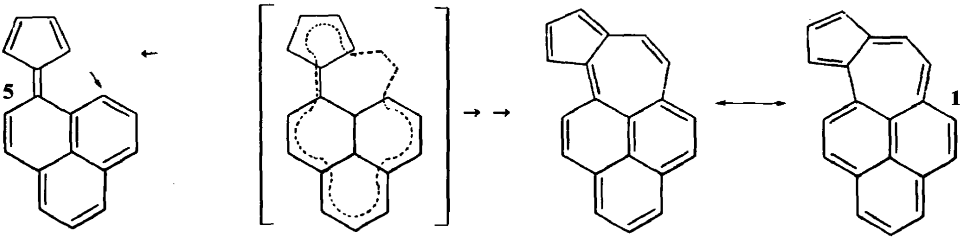
9

2



7

5



10

(1) The polyenes **1**–**5**, insofar as they are known at all, are all extremely reactive and exist only in solution and at very high dilution. Our first task, therefore, was to synthesize derivatives which were suitably substituted to enhance stability and yet would allow the possibility of an α,ω-cycloadditon.

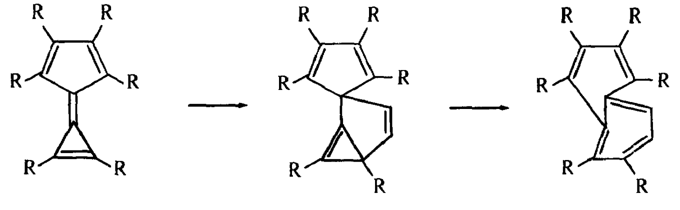
(2) The polyenes **1**–**5** can undergo additions other than the desired α,ω-type, as, for instance, additions to one and/or the other fulvene half of the structure. No reliable predictions can be made, *a priori*, as to the likelihood of one or the other alternative.

This paper gives me the opportunity to inform you of what we have accomplished and to comment on the viability of our concept of a route to the bridged annulenes **6**–**10**, using the fulvalenes **1**–**5** as starting materials.

A. CALICENES

H. Knöfel

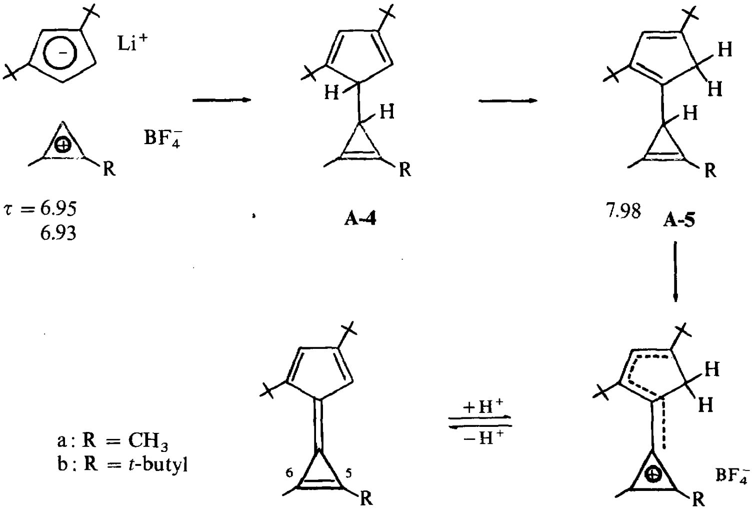
The realization of a synthesis of the type **1** → **6** depends on the availability of the parent molecule **1** or of some suitably substituted derivatives. Until recently, no such calicene was known and for good reasons. One has only to remember the difficulties encountered with the unsubstituted cyclopropenium salt[1], in order to understand why a synthesis of the parent molecule **1** has not even been attempted. The kind of substitution on the calicenes **A-1** synthesized by Bergmann[2], Jones[3], Kende[4], Kitahara[5] and collaborators, and by ourselves[6], provides thermal and chemical stability, but at the same time, however, prevents the possibility of an [8 + 2] cycloaddition. Reactions with tetracyanoethylene (TCNE), dimethyl acetylenedicarboxylate (MAD) or maleic anhydride (MA) led to a number of interesting and valuable products **A-3**, the structures of which could be explained by an addition to the triafulvene skeleton with concomitant isomerization of the unstable adducts **A-2**. Most probably, some dipolar additions take the same course[7].



A-1 **A-2** **A-3**

Only when the substitution was reduced to the methyl and *t*-butyl groups as in the calicenes **A-7a** and **A-7b**, was a cycloaddition of the [8 + 2] type feasible in principle.

These calicenes, **A-7a** and **A-7b** were constructed following the sequence **A-4** → **A-5** → **A-6** → **A-7**. The *t*-butyl groups in the 5-membered ring* made them sufficiently stable and resistant against chemical attack to allow their isolation. At the hydride elimination stage **A-5** → **A-6**, however, even the bulky *t*-butyl groups cannot prevent a competing attack of the Lewis acid upon the cyclopentadienyl moiety, ultimately causing partial polymerization. The overall yields of **A-7a** and **A-7b** are, in fact, rather poor.



$\tau = 6.95$
6.93

A-4

7.98 **A-5**

a: R = CH_3
b: R = *t*-butyl

$\tau = 7.56$
$\lambda_{max.} = 7.48$
A-7
300 nm
301 nm

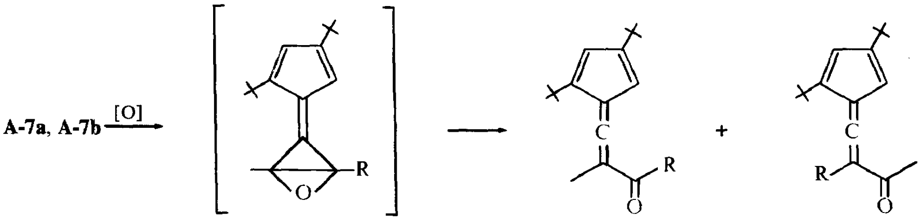
7.13
7.08
A-6
346 nm (CH_2Cl_2)
347 nm (CH_2Cl_2)

The hydrocarbons **A-7a** and **A-7b** surpass their aforementioned highly substituted analogues in their sensitivity towards oxygen. Even a very short exposure of a solution to air causes appreciable transformation. As we had published earlier[6], the reaction is very specific, only the C(5)—C(6) double

---

* The stabilizing influence of the same substituents upon the cyclopentadienone system was well known[8].

bond is involved. With **A-7a** and **A-7b**, the allene ketones **A-9**, **A-10** are the oxidation products. Probably the methylene oxabicyclo[1,1,0]butane compounds **A-8** are the intermediates[*].



A-8 **A-9** **A-10**

As the n.m.r. spectra in *Figures 1* and *2* illustrate, the crystalline salts **A-6a** and **A-6b**, and the conjugate bases **A-7a** and **A-7b** can be made in a rather pure state. The nature of such 'calicenium salts', in other words the delocalization of the charge, is evident from their u.v. absorption and from the diamagnetic shift of the methyl signals (τ = 7.13; 7.08) as compared with the dialkyl cyclopropenium salts (τ = 6.95; 6.93). From the electronic spectra of **A-7a** and **A-7b**, data are now at our disposal which allow a more critical evaluation of the many theoretical calculations done on these systems. The longest absorption maximum of **A-7a** and **A-7b** lies between 295 nm (*n*-hexane) and 301 nm (CH_2Cl_2) and is, in agreement with earlier measurements, only insignificantly dependent on solvent.

The dipole moment measured[9] for the dibenzodimethylcalicene **A-11** of $\mu = 4.9$ D and the τ-values of the CH_3-signal (τ = 7.37, $CDCl_3$) were originally accepted as qualitative evidence for a relatively electron-deficient cyclopropene ring.

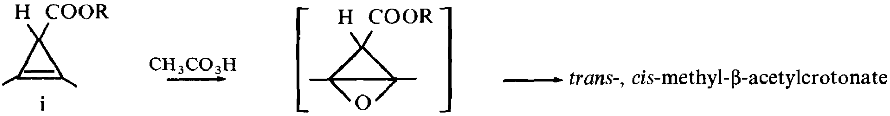
In connection with the previously not fully answered question of the importance of anisotropic influences upon the CH_3-protons in **A-11**, it is gratifying to discover that the CH_3-protons in **A-7a** and **A-7b** have very similar chemical shifts. The latter lie approximately halfway between the signals of the dihydro compounds **A-5** and the salts **A-6**.

As yet, we do not have good dipole moments for **A-7a** and **A-7b**. Two independent experimental estimations[10] gave a value of *ca.* 5.6 D for the parent calicene **1**. Should these estimations turn out to be approximately correct, agreement with the theoretical moments[†] would be excellent.

In support of a pronounced polarity in the ground states of the calicenes **A-7a** and **A-7b** or of a high polarizability of the systems, the impressive

---

[*] To achieve the analogous oxidation with i, a stronger oxidizing reagent, e.g. a peracid, is needed[6].



i

[†] 5.63 D, Dewar[11].
5.70 D, Nakajima[12].

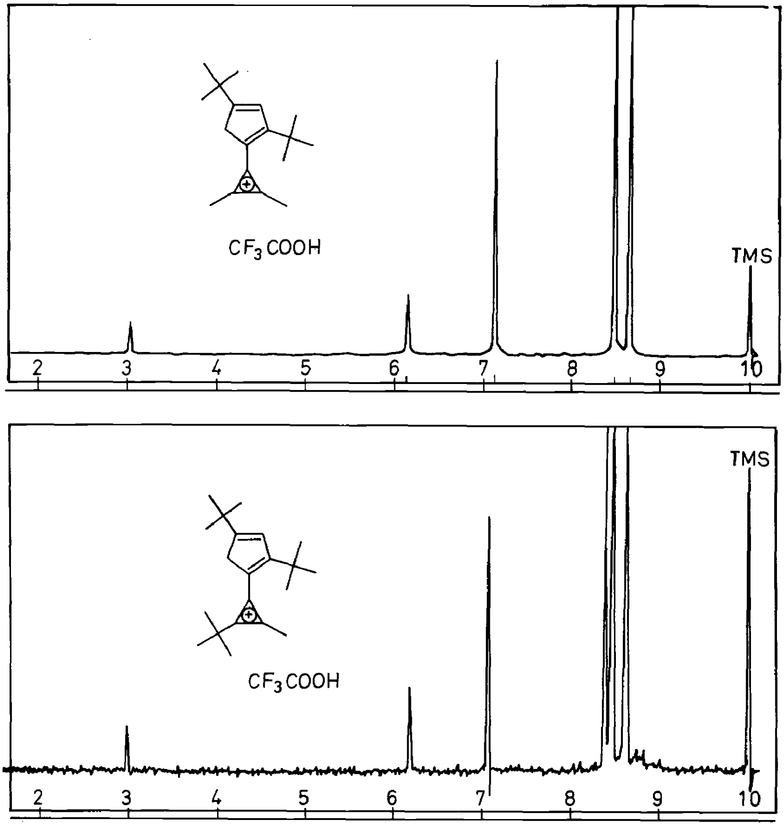


Figure 1. The n.m.r. spectra of the calicenium ions **A-6a** and **A-6b** (60 MHz; CF_3CO_2H)

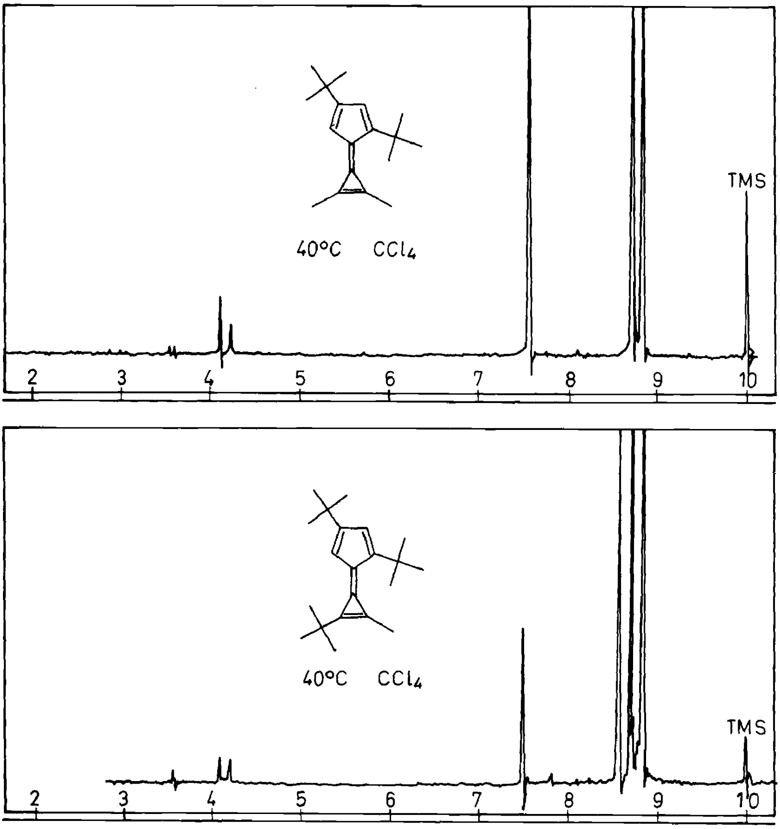
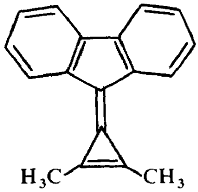
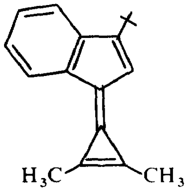


Figure 2. The n.m.r. spectra of the calicenes **A-7a** and **A-7b** (60 MHz, CCl_4; 40°C)

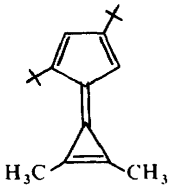


τ = 7.37
(CDCl$_3$)

A-11



7.37 7.49



7.52 (40°)

A-7a

solvent dependence of the chemical shifts of the olefinic and the CH$_3$-protons is notable. The direction and magnitude of the displacements (see below) suggest a rather tight association of the benzene molecules with the electron deficient cyclopropene ring.

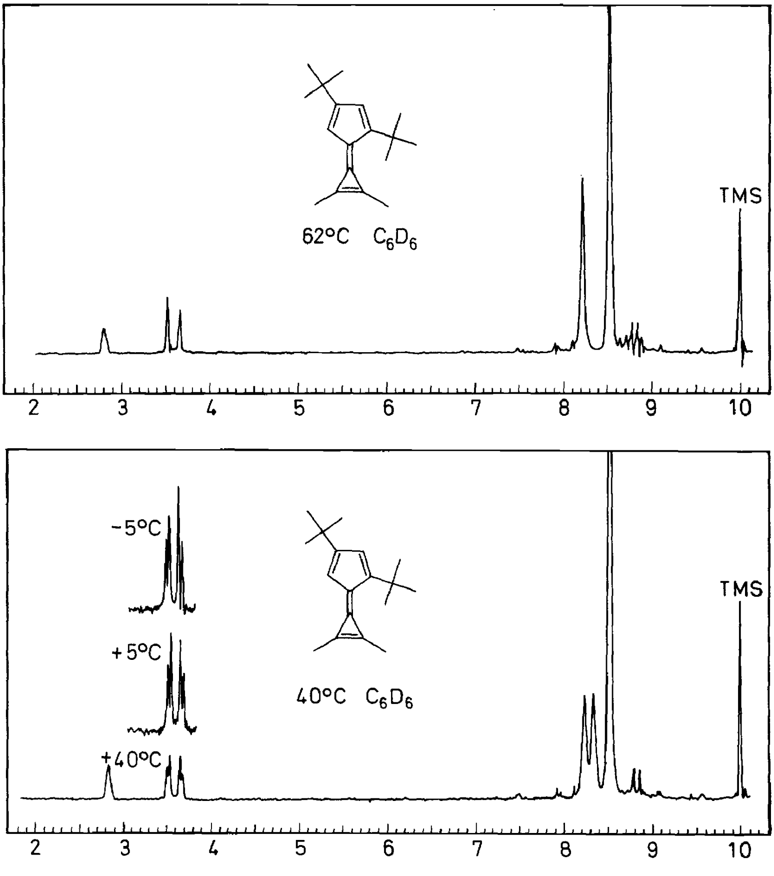


Figure 3. Temperature dependence of the n.m.r. spectrum of **A-7a** (60 MHz, C$_6$D$_6$)

Of great interest in this connection was the discovery that the n.m.r. spectra of **A-7a** and **A-7b** are temperature dependent. The experiments (*Figure 3*; *Table 1*) are still incomplete and somewhat preliminary. Nevertheless, the interpretation that this temperature dependence is a result of a rotation or possibly of a rocking motion around the C(7)—C(8) double bond seems justified.

The coalescence temperatures determined in the solvents C_6D_6, CCl_4 and $CDCl_3$

$$\begin{aligned} T_c(C_6D_6) &= +51^\circ \\ T_c(CCl_4) &= -11.5^\circ \\ T_c(CDCl_3) &= -62.5^\circ \end{aligned}$$

follow the expected trend; with increasing polarity of the solvent, the process responsible for the temperature dependence is facilitated. As has been discussed for the formyl-di-*n*-propyl calicene[13], and for a number of hetero-substituted fulvenes[14], the most reasonable transition state appears to be approximated by the perpendicular conformation **A-12** which is a dipolar rather than a diradical species. If the interpretation is correct, then **A-7a** is the hydrocarbon with a cross-conjugated π-electron system, exhibiting by far the lowest barrier to rotation around a carbon–carbon double bond.

