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FLASH VACUUM THERMOLYSIS OF DISPIRO[2.2.n.2]ALKADIENES

P.A. KRAAKMAN, E.T.J. NIBBERING, W.H. DE WOLF
and F. BICKELHAUPT* +

Scheikundig Laboratorium, Vrije Universiteit
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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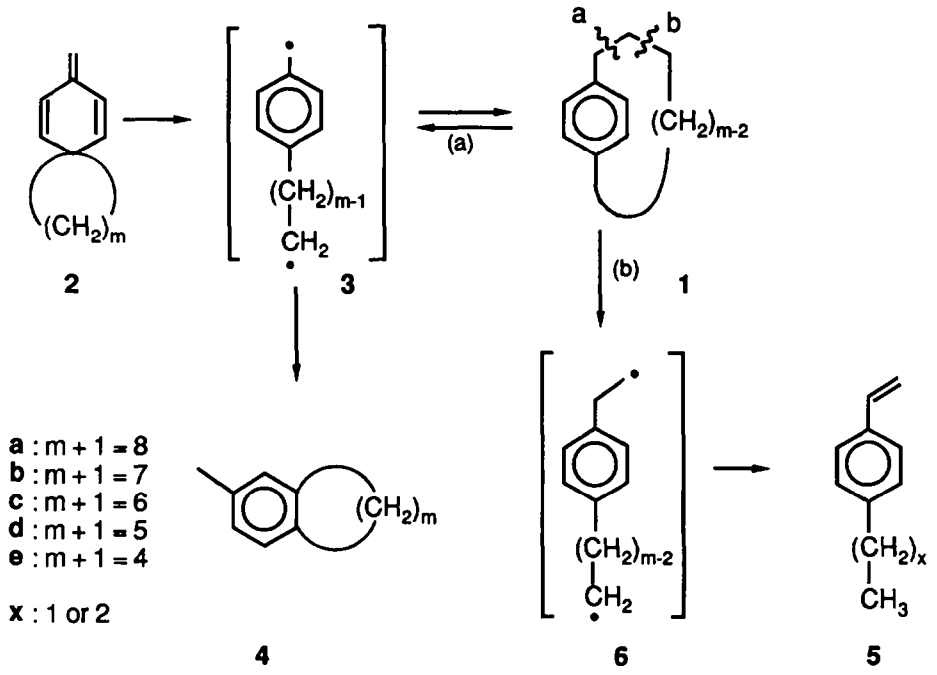
Abstract - The Flash Vacuum Thermolysis (FVT) of dispiro[2.2.6.2]-tetradeca-4,13-diene (**7a**), dispiro[2.2.5.2]trideca-4,12-diene (**7b**) and dispiro[2.2.2.2]deca-4,9-diene (**7e**) at 500 - 750 °C is reported. The complicated reaction mixture from **7a** and **7b** (Scheme 3) included at lower temperatures vinylspiroalkadienes **9**, ethylidene-spiroalkadiene **10b**, β-ethylcycloalkabenzenes **11**, while at higher temperatures, *p-n*-alkyl- (**5**) and *p-sec*-alkylstyrenes **14** and *p*-divinylbenzene (**15**) dominated. Product formation is explained by invoking diradicals **8**, **6** and **12** as well as the cyclophanes **1** and **13** as intermediates. For **7e**, the product mixture was less complicated and consisted of *p*-ethylstyrene (**5e**), **15** and, unexpectedly, *p*-isopropylstyrene (**14e**) which contains one carbon more than the starting material. The analysis and interpretation of product formation largely confirms previously suggested reaction pathways and furnishes further interesting details. However, new and unexpected features are also encountered, especially in the fragmentations of **1** and **13** which may stimulate future investigations on the thermal behaviour of these relatively simple hydrocarbons.

INTRODUCTION

As a synthetic approach towards small bridged [n]paracyclophanes (**1**), we recently reported the Flash Vacuum Thermolysis (FVT) of methylenespirocyclohexadienes **2a-c**. [1] This method was satisfactory in the case of m + 1 = 8 (**1a**; 80% yield) and less so for m + 1 = 7 (**1b**; 7% yield). In the case of m+1 = 6, [6]paracyclophane