Whether or not, and to what extent, the dynamic behaviour of **A-7a** depends on a deviation from coplanarity and a consequent higher polarity in

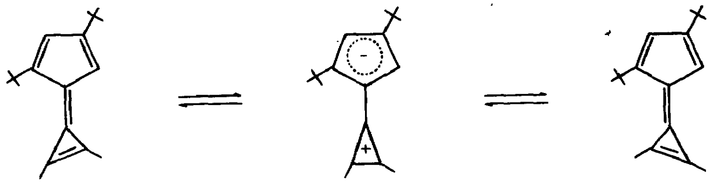
Table 1. Temperature dependence of the n.m.r. spectrum of the calicene **A-7a** (τ-values CCl_4; C_6D_6)

T (°C)	H^2	H^4	C(5)—CH_3	C(6)—CH_3	C(1)—$C(CH_3)_3$	C(3)—$C(CH_3)_3$
40	4.10 s	4.22 s	7.56		8.73	8.84
2	4.11 s	4.24 s	7.54			
− 2.5	4.13 s	4.26 s	7.54		8.73	8.84
−10	4.13 s	4.26 s	7.54		8.72	8.83
−11.5	4.13 bs	4.26 bs	7.54			
−13.5	4.13 d	4.26 d	7.53	7.55	8.73	8.83
−17.5	4.13 d	4.26 d	7.52	7.56	8.73	8.83
−21	4.13 d	4.26 d	7.53	7.59		
−33.5	4.13 d	4.26 d	7.52	7.60	8.75	8.85

(CCl_4)

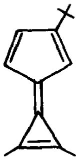
T (°C)	H^2	H^4	C(5)—CH_3	C(6)—CH_3	$C(CH_3)_3$
62	3.54 s	3.68 s	8.23		8.54
54	3.52 s	3.67 s	8.24		8.54
51	3.51 s	3.66 s	8.24		8.53
49	3.51 bs	3.65 bs	8.23	8.27	8.52
46.5	3.51 d	3.65 d	8.23	8.30	8.52
44	3.51 d	3.65 d	8.21	8.31	8.52
40	3.52 d	3.66 d	8.24	8.35	8.53

(C_6D_6)



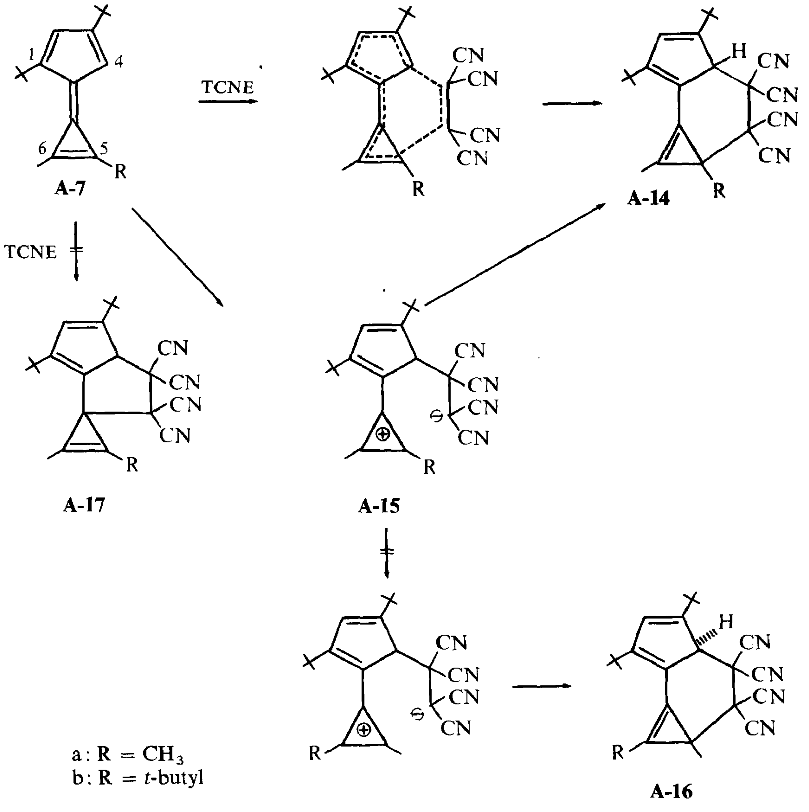
A-12

the sense of **A-12**, will have to be tested with the help of the mono-*t*-butylcalicene **A-13**.



A-13 $\lambda_{max.}(CH_2Cl_2)$ 300 nm

With TCNE, at 20°, both calicenes **A-7a** and **A-7b** undergo a clean, rapid and nearly quantitative addition reaction. For the crystalline, stable, 1:1 adducts we propose the structures **A-14a** and **A-14b**, mainly on the basis of



a: R = CH_3
b: R = *t*-butyl

their n.m.r. spectra (*Figure 4*). The large diamagnetic displacements of the signals for one cyclopentadienyl proton and for one methyl or one *t*-butyl group, respectively (cf. *Figure 2*), make alternative structures like **A-16** and **A-17** highly improbable. The stereochemistry, as formulated in **A-14**, is not proved; it is based on the prediction, made for a 10π-transition state[15].

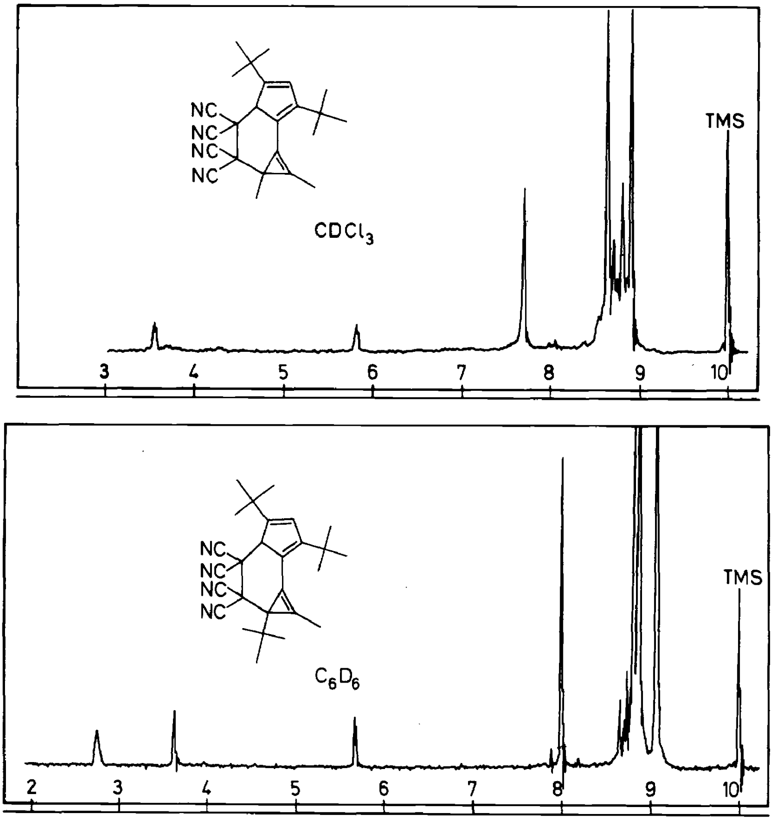


Figure 4. The n.m.r. spectra of the adducts **A-14a** and **A-14b** (60 MHz; $CDCl_3$, C_6D_6)

From mechanistic principles, as well as from earlier experimental findings, one would expect an attack of the π-acid at position 4 in **A-7**, likewise the position of protonation (**A-5**). Ring closure takes place at C(5) irrespective of the kind of substitution at this position; however, this specificity can hardly be an argument for a concerted pathway, at least not for **A-7b**. Even by a nonconcerted route (**A-15**), cyclization at C(6), to give **A-16b**, should be rather unlikely, since it would bring the two *t*-butyl groups at C(5) and C(1) into too close a proximity.

REFERENCES

[1] R. Breslow, J. D. Groves and G. Ryan, *J. Amer. Chem. Soc.* **89**, 5048 (1967); **92**, 984, 988 (1970).
[2] E. D. Bergmann and I. Agranat, *Chem. Commun.* 512 (1965).

[3] W. M. Jones and R. S. Pyron, *J. Amer. Chem. Soc.* **87**, 1608 (1965).

[4] A. S. Kende and P. T. Izzo, *J. Amer. Chem. Soc.* **87**, 4162 (1965);
A. S. Kende, P. T. Izzo and P. T. McGregor, *J. Amer. Chem. Soc.* **88**, 3359 (1966).

[5] M. Ueno, I. Murata and Y. Kitahara, *Tetrahedron Letters*, 2967 (1965);
I. Murata, M. Ueno, Y. Kitahara and H. Watanabe, *Tetrahedron Letters*, 1831 (1966);
Y. Kitahara, I. Murata, M. Ueno, K. Sato and H. Watanabe, *Chem. Commun.* 180 (1966);
H. Shimanouchi, T. Ashida, Y. Sasada, M. Kakudo, I. Murata and Y. Kitahara, *Tetrahedron Letters*, 61 (1967).

[6] H. Prinzbach, *Angew. Chem.* **76**, 235 (1964);
H. Prinzbach, D. Seip and U. Fischer, *Angew. Chem.* **77**, 258 (1965);
H. Prinzbach and U. Fischer, *Angew. Chem.* **77**, 621 (1965);
H. Prinzbach and U. Fischer, *Helv. Chim. Acta*, **50**, 1669 (1967);
H. Prinzbach and E. Woischnik, *Helv. Chim. Acta*, **52**, 2472 (1969).

[7] H. Prinzbach and U. Fischer, *Helv. Chim. Acta*, **50**, 1692 (1967);
cf. J. Ciabattoni and P. J. Kocienski, *J. Amer. Chem. Soc.* **91**, 6534 (1969).

[8] E. W. Garbisch Jr and R. F. Sprecher, *J. Amer. Chem. Soc.* **91**, 6785 (1969).

[9] E. Woischnik, *Diplomarbeit*, University of Freiburg i.Br. (1967).

[10] Y. Kitahara, I. Murata and S. Katagiri, *Tetrahedron*, **23**, 3613 (1967);
H. Prinzbach, H. Knöfel and E. Woischnik, *Proceedings* of the Third Jerusalem Symposium on 'Aromaticity, Pseudoaromaticity, Antiaromaticity', p 269. Israel Academy of Sciences and Humanities: Jerusalem (1971).

[11] M. J. S. Dewar, personal communication.

[12] T. Nakajima, S. Kohda, A. Tajiri and S. Karasawa, *Tetrahedron*, **23**, 2189 (1967).

[13] A. S. Kende, P. T. Izzo and W. Fulmor, *Tetrahedron Letters*, 3697 (1966).

[14] A. Mannschreck and U. Koelle, *Tetrahedron Letters*, 863 (1967);
J. A. Crabtree and D. J. Bertelli, *J. Amer. Chem. Soc.* **89**, 5384 (1967);
A. P. Downing, W. D. Ollis and I. O. Sutherland, *J. Chem. Soc. B*, 111 (1969);
K. Hartke and G. Salomon, *Chem. Ber.* **103**, 133, 147 (1970);
T. Eicher and N. Pelz, *Chem. Ber.* **103**, 2697 (1970).

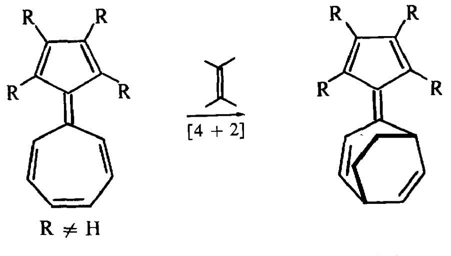
[15] R. B. Woodward and R. Hoffmann, *Angew. Chem.* **81**, 797 (1969).

B. SESQUIFULVALENES

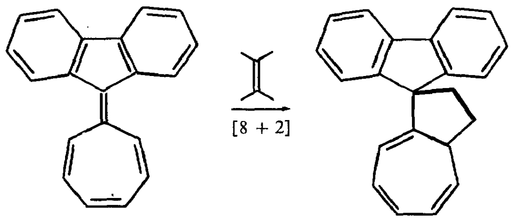
H. KNÖFEL

Attractive as it looks to us, to construct the annulene **8** via a [12 + 2] cycloaddition to sesquifulvalenes, the fact that the parent hydrocarbon **2** is manageable only as a very dilute solution (*ca.* 10^{-3} mol)[1] and that suitable derivatives were lacking, made the prospect appear rather remote.

As for the calicenes, several highly substituted derivatives were known, e.g. sesquifulvalenes bearing four substituents (**B-1**)[2,3] or two fused benzene rings (**B-3**)[3], but none would allow the desired α,ω-cycloaddition. A few investigations dealt with reactions of **B-1** and **B-3** with TCNE, MAD and MA to give products of the type **B-2** and **B-4**[3,4].



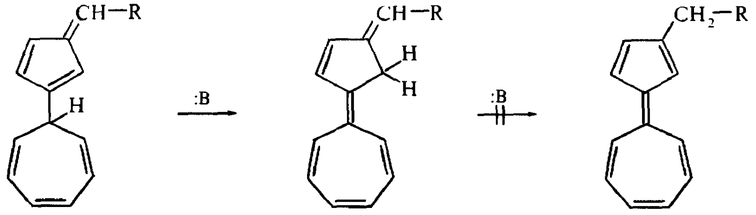
B-1 **B-2**



B-3 **B-4**

Below we outline four different approaches by which it was hoped to make derivatives of **2**, specifically substituted for the intended chemical reactions. Our intensive efforts, however, were only partially successful.

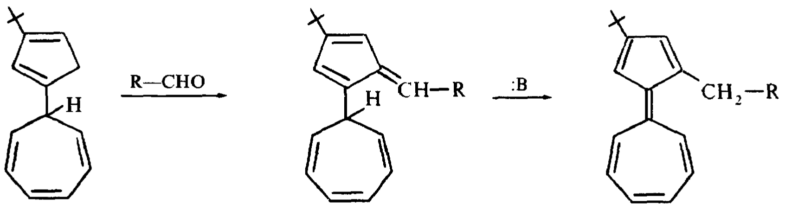
(1) The prototropic rearrangement of the 3-cycloheptatrienylfulvenes **B-5**—in contrast to the corresponding benzoanalogues which underwent facile isomerization to the benzosesquifulvalenes—gave the conjugated heptafulvenes **B-6** instead of the sesquifulvalenes **B-7**[4, 5].



B-5 **B-6** **B-7**

(R = alkyl-, aryl-)

(2) Beginning with the fulvenes **B-9** having the cycloheptatrienyl group in 2-position—obtainable after introduction of a voluminous group at C(3′) of **B-8**—the relative stabilities of the possible tautomeric conjugated systems are changed in such a way that the prototropic rearrangement now leads preferentially to the dialkylated sesquifulvalenes **B-10**.

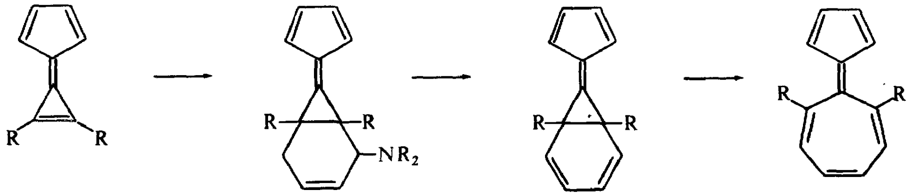


B-8 **B-9** **B-10**

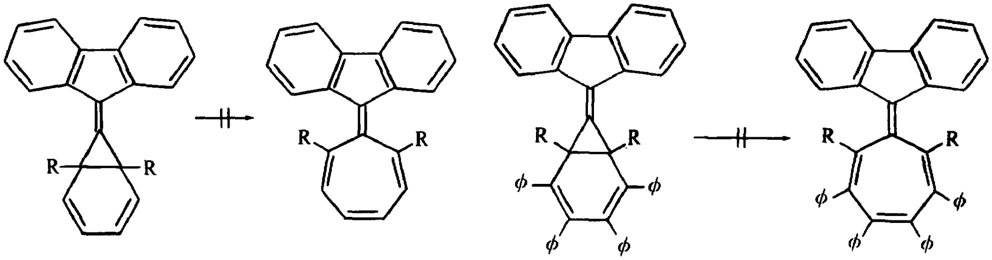
(R = aryl-)

(3) Initial attempts to transform calicenes into sesquifulvalenes according to the sequence **B-11** → **B-12** → **B-13** → **B-14** have been made with dibenzo-dimethyl- and tetraphenyldimethyl-calicene[6]. As it turned out, these two calicenes were poor models, because the intermediate norcaradienes **B-15** and **B-17** are unusually stable and resisted all attempts at thermal or photochemical scission to the sesquifulvalenes **B-16** and **B-18**, in which steric

compression is evidently prohibitive[3]. It will be interesting to see how the *t*-butylcalicenes **A-7a** and **A-7b** behave.

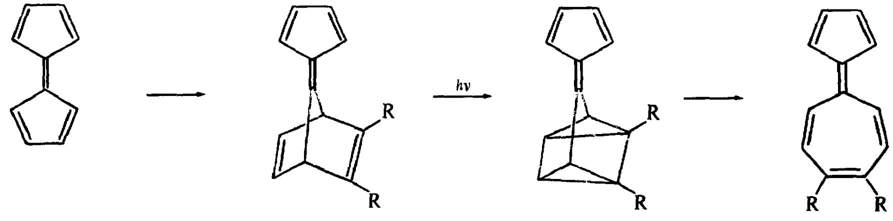


B-11 **B-12** **B-13** **B-14**



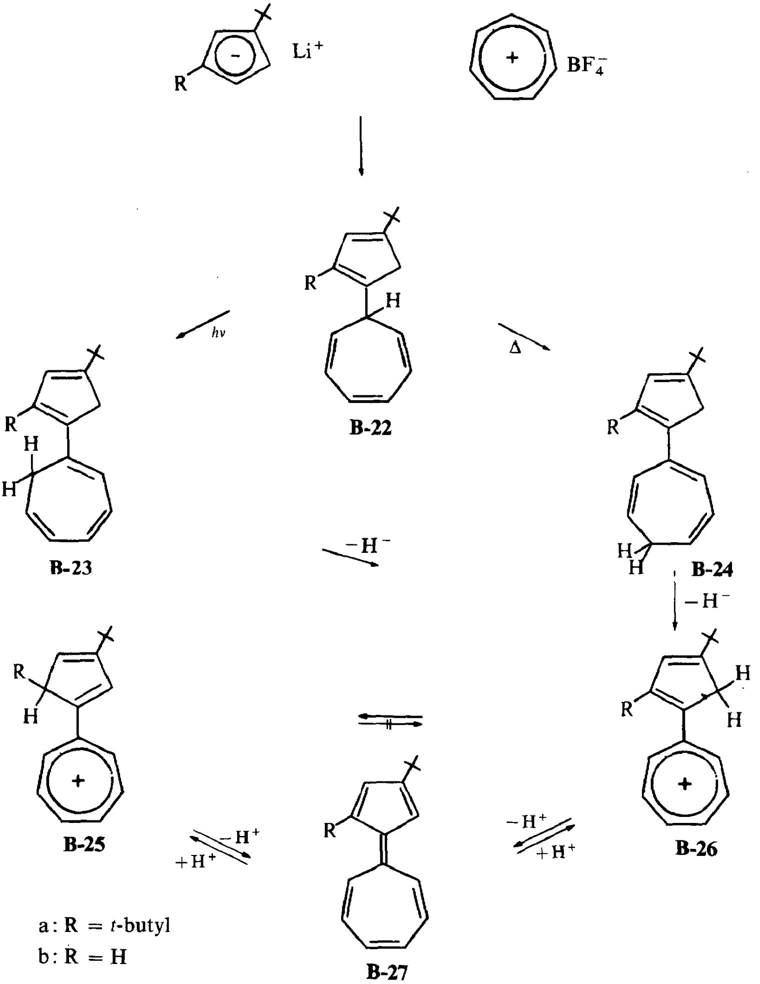
B-15 **B-16** **B-17** **B-18**

(4) Some details of another sesquifulvalene synthesis, using pentafulvalenes as starting materials and going through the intermediate stages **B-19** and/or **B-20**, will be given in section D.



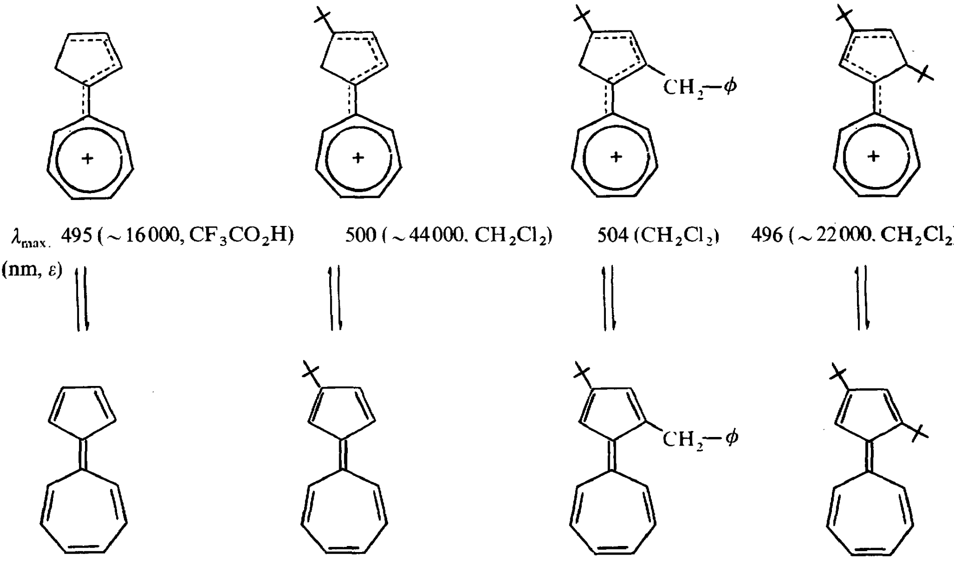
B-19 **B-20**

Again it proved most advantageous to stabilize the sesquifulvalene molecule by introduction of *t*-butyl groups into its five-membered ring. The critical step in the synthesis of 7,9-di-*t*-butyl-(**B-27a**) and 8-*t*-butyl-sesquifulvalene (**B-27b**) proved again to be the elimination of the hydride ion, because of the sensitivity of the dihydro compounds **B-22** towards acids. Prior thermal (of **B-22a**) or photochemical (of **B-22a**, **B-22b**) isomerization to **B-24** and **B-23**, respectively, sufficiently increases the rate of hydride abstraction. Yields averaging 30 to 50 per cent of the sesquifulvalenium salts **B-26** are quite satisfactory. Deprotonation and careful chromatography yield the hydrocarbons **B-27**, stable as 0.6 to 1.0 mol solutions. Higher concentrations are attainable only at the cost of partial decomposition. The protonation–deprotonation, nonetheless, can be repeated several times without great loss of material. Protonation to **B-26** is the kinetically favoured process[7].



a: R = *t*-butyl
b: R = H

The electronic spectra—the extinction coefficients are estimated—of **B-27a** and **B-27b** are in good agreement with the data we had reproducibly collected for the parent molecule **2**. The blue shift, on going from **2** or **B-27b** to **B-27a**, is a reflection of the changes in geometry caused by the substituent at C(7). Some of the differences noted for the conjugate acids, especially of **2**, are certainly due to solvent effects. The 7-benzyl-9-*t*-butylsesquifulvalene **B-10** (and its conjugate acid), one of the examples synthesized, fits very nicely into this picture, though with moderate yield as yet, by way of a prototropic rearrangement.



2 **B-27b** **B-10** **B-27a**

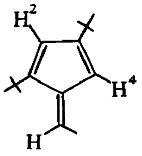
With the knowledge that an n.m.r. spectrum of the parent compound **2** was not to be had, even with integrating equipment, it was especially pleasing to get spectra of the pure alkylated derivatives (*Figures 5, 6*). The magnitude of the coupling constants determined for the cyclopentadienyl protons reflects once more the polyene character of these hydrocarbons*.

B-27a undergoes, with both TCNE and MAD, surprisingly specific addition reactions.

The deep red solution of **B-27a** rapidly changes to yellow upon addition of TCNE (20°). Elemental analysis proves a 1:1 composition of the solid adduct which is formed in practically quantitative yield. Structure **B-28**, arising from the desired α,ω addition to the sesquifulvalene bond system, was deduced from the following evidence. The strong absorption maximum at 331 nm (methanol, ε = 32 700) is indicative of an effective conjugation

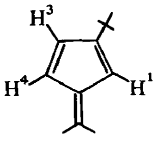
---

* Compare the data measured for the models **i**, **ii**, **iii** and **iv**.



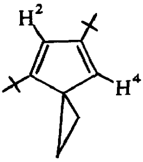
i

$J^{2,4} = 2.0$



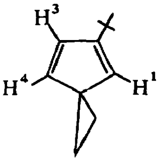
ii

$J^{1,3} = J^{1,4} = 2.0$



iii

$J^{2,4} = 2.2$



iv

$J^{1,3} = 1.8$ Hz
$J^{1,4} = 2.1$ Hz
$J^{3,4} = 5.1$ Hz

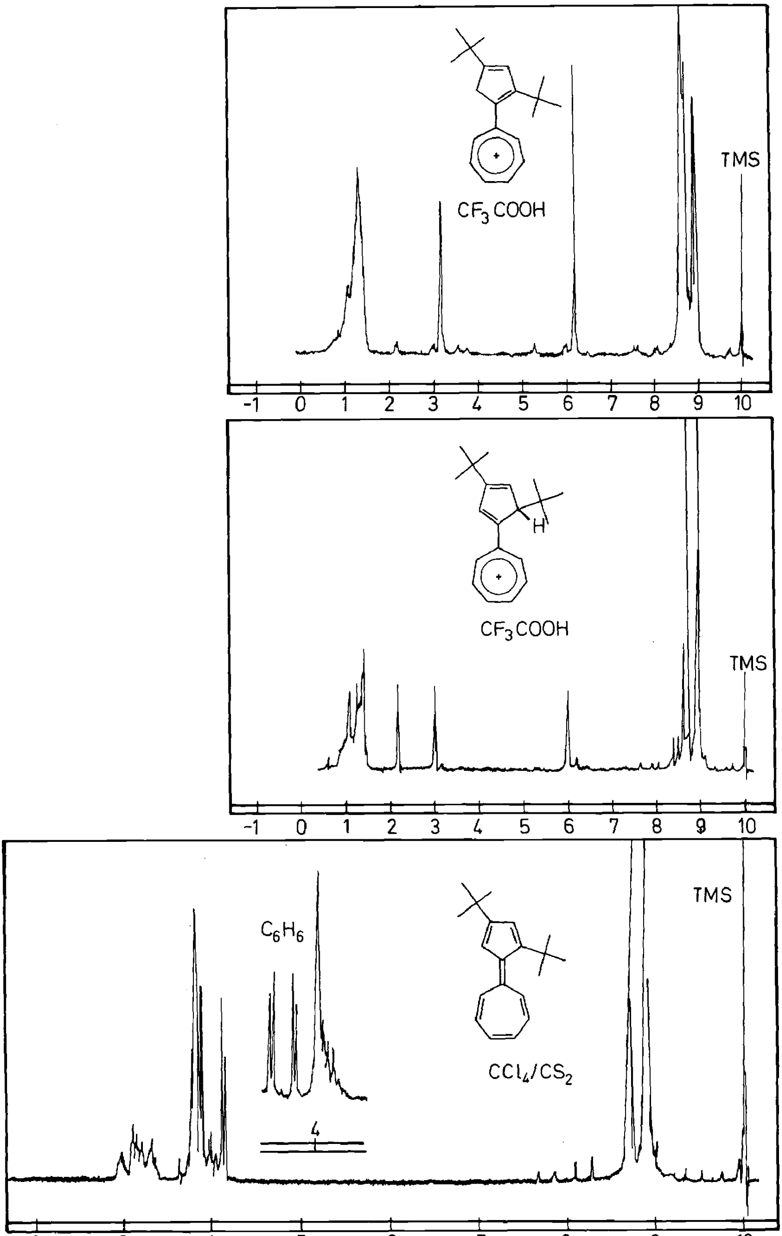


Figure 5. The n.m.r. spectra of the sesquifulvalenium salts **B-26a**, **B-25a** (CF_3CO_2H) and of the sesquifulvalene **B-27a** (60 MHz, CCl_4/CS_2; C_6H_6)

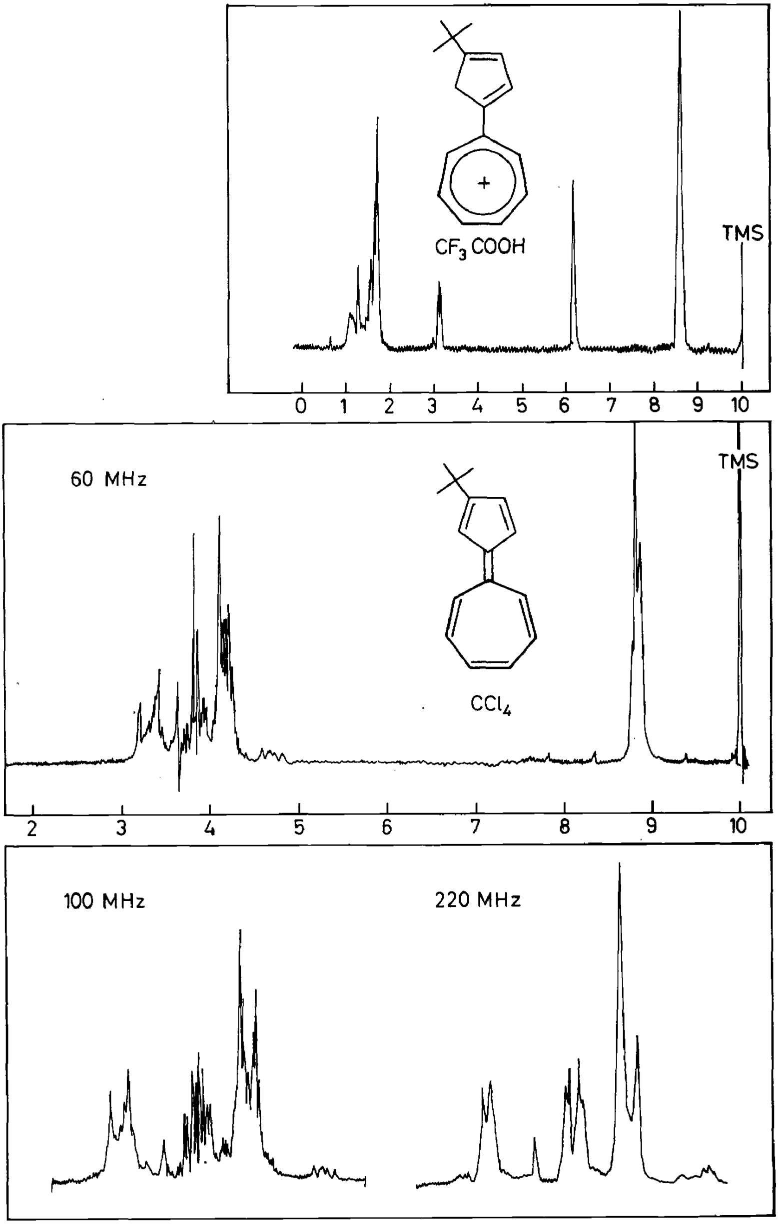
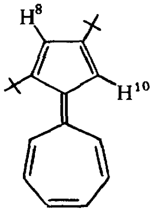
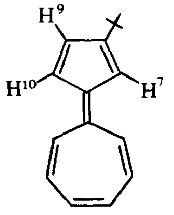


Figure 6. The n.m.r. spectra of the sesquifulvalenium salt **B-26b** (CF_3CO_2H) and of the sesquifulvalene **B-27b** (60, 100, 220 MHz; CCl_4)



B-27a



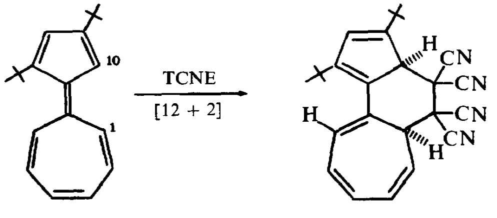
B-27b

τH^8: 3.85
τH^{10}: 4.11

$J^{8,10} = 2.3$ Hz

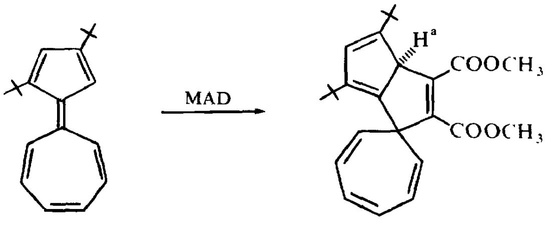
τH^9 : 3.75
τH^{10}: 3.88
τH^7: 4.20
$J^{7,10} = 2.3$ Hz
$J^{7,9} = 1.8$ Hz
$J^{9,10} = 5.3$ Hz

between the two unsaturated rings. The pentaene chromophore in **B-23b** might serve as a model for that in **B-28**, since the ethano bridge in **B-28** enforces a coplanarity better approximated in **B-23b** than in **B-23a**. The $\lambda_{max.}$ of 343 nm (ether) is as close as one can reasonably expect. The points of fixation of the TCNE in the two rings were established by the n.m.r. spectrum



B-27a **B-28**

(*Figure 7*). A comparison with the spectrum of **B-27a** (*Figure 5*) and with the spectrum of the adduct **A-14** (*Figure 4*) convinces one that the lower of the two newly appearing aliphatic-proton-signals stems from the original H^{10}, the higher one from H^1. The details of the spectrum—coupling constants, chemical shifts—all are in line with experience. They allow, however, no firm decision as to stereochemistry of the addition reaction. The *cis* geometry as formulated in **B-28** is symmetry allowed for a $[\pi 12\ s + \pi 2\ s]$ addition type. One is tempted to add, furthermore, that the intensity of the 331 nm maximum is in favour with this geometry in which the pentadiene chromophore



B-27a **B-29**

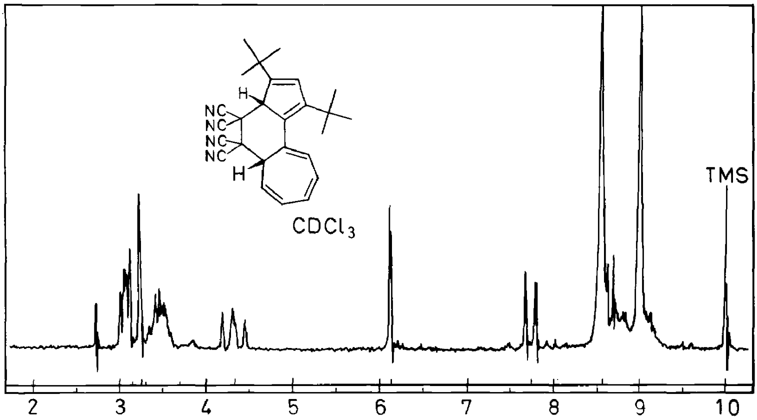


Figure 7. The n.m.r. spectrum of the adduct **B-28** (60 MHz; $CDCl_3$)

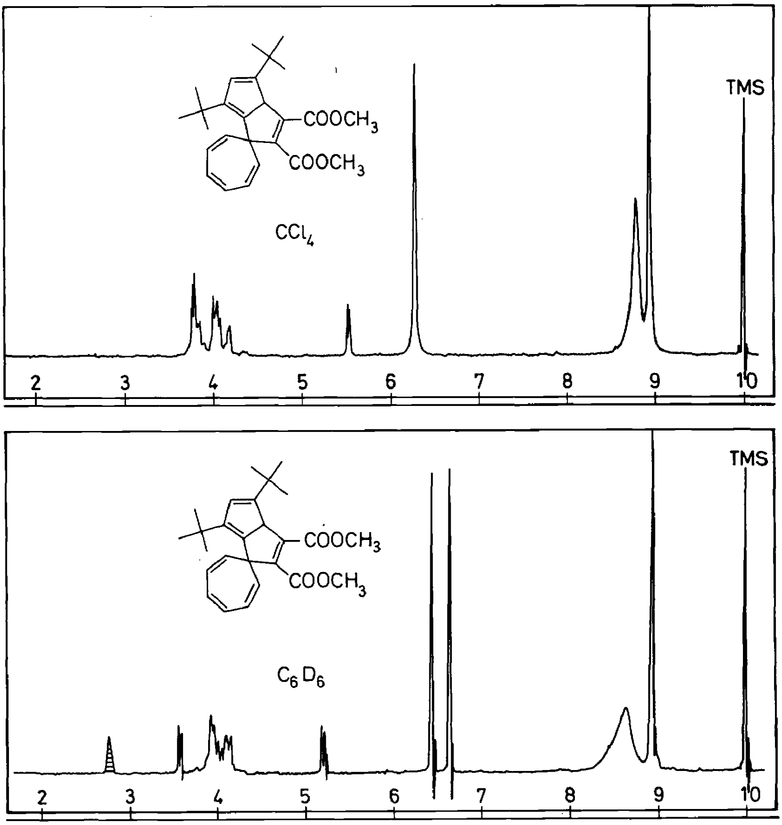


Figure 8. The n.m.r. spectrum of the adduct **B-29** (60 MHz; CCl_4, C_6D_6)

remains as coplanar as the steric interaction between the opposed *t*-butyl group and the cycloheptatriene hydrogen atom allows it to be.

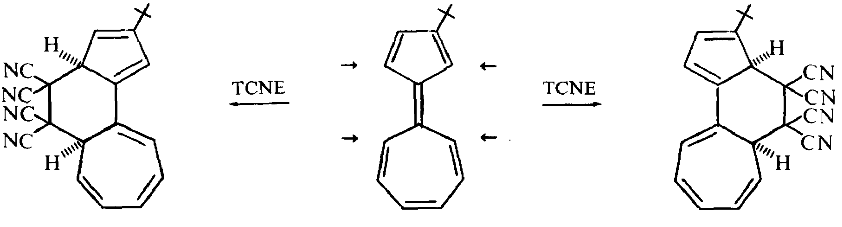
At somewhat higher temperatures, but still in an acceptable range (80°–90°) **B-27a** reacts with MAD yielding again the 1:1 adduct. However, much to our regret, a [12 + 2] product is clearly eliminated by u.v. and n.m.r. studies; the adduct has the spiro structure **B-29**.

The u.v. absorption curve (ethanol) shows two maxima [280 nm ($\varepsilon = 7900$); 223 nm (21950)] attributable to the cycloheptatrienyl- and cyclopentadienyl/maleic chromophoric units, and in addition, a shoulder at 334 nm ($\varepsilon = 1300$) which, with some reservation, we ascribe to a spiro conjugational effect.

According to the n.m.r. spectrum (*Figure 8*) there is only one aliphatic proton (H^a) directly attached to the cyclic system, this one being the original H^{10}.

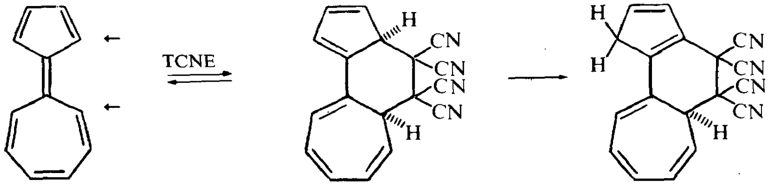
In Section C we will learn of another example of this type of addition. Several explanations could be advanced to account for the differing modes of addition of TCNE and MAD—change of mechanism, bond length in the dienophil, etc. At present, all these explanations are nothing more than conjecture.

The addition studies with **B-27b** and with the parent sesquifulvalene **2**—though still in a preliminary stage—leave no doubt that the [12 + 2] addition of TCNE to the sesquifulvalene system is rather general. Apparently, **B-27b** adds TCNE from both sides with roughly equal probability, giving **B-30** and **B-31**, both of which experience a slow hydrogen migration in the five-membered ring on standing in solution.



B-30 **B-27b** **B-31**

From very similar spectral data we conclude that the parent sesquifulvalene **2** adds TCNE—preferentially, if not exclusively—in the same [12 + 2] fashion. From the necessarily very dilute solution of **2**—the reaction is nevertheless very rapid—a solid 1:1 adduct precipitates out which is stable in relatively nonpolar solvents but quickly dissociates to its components in a

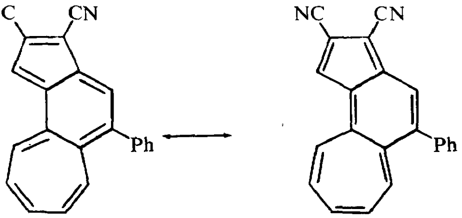


2 **B-32** **B-33**

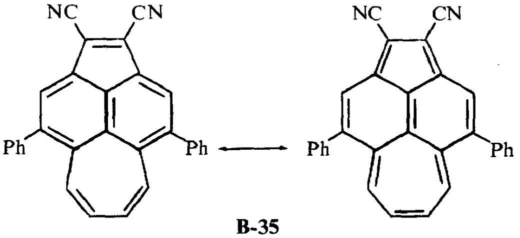
solvent like tetrahydrofuran. The 345 nm maximum ($CDCl_3$) compares well with the absorption of the model **B-23**; **B-32**—the stereochemistry is postulated—tautomerizes in solution to what is thought to be **B-33**. The n.m.r. spectrum allows no clear decision between the three tautomers having a methylene group in the five-membered ring[8].

Note added in proof

The 7,9-diphenylsesquifulvalene synthesized recently adds TCNE in the [12 + 2] manner, whilst all the evidence with MAD points towards the formal [6 + 2] addition observed with **B-27a**. In contrast, the 8,9-dicyanosesquifulvalene, a stable crystalline compound, does not react with TCNE or MAD under comparable conditions. With electron-rich olefins, e.g. piperidinostyrene, an almost instantaneous reaction takes place. Depending on the experimental conditions a 1:1 or 1:2 adduct is formed preferentially, allowing the isolation of the bridged annulenes **B-34**, **B-35**[9].



B-34



B-35

REFERENCES

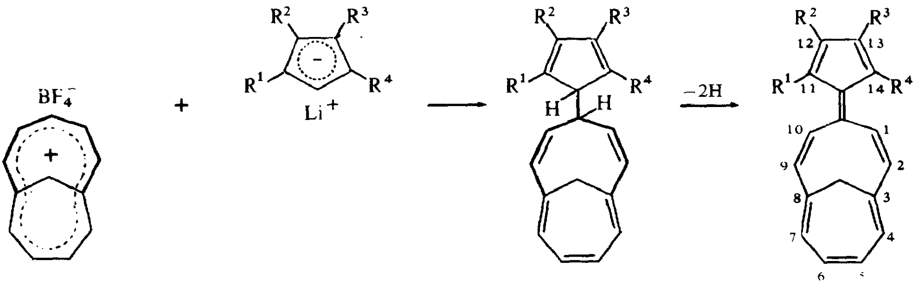
[1] W. Rosswog, *Dissertation*, University of Freiburg i.Br. (1964).
[2] Y. Kitahara, I. Murata and S. Katagiri, *Angew. Chem.* 77, 345 (1965); G. Seitz, *Angew. Chem.* **79**, 96 (1967).
[3] H. Prinzbach, D. Seip, L. Knothe and W. Faisst, *Liebigs Ann. Chem.* **698**, 54 (1966).
[4] H. Prinzbach, D. Seip and G. Englert, *Liebigs Ann. Chem.* **698**, 57 (1966).
[5] Our earlier report has to be revised in this sense. [H. Prinzbach and W. Rosswog, *Tetrahedron Letters*, 1217 (1963).].
[6] L. Knothe, *Dissertation*, University of Freiburg i.Br. (1969).
[7] H. Prinzbach and H. Knöfel, *Angew. Chem.* **81**, 900 (1969); H. Prinzbach, H. Knöfel and E. Woischnik, *Proceedings* of the Third Jerusalem Symposium on 'Aromaticity, Pseudoaromaticity, Antiaromaticity', p 269. Israel Academy of Sciences and Humanities: Jerusalem (1971).
[8] U. Fischer, *Dissertation*, University of Freiburg i.Br. (1966).
[9] H. Prinzbach, V. Blumenstock, L. Knothe, H. Knöfel, H.-W. Schneider and E. Woischnik, unpublished.

C. FIDECENES

L. KNOTHE and D. FORSTER

'Fidecene'* is the most recently synthesized example of the 'mixed fulvalenes'. Since the experimental results obtained for this class of cross-conjugated hydrocarbons have been published in a very incomplete way, we would like to present a short résumé about what is known to date.

All synthetic approaches to this system were patterned after the following sequence. For obvious reasons it was Vogel's bicyclo[5,4,1]dodecapentaenyliumfluoroborate **C-1** which was used as 11-ring cation in all instances.



and isomers

and isomers

C-1

C-2

In the cation **C-1**, because of the bridge, six different positions are open to an attacking nucleophile. Judged by the localization energies[2] the addition in the 4-position, leading to the symmetrical and desired form, was predicted to be favoured. However, in those cases where several positional isomers have been isolated from the reaction between **C-1** and a cyclopentadienyl anion **C-2** we had to note a rather strong preference for nucleophilic attack at position 2.

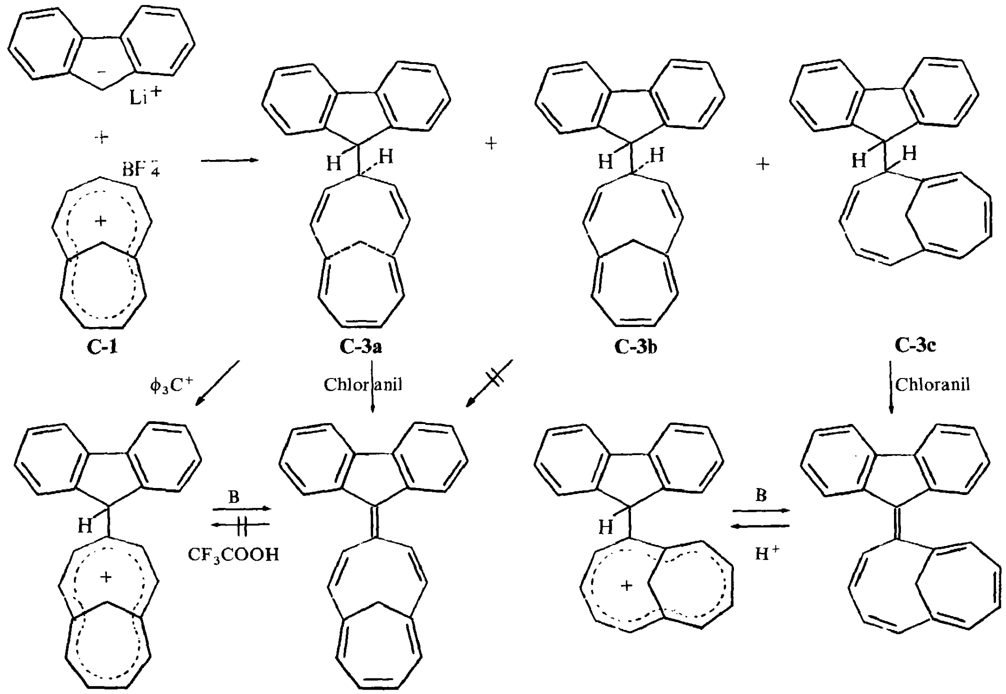
To give you some insight into the experimental problems involved, consider that some of the dihydromethanofidecenes may exist in several tautomeric forms and, furthermore, that still another kind of isomerism may result from the fact that the cyclopentadienyl substituent may be *syn* or *anti* to the methano bridge. For the unsubstituted dihydromethanofidecene, not less than 168 isomeric structures are theoretically possible.

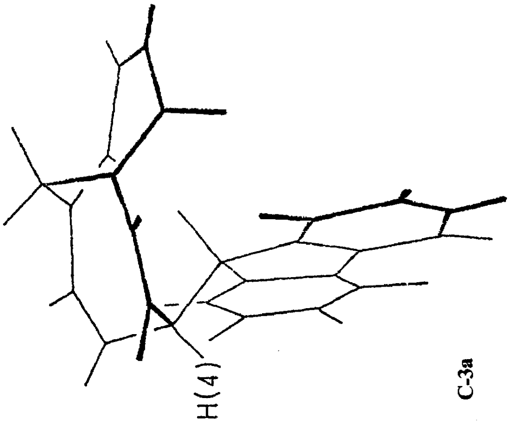
For the foregoing reasons only a few dihydro compounds were isolated and characterized; more often the crude products from the reaction between the ions **C-1** and **C-2** were oxidized directly.

From our experiences with the calicenes and sesquifulvalenes we felt it wise to begin with the synthesis of the predictably stable and more manageable dibenzo- and tetraphenyl-methanofidecenes. These would be followed by the di-*t*-butyl-substituted derivatives, and finally by the parent compounds[3].

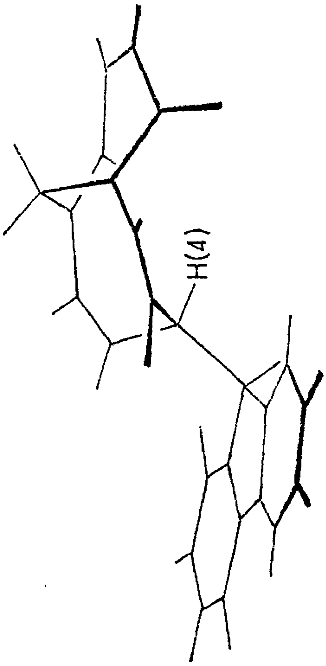
---

* 'Fidecene' is the trivial name proposed by us[3] for the cyclopentadienylidene-cycloundecapentaene ('Pentahendecafulvalene') because of the formal resemblance of its ctctc-structure to a well known musical instrument (lat. *fides*). The isomeric methano-fidecenes can be named by indicating the position of the methano bridge.


Li+
+
BF$_4^-$
C-1
H
H
C-3a
+
C-3b
+
C-3c
ϕ_3C^+
Chloranil
Chloranil
C-6
B
CF$_3$COOH
C-4
C-7
B
H$^+$
C-5

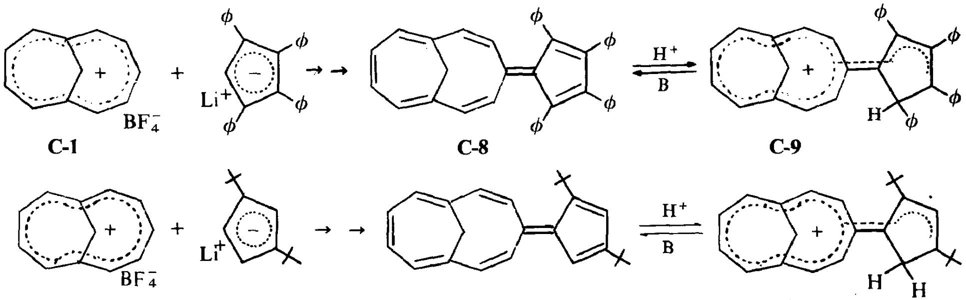


C-3a



C-3b

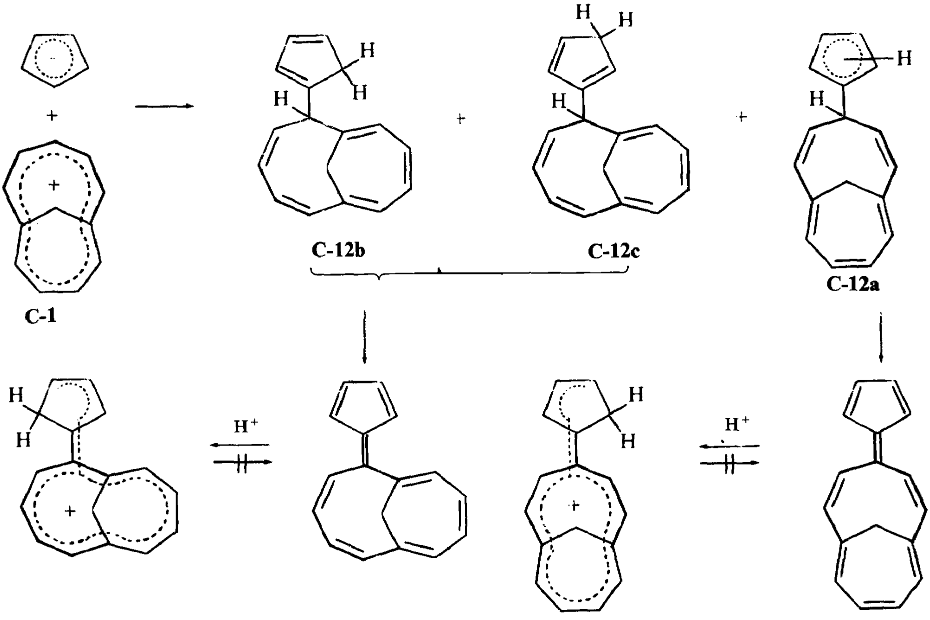
In the reaction with fluorene we were able to separate **C-3a**, **C-3b** and **C-3c** as major dihydro products. Isomer **C-3a** gave, upon oxidation with chloranil, the symmetrical methanofidecene **C-4**, and isomer **C-3c** gave the unsymmetrical **C-5**. Under identical conditions **C-3b** was resistant to oxidation. An examination of models suggests that geometrical factors are responsible. In the *syn*-arrangement H(4) is effectively screened by the molecular framework. An effective separation of **C-4** and **C-5** can be readily achieved by taking advantage of their differing basicities; with HBF_4 (ether) **C-5** is protonated to form the rather insoluble salt **C-7**, while **C-4** remains unchanged in solution. In practice, therefore, there was no necessity to go through the tedious and product-destroying separation at the dihydro stage (**C-3**).



C-1 **C-8** **C-9**

C-1 **C-10** **C-11**

In the reactions between **C-1** and tetraphenylcyclopentadiene and di-*t*-butylcyclopentadiene, respectively, we secured only the symmetrical systems **C-8** and **C-10**, both in low yields (3 to 7 per cent). A possible explanation

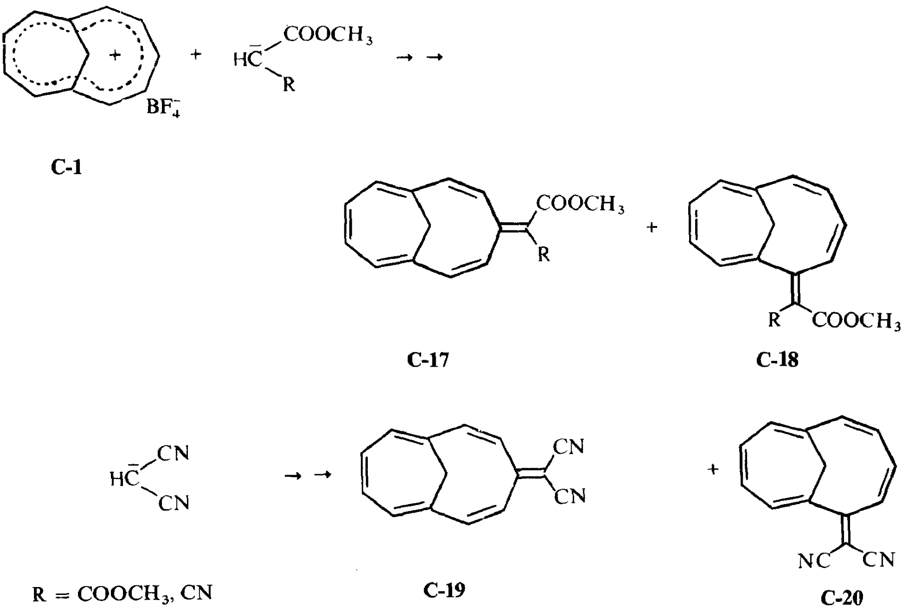


C-1 **C-12b** **C-12c** **C-12a**

C-16 **C-14** **C-15** **C-13**

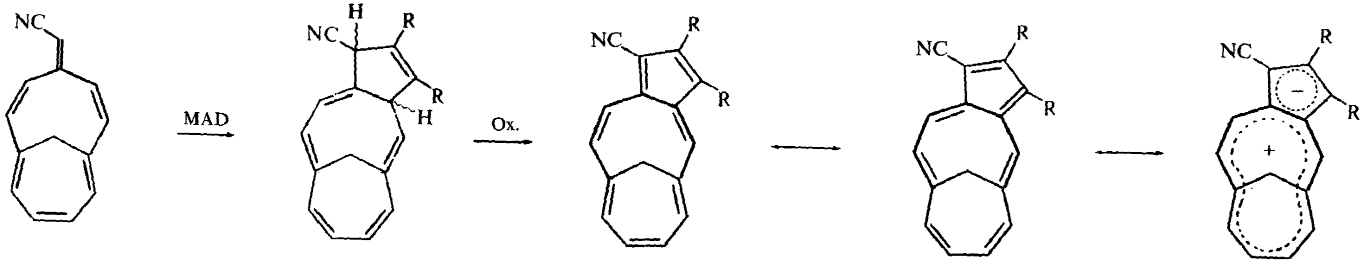
came to mind in the experiments with unsubstituted cyclopentadiene. Systematic control experiments made it clear that, to a limited extent, the relative amount of the symmetrical dihydro product **C-12a** could be increased by raising the reaction temperature and that the rates of oxidation for the symmetrical and unsymmetrical dihydro products varied appreciably; **C-12b, c** were being oxidized faster than **C-12a** by a factor of about seven. In addition, the methanofidecene **C-14** is not stable under the reaction conditions and gradually disappears with longer reaction times. Thus, it turns out that by careful manipulation of the experimental procedures, solutions of pure **C-13** and **C-14** could be made available.

In order to gain additional spectral information (*vide infra*) the hendecafulvenes **C-17**–**C-20** were synthesized from **C-1** and the appropriate malonic acid derivatives[4]. A second motive for the synthesis of these fulvenes

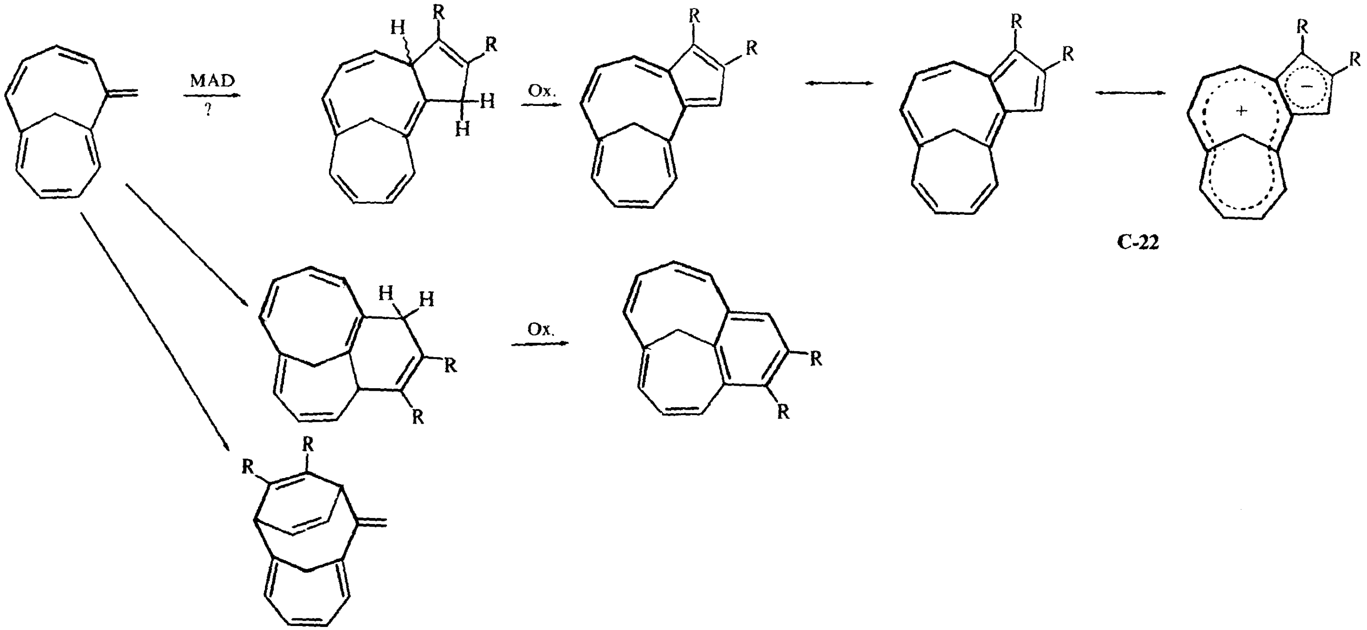


is their potential application in [12 + 2] cycloaddition reactions leading ultimately to the new azulene-analogous **C-21** and **C-22**. At present, such a route seems to be restricted to the use of the unsymmetrical products, since the malonyl anions, like the cyclopentadienyl anions, seem to have an overwhelming preference for attachment at position 2 in **C-1**.

The n.m.r. spectra of the *symmetrical* methanofidecenes **C-4**, **C-8**, **C-10** and **C-13** and of the *symmetrical* hendecafulvenes **C-17** and **C-19** are all remarkably similar. In the olefinic region they all exhibit an AA′BB′ multiplet and an AB quartet for the eleven-membered ring protons, and two doublets at higher field (τ = 6–7; τ = 9.5–10.5) for the methano-bridge protons. As an example, the spectrum of **C-13** is shown in *Figure 9*.



C-21



C-22

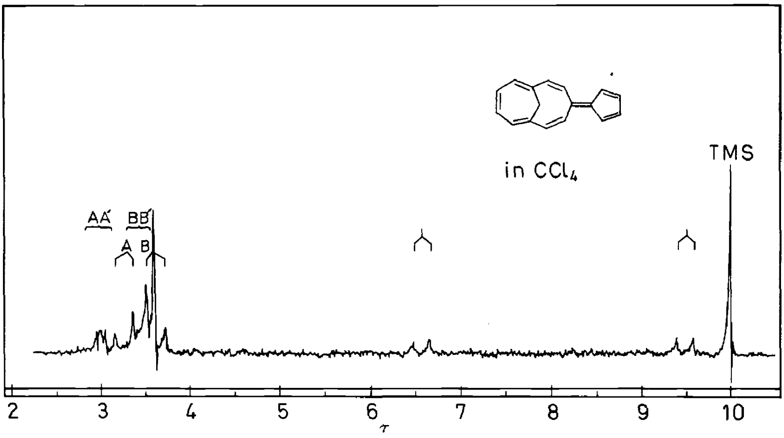
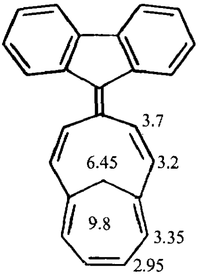
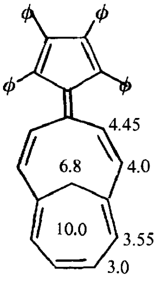


Figure 9. The n.m.r. spectrum of **C-13** (60 MHz, CCl_4)

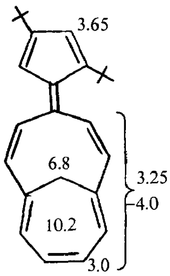
The great similarity of the chemical shifts for those protons not influenced by anisotropic effects is evident from a comparison of the data given below:



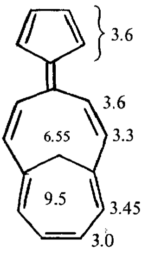
C-4



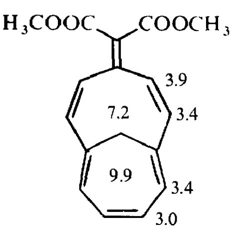
C-8



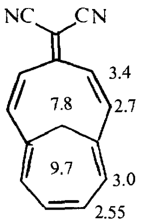
C-10



C-13

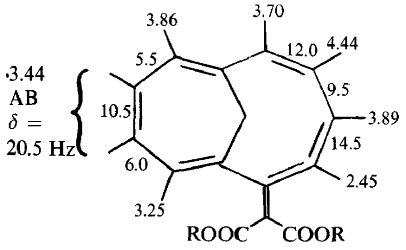


C-17



C-19

The spectra of the unsymmetrical methanofidecenes **C-5** and **C-14** are much more complicated. Because a satisfactory analysis was not possible, a reliable assignment as to the point of attachment of the cyclopentadienylidene moiety could not be made until the biscarbomethoxyhendecafulvene **C-18** was at our disposal. The 220 MHz spectrum (*Figure 10*) of the latter can be



C-18

(in C_6D_6)

interpreted as a pseudo-first order spectrum and allows an assignment of all the signals. In the result, there are two groups of four protons each, showing spin–spin coupling *within* the groups only. This excludes all possible structures but **C-18**.

The chemical shifts and coupling constants determined for **C-5** and **C-14** are presented in *Table 2*. The good agreement leaves little doubt that **C-5**, **C-14** and **C-18** all are substituted in the same position. By applying the same reasoning as in the case of the symmetrical analogues and of the lower vinylogues, the magnitude of the coupling constants is indicative of a system with alternating single and double bonds. As far as the ultra-violet and visible spectra are concerned, the unsymmetrical methanofidecene and hendecafulvene absorbances are consistently red-shifted compared to the symmetrical analogue; the difference is especially great for the dibenzo compounds **C-4** and **C-5**.

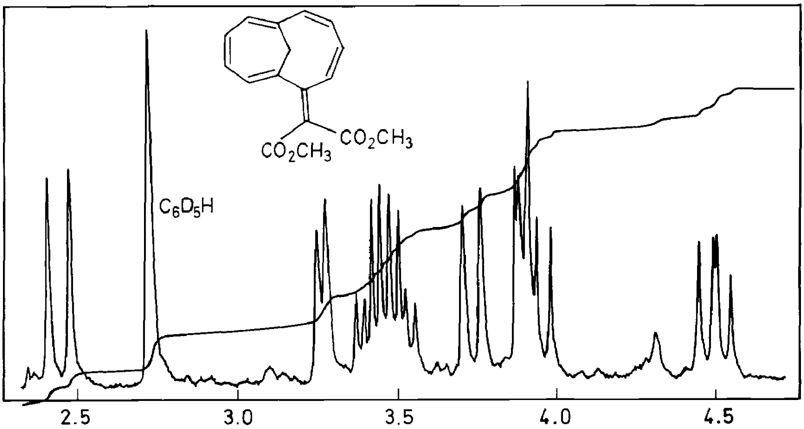


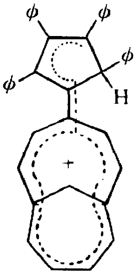
Figure 10. The n.m.r. spectrum of **C-18** (220 MHz, CCl_4)

The behaviour of the methanofidecenes and hendecafulvenes towards strong acids brought no surprises. With the exception of **C-4** and **C-19**, all the cross-conjugated systems described in this section are protonated by trifluoroacetic acid or perchloric acid in ethanol. For **C-4**, a stronger acidic medium such as sulphuric–glacial acetic acid is necessary. As was expected, and thus confirming the correctness of our structural assignments, the u.v.

Table 2. The n.m.r. data for **C-18**, **C-14** and **C-5**

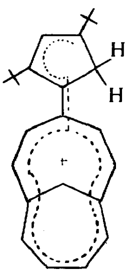
Cpd		H(3)		H(4)		H(5)		H(6)	
C-18	τ =	3.59		3.40		3.30		3.75	
(CCl_4)	J =		6		10.5		5.5		Hz
		H(2)		H(3)		H(4)		H(5)	
C-14	τ =	3.53		3.39		3.21		(3.57–3.84)	
(CCl_4)	J =		6		11		5.5		Hz
C-5	τ =	3.13		3.40		3.25		3.71	
($CDCl_3$)	J =		6.5		10.5		5.5		Hz
Cpd		H(8)		H(9)		H(10)		H(11)	
C-18	τ =	3.57		4.30		3.83		2.90	
(CCl_4)	J =		12		9.5		14.5		Hz
		H(7)		H(8)		H(9)		H(10)	
C-14	τ =	(3.57–3.84)		4.33		4.00		3.20	
(CCl_4)	J =		12		9.5		14.5		Hz
C-5	τ =	3.60		4.27		3.90		(2.65–2.98)	
($CDCl_3$)	J =		12		9.5		14		Hz

and n.m.r. data for the conjugate acids **C-6** and **C-7** very closely resemble those of the fluoroborate **C-1**. The position of the added proton in the fidecenium salts **C-9**, **C-11**, **C-15** and **C-16**, as well as the delocalization of the positive charge through the five-membered ring, are established by the change in the electronic spectra on going from the fidecenes to their conjugate acids; furthermore, the chemical shifts of the eleven-membered ring protons and of the methano protons lie between the values for the salt **C-1** and the corresponding hydrocarbons.



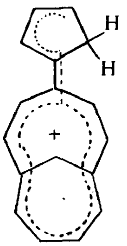
$\lambda_{max.}$: 610 nm

C-9



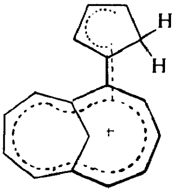
564 nm

C-11



523 nm

C-15



553 nm

C-16

Qualitative statements as to the charge distribution in the methano-fidecene molecules are based on dipole moment measurements and the chemical shifts of the methano protons.

For the dibenzofidecene **C-4** we have measured a dipole moment (benzene) of $\mu = 1.2$ D. The moment calculated on the basis of complete charge separation in **C-4** is $\mu = 26$ D. Apparently the contribution of the dipolar limiting structure to the description of the ground state electron configuration cannot be important.

The very same conclusion is reached from a consideration of the chemical shift changes observed for the methano protons. In the fidecenes, in their dihydroforms, as well as in the bicyclo[5,4,1]dodecapentaene-2,5,7,9,11 [ref. 6], the lower field half of the AX quartet belongs to the proton above the larger ring. In the case of the delocalized cation **C-1** the situation is reversed; the proton above the larger ring is situated closer to the centre of the eleven-membered ring and therefore is more screened by the ring current. This interpretation is supported by the fidecenium salts, for which the methano protons are found somewhere in between.

Clearly, the chemical shift of the proton above the smaller ring (see *Figure 11**)—*cum grano salis*—remains constant for all compounds, while the proton above the larger ring varies between $\tau = 6.15$ (in the dihydro form **C-3a**) and $\tau = 11.8$ (in **C-1**). The τ values of these geminal protons may be regarded, albeit very qualitatively, as a measure of the electron delocalization in the system.

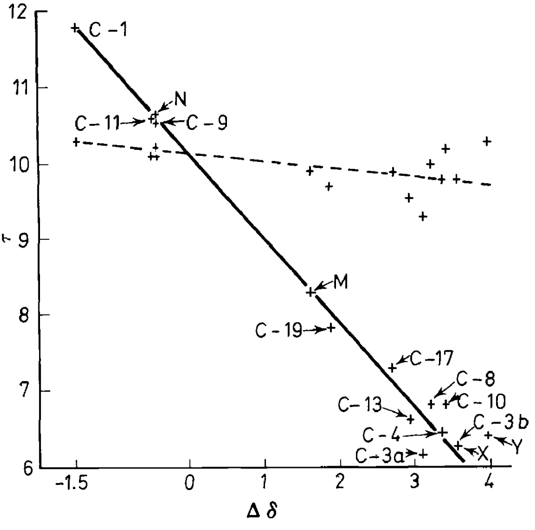
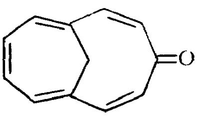


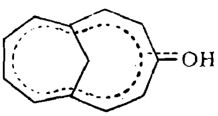
Figure 11. Chemical shift of the methano-bridge protons of symmetrically substituted bicyclo[5,4,1]dodecapentaene derivatives

---

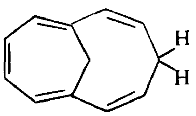
* In *Figure 11* values for the following compounds have been included[6].



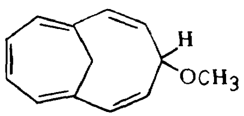
M



N



X



Y

Our efforts to achieve cycloaddition reactions with the methanofidecenes and hendecafulvenes mentioned above, have so far been restricted to two examples.

The dibenzofidecene **C-4** undergoes a reaction with maleic anhydride (140°; bromobenzene). The n.m.r. data are compatible with the structure **C-24**; this would mean that the dienophile adds to the norcaradiene tautomer **C-23**.

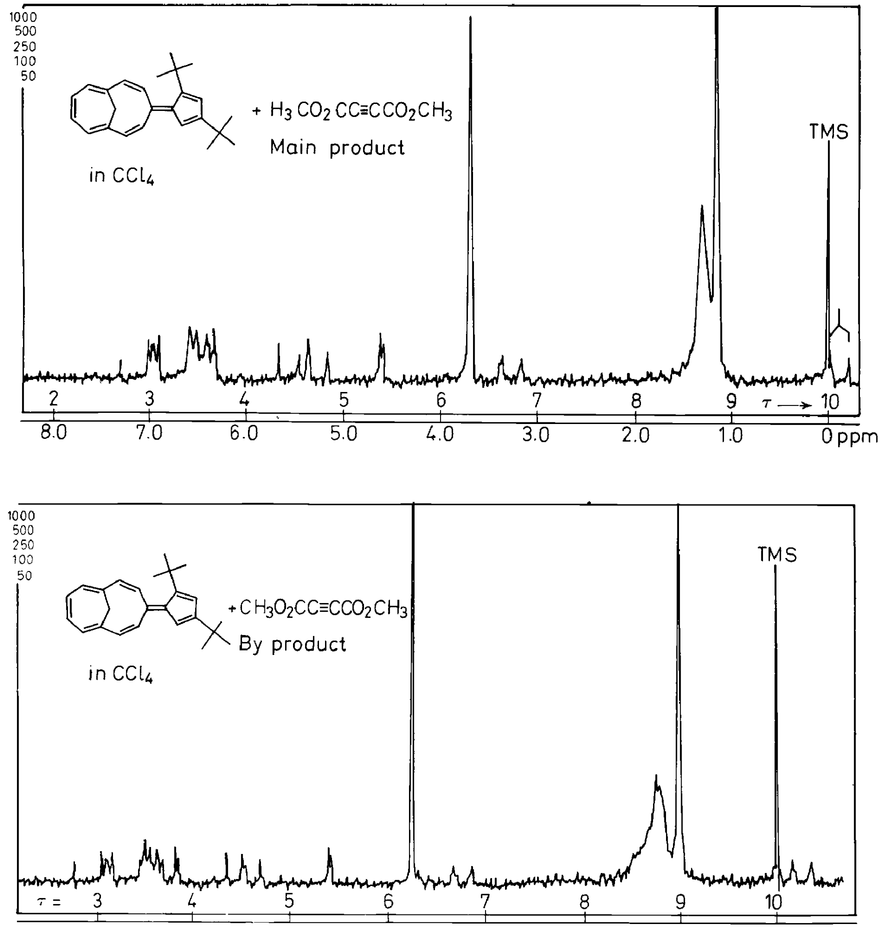
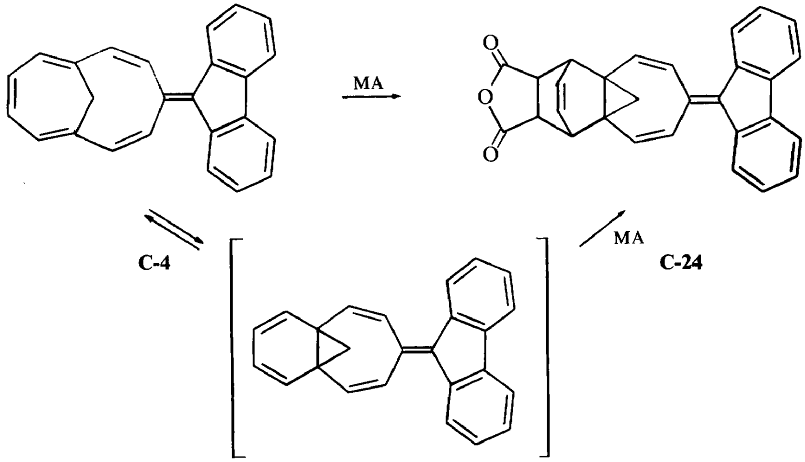


Figure 12. The n.m.r. spectra of **C-27a** and **C-27b** (60 MHz, CCl_4)

The di-*t*-butyl-compound **C-10** adds MAD (in a manner analogous to that established for the sesquifulvalene **B-27a**). By careful chromatographic work-up the mixture of the *syn*/*anti* isomers **C-27a**/**C-27b** (7 : 3) was separated.

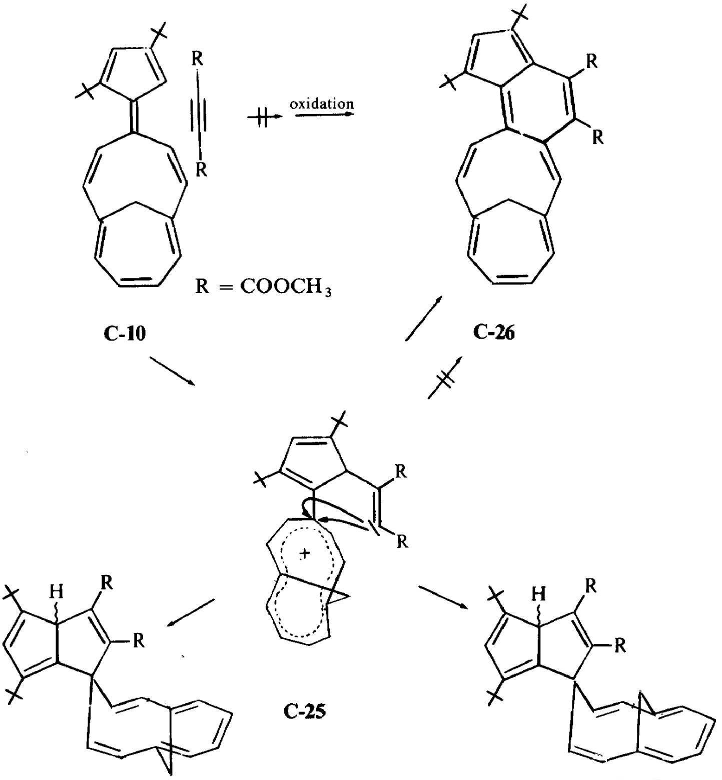


C-4

C-24

C-23

A possible rationale is the formation of the intermediate **C-25** by electrophilic attack at C(14) followed by ring closure either *syn* or *anti* to the methano bridge. No **C-26** was observed. It is not certain which is which,



C-10

C-26

C-25

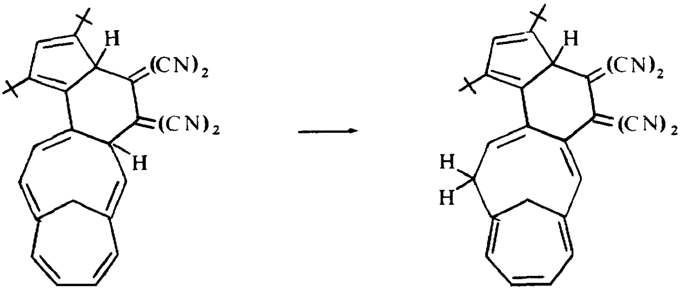
C-27a

C-27b

but it seems plausible to ascribe the sterically less hindered structure (**C-27a**) to the major component of the mixture. The considerable broadening of one of the two *t*-butyl n.m.r. signals in the spectrum of what is believed to be **C-27b** is also in agreement with this.

Note added in proof

We recently gathered convincing evidence that **C-10** with TCNE undergoes a [16 + 2] cycloaddition; because of a rapid 1,9-hydrogen migration in the primary product **C-28** nothing can be said about the stereochemical aspect of this process.



C-28

REFERENCES

[1] E. Vogel and H. D. Roth, *Angew. Chem.* **76**, 145 (1964);
W. Grimme, H. Hoffmann and E. Vogel, *Angew. Chem.* **77**, 348 (1965).

[2] M. J. S. Dewar, G. J. Gleicher and C. C. Thompson Jr, *J. Amer. Chem. Soc.* **88**, 1349 (1966);
D. H. Lo and M. A. Whitehead, *J. Chem. Soc.* (*B*),480 (1970).

[3] H. Prinzbach and L. Knothe, *Angew. Chem.* **79**, 620 (1967);
U. Fischer, L. Knothe and H. Prinzbach, *Chimia*, **21**, 589 (1967);
H. Prinzbach and L. Knothe, *Angew. Chem.* **80**, 698 (1968);
H. Prinzbach, L. Knothe and A. Dieffenbacher, *Tetrahedron Letters*, 2093 (1969).

[4] L. Knothe, D. Forster, H. Friebolin, H. Achenbach and H. Prinzbach, *Tetrahedron Letters*, 3075 (1970).

[5] H. Günther and H.-H. Hinrichs, *Tetrahedron Letters*, 787 (1966);
M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.* **91**, 6325 (1969).

[6] W. Grimme, personal communication;
E. Vogel, R. Feldmann and H. Düwel, *Tetrahedron Letters*, 1941 (1970).

D. PENTAFULVALENES

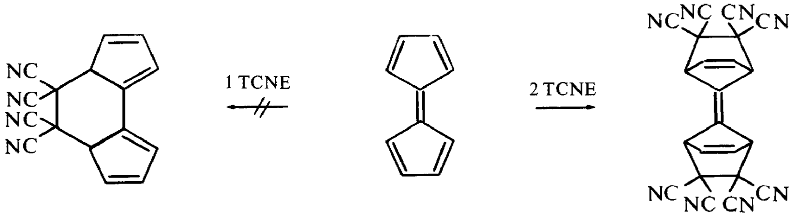
H. SAUTER

We became engaged in work on pentafulvalenes mainly for the two reasons mentioned above: use in a synthesis of *as* indacenes (**2** → **7**) and of specifically substituted sesquifulvalenes (see Part B).

A hint that the chances of accomplishing such a synthesis of **7** would be rather dim, comes from the work of Doering and Matzner[1], according to whom the parent molecule **2**, with TCNE, undergoes not a [10 + 2] cycloaddition to **D-1** but a double Diels–Alder reaction to **D-2**. This failure of **2** to take part in an α,ω-cycloaddition, in contrast to the behaviour of the calicenes **A-7a**, **A-7b** and of the sesquifulvalenes **3**, **B-27a**, **B-27b** may be traced back to the fact that in a concerted reaction going through an antiaromatic 12π-transition state, the *cis* addition is not allowed on symmetry grounds while the allowed *trans* addition is apparently hindered for steric reasons.

It is our hope that by introducing appropriate substituents into **2**, and thereby forcing the molecule to assume a somewhat twisted geometry, the Diels–Alder addition can be retarded in favour of a [π10 *a* + π2 *s*] addition.

A survey of the literature makes it clear that suitable pentafulvalenes are not very numerous. Most of the derivatives which have been described are substituted in such a way that an α,ω-addition would be impossible[2].



D-1 **2** **D-2**

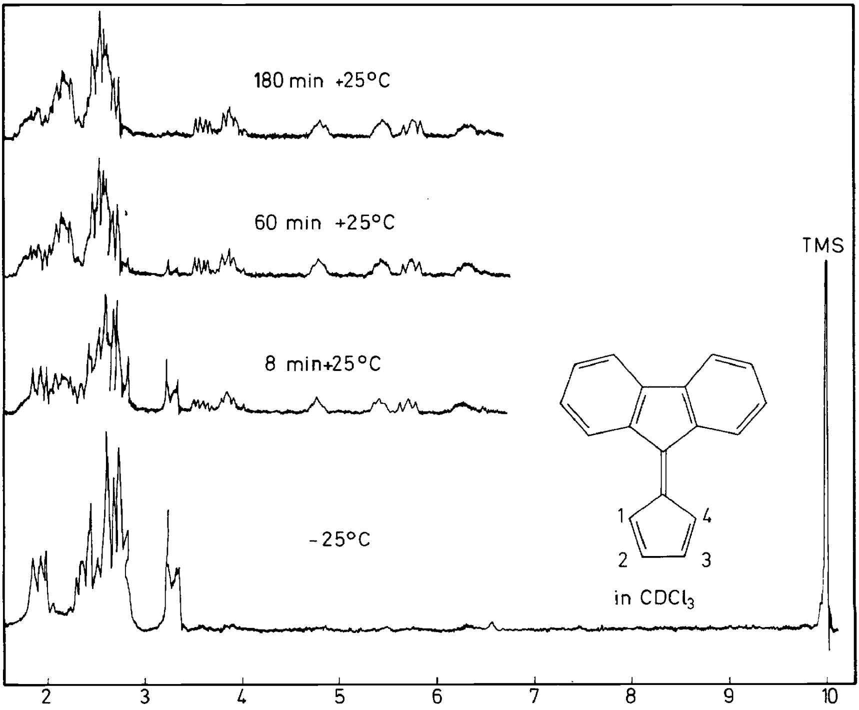
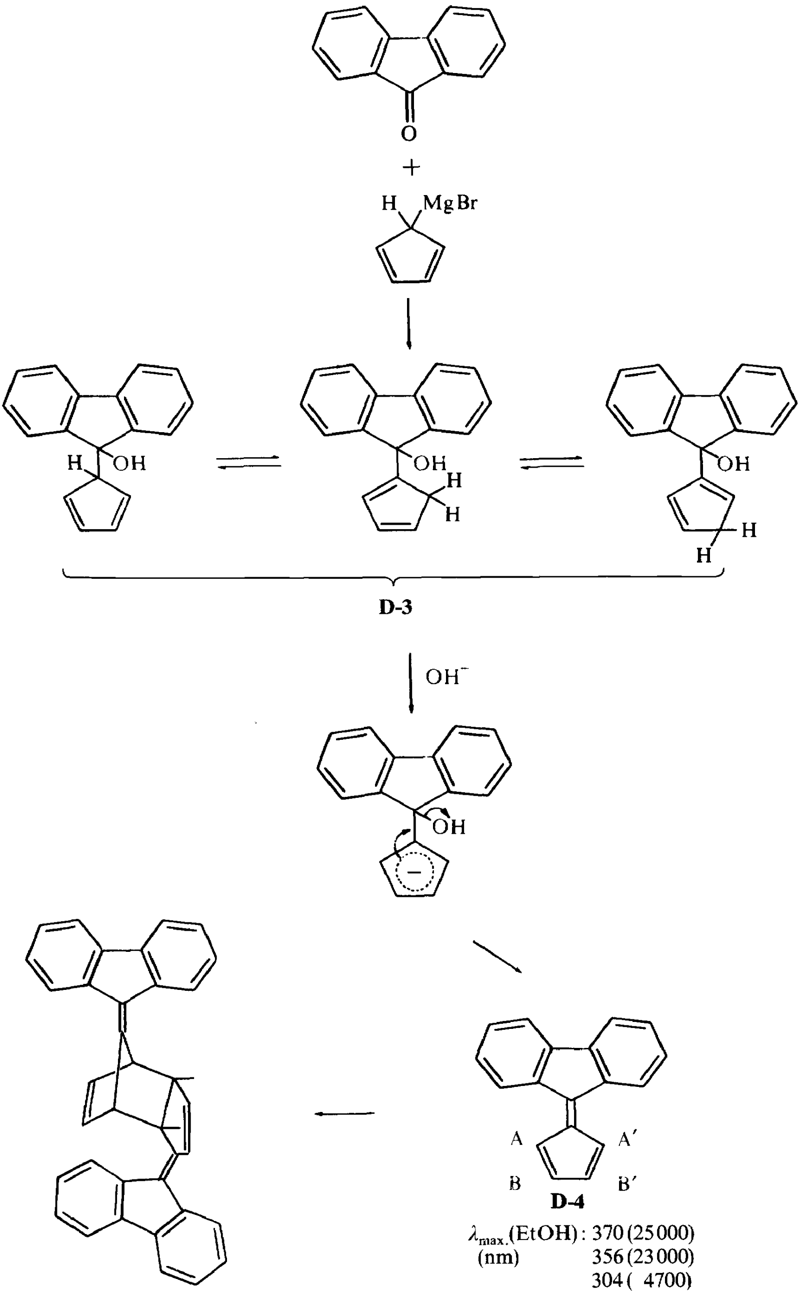


Figure 13. The n.m.r. spectra of the pentafulvalene **D-4** and of the dimerization to **D-5** (60 MHz, $CDCl_3$)



D-3

D-4

D-5

$\lambda_{\text{max.}}$(EtOH): 370 (25 000)
(nm) 356 (23 000)
304 (4700)
293 (5000)
272 (33 000)
263 (28 800)
256 (23 000)
237 (27 000)

Our primary concern to date, then, has been to devise synthetic routes, and we report here some of our results.

In order to gain some feeling for, and some information on, these undoubtedly very reactive and unstable polyenes we began by repeating the reported preparations of 1,2,3,4-dibenzo- (**D-4**) and of 1,2,3,4-tetraphenylpentafulvalene (**D-9**). As we soon learned, some of this earlier work needs revision.

Bergmann[3], by following the procedure prescribed by Courtot[4]—condensation of fluorenone with cyclopentadiene—was not able to verify the formation of the 'red hydrocarbon' claimed to be formed in low yield. In our hands, the original prescription does indeed lead to the formation of a deeply coloured red solution—later on proved to contain dibenzopentafulvalene (**D-4**)—from which the isolation of the pure polyene could not be realized; dimerization is too rapid in solution. A modification, outlined below, circumvents the problem of dimerization by effecting the base catalysed dehydration **D3** → **D4** under such conditions that **D-4** is precipitated rapidly from the solution in crystalline form in yields of 30 to 40 per cent. These brilliant red crystals can be stored at −20° for a considerable time. From an n.m.r. experiment at −25° (*Figure 13*) data on the monomeric **D-4** could be collected*, and its disappearance with increasing temperature could be followed. As is evident from this experiment, the thermal reaction of **D-4** leads cleanly to a dimer for which the structure of a normal Diels–Alder adduct **D-5** is established (*Figure 14*).

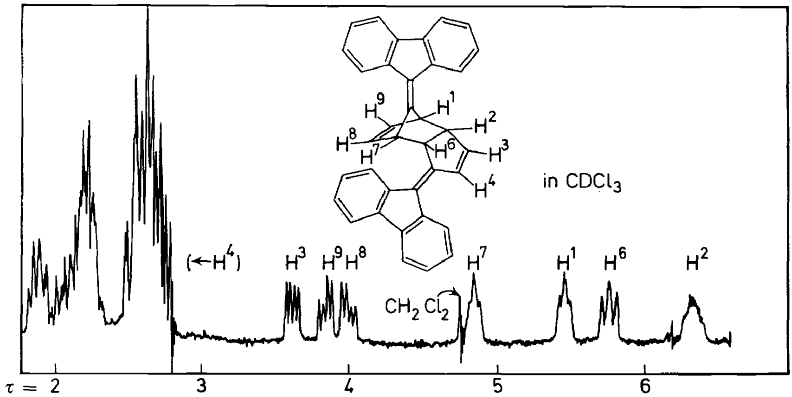


Figure 14. The n.m.r. spectrum of the dimer **D-5** (100 MHz, $CDCl_3$)

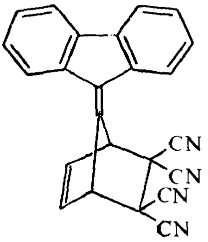
---

* The calculated AA′BB′-spectrum using the following set of coupling constants reproduces the experimental spectrum, giving excellent agreement regarding peak positions and line intensities.

$$J^{1,2} = J^{3,4} = 5.5 \text{ Hz}$$
$$J^{1,3} = J^{2,4} = 1.3 \text{ Hz}$$
$$J^{2,3} = J^{1,4} = 2.1 \text{ Hz.}$$

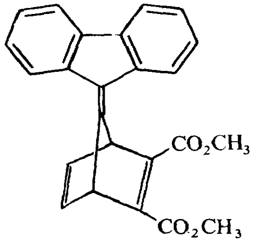
$J^{1,2} = 4.5$ Hz $\qquad J^{6,7} = 4.0$ Hz
$J^{2,6} = 5.7$ Hz $\qquad J^{7,8} = 3.0$ Hz
$J^{3,4} = 6.0$ Hz $\qquad J^{8,9} = 6.0$ Hz

With TCNE and MAD the adducts **D-6** and **D-7** are obtained; the latter one conveniently by heating the dimer in the presence of MAD.



D-6

τ = 4.2 –4.35 (2, 't')
2.85–3.1 (2, 't')
1.7 –2.7 (8, m)
(CD_3CN)



D-7

τ = 4.5–4.7 (2, 't')

2.0–2.9 (10, m)
($CDCl_3$)

Using the same approach which proved successful in the case of **D-4**, we carried out the condensation with tetraphenylcyclopentadienone and obtained by way of the mixture **D-8** a 60 to 70 per cent yield of tetraphenylpentafulvalene **D-9**. The physical and chemical properties of our violet crystalline material are in conflict with those reported[5].

Our product, which shows a tendency for dimerization at 80°, has been unequivocally identified as **D-9** by spectral analysis (cf. *Figure 15*) as well as by isolation of the addition products **D-10**, **D-11** and **D-12**.

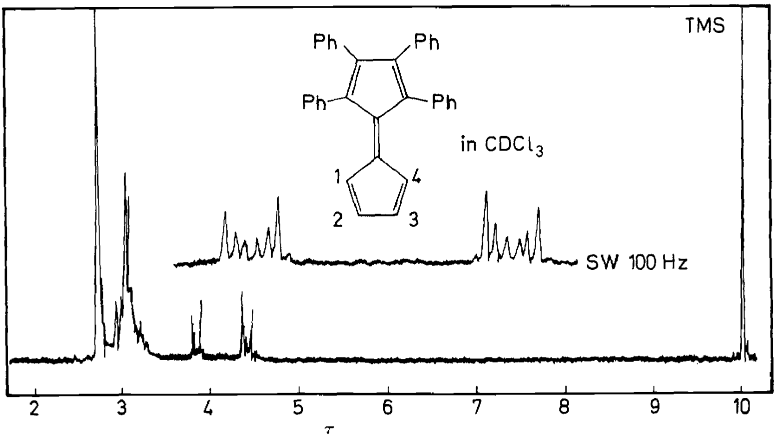
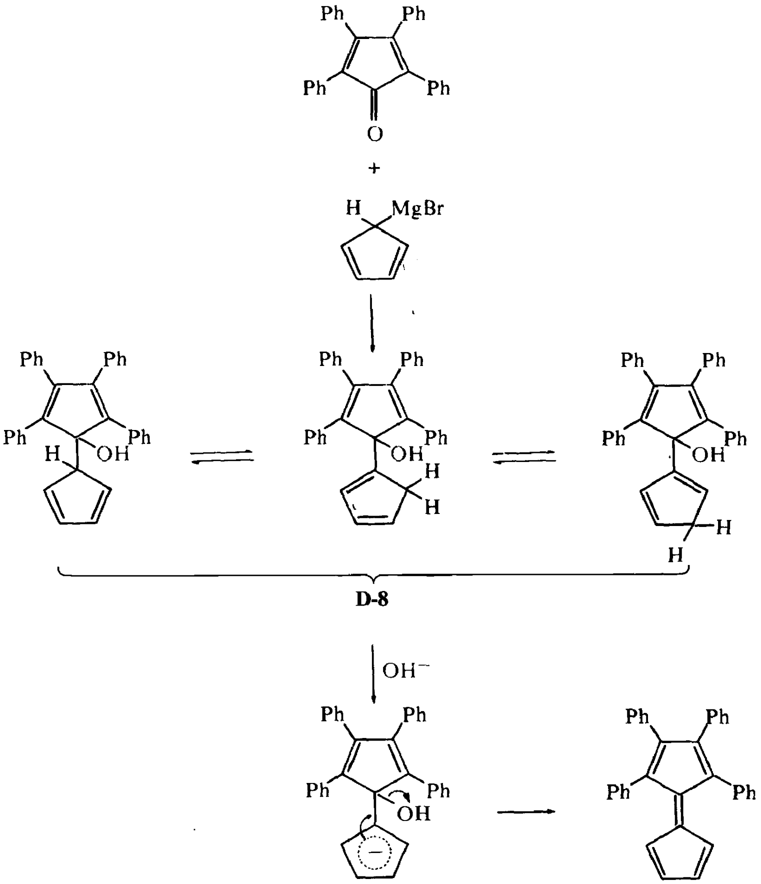


Figure 15. The n.m.r. spectrum of the pentafulvalene **D-9** (60 MHz, $CDCl_3$)



D-8

$\lambda_{max.}$(EtOH): 480 (s, 450)
(nm) 357 (20000)
258 (15500)

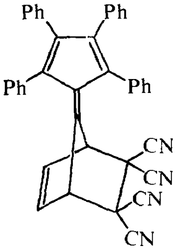
Calculated and experimental AA′BB′ spectra correspond well using practically the same coupling constants as for **D-4**.

$$J^{1,2} = J^{3,4} = 5.6\ \text{Hz}$$
$$J^{1,3} = J^{2,4} = 1.3\ \text{Hz}$$
$$J^{2,3} = J^{1,4} = 2.1\ \text{Hz}$$

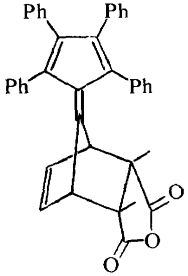
Very similar magnitudes for vicinal and long range coupling constants have been deduced for a number of fulvenes[6].

The u.v. and n.m.r. measurements clearly support the structures of the addition products with TCNE, MA and MAD.

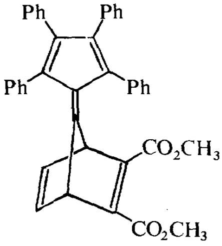
Using the adduct **D-12**, we have tried, with no success, to achieve a pentafulvalene → sesquifulvalene transformation by the sequence **2** → **B-19** → **B-20** → **3** outlined in section B. If oxygen is strictly excluded,



D-10



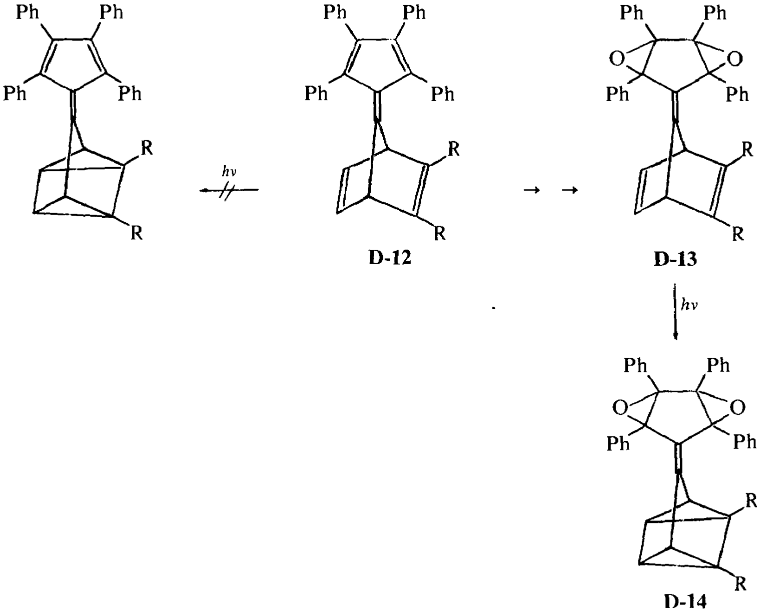
D-11



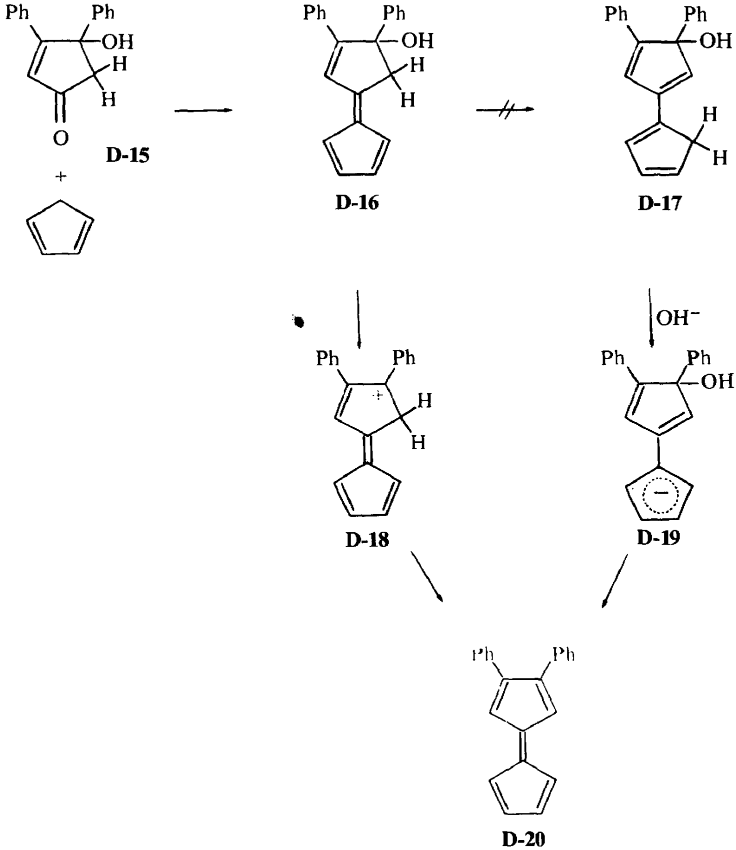
D-12

τ = 6.2–6.35 (2, 't) 3.3–3.45 (2, 't') 2.5–3.2 (20, m)	τ = 7.1 –7.2 (2, m), 6.65–6.9 (2, m) 4.1 –4.25 (2, 't') 2.65–3.20 (20, m)	τ = 6.41 (6, s) 6.2 –6.3 (2, 't') 3.2 –3.3 (2, 't') 3.1 (10, br. s) 2.75 (10, br. s)
(CD_3CN)	(C_6D_6)	(CCl_4/C_6D_6)
$\lambda_{max.}$: 400 (s, 1000) (nm) 308 13500) 257 (26500)	385 (s, 1000) 295 (s, 17000) 260 (27000)	377 (s, 1250) 309 (19500) 261 (24500)
(CH_3CN)	(CH_3CN)	(EtOH)

the direct photolysis of **D-12** results in no reaction; in the presence of oxygen, the quadricyclan **D-14** is formed. This suggests that prior formation of the bis-epoxide **D-13**, i.e. prior destruction of the fulvene chromophore in **D-12**, is a prerequisite for the photochemical ring closure to **D-14**.

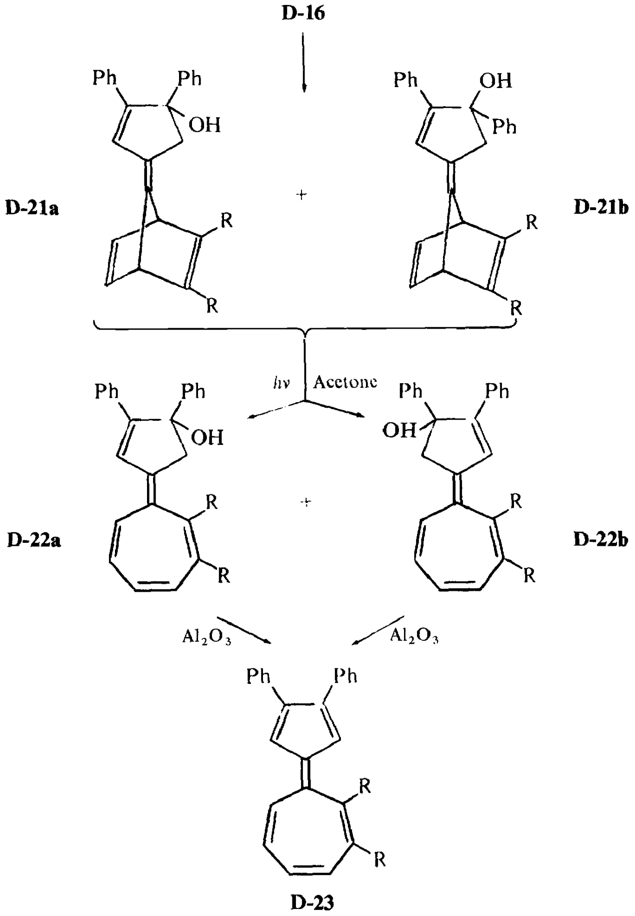


An easy route to the diphenyl-pentafulvalene **D-20** appeared to be opened when the condensation of the ketone **D-15** with cyclopentadiene led to the crystalline vinylogous fulvene **D-16** in good yields. However, several attempts to eliminate the elements of water from **D-16** were unsuccessful. A base catalysed dehydration, by way of the anion **D-19**—the method which had turned out to be the one of choice in the synthesis of **D-4** and **D-9**—could not be applied here because of our failure to bring about the isomerization **D-16** → **D-17**.



Note added in proof

We have found that **D-16** can be dehydrated over aluminium oxide yielding the very reactive deep red pentafulvalene **D-20**, which is very prone to dimerization. With MAD **D-16** gives the two isomeric adducts **D-21a**, **D-21b**. Upon acetone sensitized excitation one obtains the vinylogous heptafulvenes **D-22a**, **D-22b** (7 : 3). Each of the isomers over aluminium oxide is dehydrated to the sesquifulvalene **D-23**.



REFERENCES

[1] W. v. E. Doering, in *Theoretical Organic Chemistry*, p 35. Butterworths: London (1959).
[2] E. D. Bergmann, *Chem. Rev.* **68**, 41 (1968).
[3] E. D. Bergmann and E. Fischer, *Bull. Soc. Chim. France*, **17**, 1084 (1950).
[4] Ch. Courtot, *Ann. Chim.* [9], **4**, 218 (1915).
[5] E. C. Schreiber and E. I. Becker, *J. Amer. Chem. Soc.* **76**, 3354, 6125 (1954).
[6] P. Yates, 'Fulvenes', in *Advances in Alicyclic Chemistry* (H. Hart and G. J. Karabatsos, eds), Vol. II, pp 117 ff. Academic Press: New York (1968).

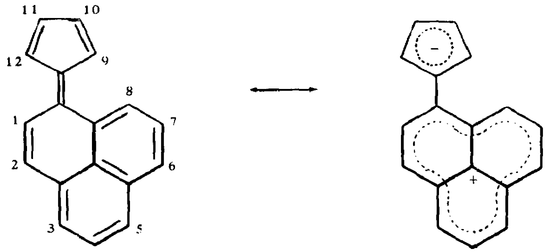
E. PENTAPHENAFULVALENES

E. WOISCHNIK

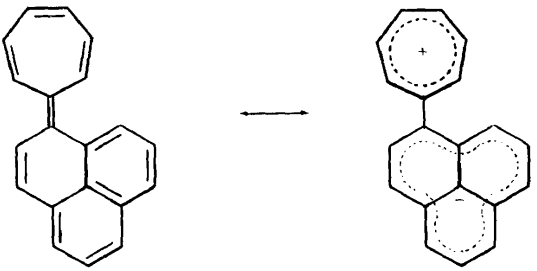
Concerning the last projected synthesis (**5** → **10**), in spite of rather intensive efforts, our progress has been limited to the synthesis of the two starting materials[1], with which this section will be dealing.

In view of the theoretically predicted and experimentally well established stability of the phenalenium cation and anion[2], the synthesis of the cyclic cross-conjugated systems **5** and **E-1** having the phenalene molecule as a component seemed only to be a matter of time.

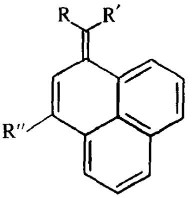
In working toward the synthesis of the heptaphenafulvalene **E-1**[3] and of the phenafulvenes **E-2**[4] it soon became clear that systems in which the phenalene ring has to accept a partial negative charge are very sensitive to oxidation. In fact, the experimentation became so frustrating that, for the time being, we have given up.



5



E-1



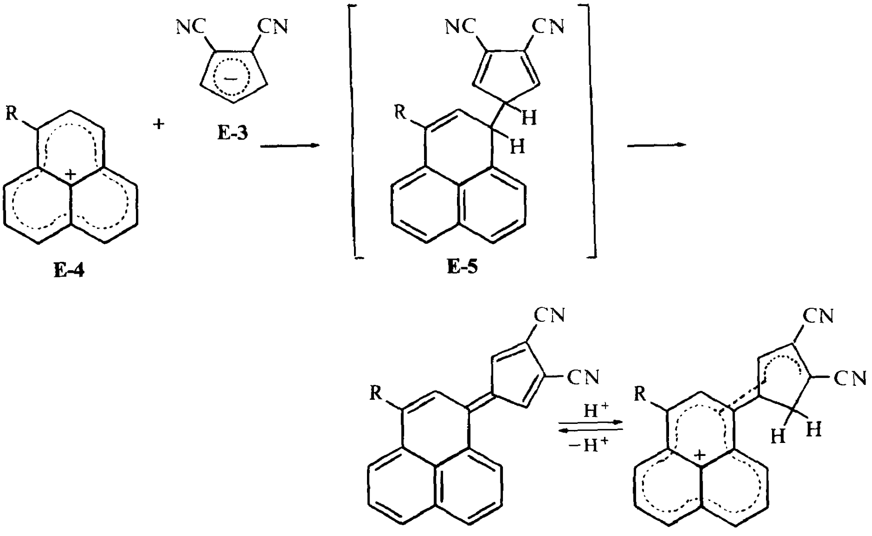
E-2

a: R = CN R′ = CN R″ = H
b: R = CO_2CH_3 R′ = CN R″ = OC_2H_5

The synthesis of the pentaphenafulvalene in which the phenalene part functions as an electron-donating ring appeared much more promising, as judged by the relative stability of the phenafulvenes with electron-attracting groups at C(10).

In fact, when the 1,2-dicyanocyclopentadienide **E-3** was allowed to react with an excess of the ethoxyphenalenium cation **E-4a**, a deeply coloured blue crystalline material precipitated; this turned out to be the pentaphenafulvalene **E-6a**. As is often observed[5], the nucleophile **E-3** attacks the cation **E-4a**, not at the carbon atom bearing the ethoxy group but at C(3), yielding a product which, under the reaction conditions, is oxidized by the phenalenium cation **E-4a**; the resulting conjugate acid then loses a proton to the medium.

The pentaphenafulvalene **E-6a** is sensitive toward oxygen; all manipulations, therefore, have to be done with strict exclusion of air.



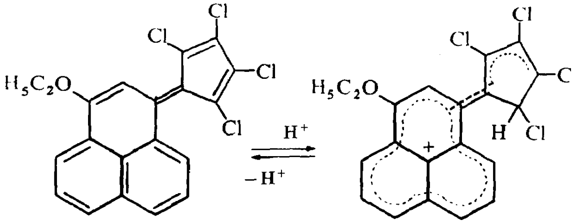
E-6 **E-7**

a: R = OC_2H_5 $\lambda_{max.}$ 600 (CH_3CN) 423 ($HClO_4$, 70%)
(nm) 588 (CCl_4) 396

b: R = H $\lambda_{max.}$ 587 (CH_3CN) 458 (H_2SO_4, 80%)
(nm) 560 (CCl_4) 401

The 10,11-dicyanopentaphenafulvalene **E-6b** is obtained by following the same procedure. The blue–black crystals can be stored for some time in the absence of oxygen.

Starting from the sodium tetrachlorocyclopentadienide and **E-4a**, again without interception of any intermediate products, Murata *et al.*[6] isolated the derivative **E-8**.



E-8 **E-9**

$\lambda_{max.}$: 606 (CH_3CN) 417 (H_2SO_4, 80%)
(nm) 587 (*n*-pentane) 368

All three pentaphenafulvalenes are quite alike in their properties. They are weak bases, and protonation requires, e.g. 80 per cent sulphuric acid; this transformation is reversed by the addition of water. It was shown by an H/D exchange experiment and by spectral data that the proton is added at C(9) or C(12), as one would expect (**E-7**, **E-9**). They all experience a large blue shift with protonation and a considerable positive solvatochromism*. This latter effect may be taken as an indication that charge separation in the

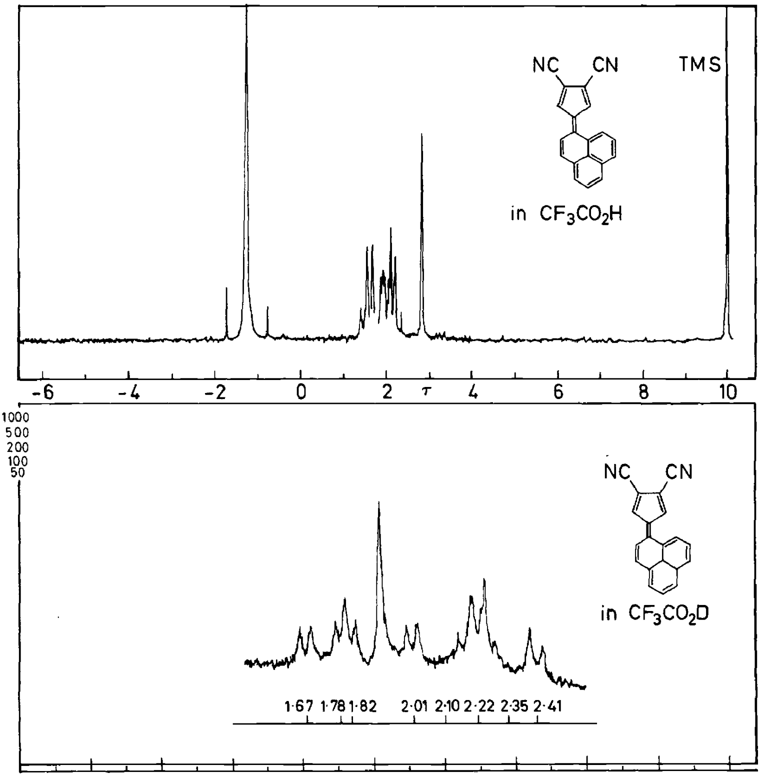
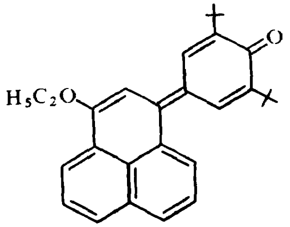


Figure 16. The n.m.r. spectra of **E-6b** (60 MHz, 220 MHz, CF_3CO_2H)

---

* A $\lambda_{max.}$ of 605 nm (CH_3CN; $\varepsilon = 20700$) was very recently reported[5] for the 'quinophenalene' **i**.



i

Table 3. The n.m.r. data (τ values; $CDCl_3$) of the pentaphenafulvalenes **E-6a**, **E-6b**, **E-8** and of some model compounds

	E-2b	**E-8***	**E-6a***	Phenalenone	**E-2a**	**E-6b†**
H^1	1.78	2.68	2.42	3.34	2.50	2.41
H^2	—	—	—	2.37	2.50	2.22
H^3	1.86	1.70	1.38	2.37	2.23	2.01
H^4	2.45	2.34	2.02	2.52	2.36	2.22
H^5	2.06	1.93	1.67	2.09	1.98	1.82
H^6	1.98	1.93	1.50	1.92	1.77	1.78
H^7	2.38	2.34	2.10	2.33	2.22	2.22
H^8	0.60	1.70	1.38	1.48	0.61	1.67
H^9			2.74			2.94
H^{12}			2.74			2.94
OCH_2CH_3		5.64 8.42	5.44 8.41			

* CD_3CN
† CF_3COOH

excited states of **E-6** and **E-8** is much more pronounced than in their ground states.

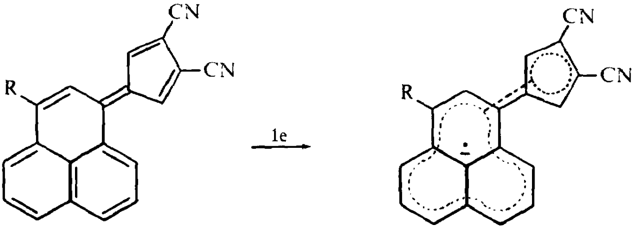
The 220 MHz n.m.r. spectra of **E-6a** and **E-6b** (*Table 3*; *Figure 16*) allow a complete analysis. In *Table 3* the chemical shifts of the pentaphenafulvalenes are summarized with inclusion of the data we had published for the phenafulvenes **E-2a**, **E-2b** and for the phenalenone.

If solvent effects are ignored, the protons in **E-6a** which are free of anisotropic influences are consistently found at lower field than the corresponding protons in **E-6b** and **E-8**; the situation in the latter being comparable to the one in **E-2a** and **E-2b** respectively. Consequently, the importance of charge separation in these molecules must follow the same order.

In this connection, it should be mentioned that a dipole moment of $\mu = 5.95$ D and a first singlet transition at 1.76 eV have been calculated[6] for the parent molecule **5**. From SCF calculations it was concluded that the dipolar resonance contribution to the ground state of **5** is 28.4 per cent compared with 11.1 per cent for fulvene and 30.8 per cent for sesquifulvalene[7].

The structures of the pentaphenafulvalenes **E-6a** and **E-6b** were further confirmed by e.s.r. measurements[8] of their anion radicals (*Figure 17*). The anion radicals **E-10a**, **E-10b** were generated by reacting a degassed solution of **E-6a**, **E-6b** in dimethoxyethane with highly purified metallic potassium. In the case of **E-10b** the reaction must be stopped as soon as the solution has a deep green colour in order to avoid the formation of the cherry-red bis-anion.

Calculated spectra using values varying between 5.75 and 6.00 gauss for the coupling with the protons H^3, H^5, H^6, H^8, (H^2), of 1.60 gauss for the coupling with H^1, H^4, H^7 and of 0.80 gauss for the coupling with H^9, H^{12}, gave, if not a perfect, a quite satisfactory fit with the experimental spectra. (The couplings with the ^{14}N nuclei and with the protons of the alkoxy group (**E-10a**) are too small to be resolved.)



a: R = OC_2H_5
b: R = H

E-10

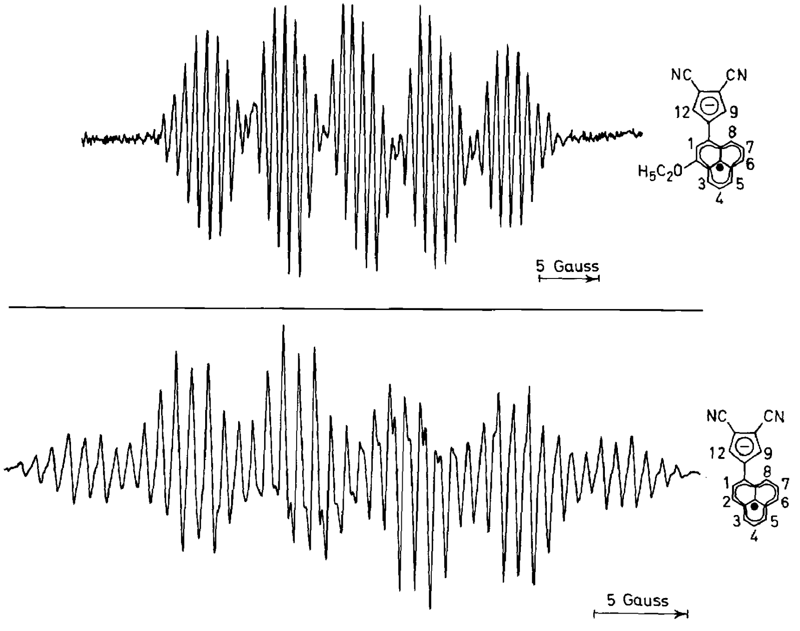


Figure 17. The e.s.r. spectra of the anion radicals **E-10a** and **E-10b** (K^+, dimethoxyethane, −40°C)

Thus, as is expected because of the partial delocalization of the unpaired electron into the five-membered ring, the coupling with the protons on the phenalene periphery is somewhat weaker than in the case of the related 1-hydroxyphenalenyl radical (7.1 and 1.8 gauss)[9], or of the parent phenalenyl radical (6.29 ± 0.04 and 1.805 ± 0.015 gauss)[10].

Systematic studies as to the ability of the pentaphenafulvalenes **E-10a** and **E-10b** to participate in cycloaddition reactions have been hampered by lack of sufficient material. There are, however, indications that **E-10b** undergoes an α,ω-addition with TCNE, but any discussion at the moment would be premature.

REFERENCES

[1] H. Prinzbach and E. Woischnik, *Angew. Chem.* **81**, 901 (1969).

[2] D. H. Reid, *Quart. Rev.* **19**, 274 (1965).

[3] H. Prinzbach and V. Freudenberger, *Angew. Chem.* **77**, 346 (1965); H. Prinzbach, *Chimia*, **19**, 352 (1965).

[4] H. Prinzbach, V. Freudenberger and U. Scheidegger, *Helv. Chim. Acta*, **50**, 1087 (1967).

[5] S. Hünig and E. Wolff, *Chimia*, **22**, 33 (1968); *Liebigs Ann. Chem.* **732**, 7, 26 (1970).

[6] I. Murata, T. Nakazawa and M. Okazaki, *Tetrahedron Letters*, 1921 (1969).

[7] D. H. Lo and M. A. Whitehead, *J. Chem. Soc.* (*B*), 480 (1970).

[8] In cooperation with K. Volkamer and E. Ohmes.

[9] P. B. Sogo, M. Nakazaki and M. Calvin, *J. Chem. Phys.* **26**, 1343 (1957); T. K. Mukherjee and A. Golubovic, *J. Org. Chem.* **30**, 3166 (1965).

[10] F. Gerson, *Helv. Chim. Acta*, **49**, 1463 (1960); cf. N. L. Bauld *et al.*, *J. Amer. Chem. Soc.* **91** 6666 (1969).

CONCLUSION

One has only to glance back at the scheme on pages 282–3 to see that our advancement toward the proposed syntheses of bridged annulenes (**6**–**10**) has not yet gone very far. Still, some surprisingly simple, yet sufficiently manageable calicenes, fidecenes and pentaphenafulvalenes could be made available. The recognition that some of these, at least with TCNE, undergo the desired α,ω-cycloaddition reactions, sustains, on the part of my co-workers, the enthusiasm and perseverance necessary to continue. My co-workers Dr L. Knothe, Dipl.Chem. H. Knöfel, H. Sauter, E. Woischnik and Ref. D. Forster deserve the credit for the achievements described here. My personal thanks go to Prof. Dr D. F. Tavares who, as a guest in our laboratory, was very helpful in the preparation of this manuscript.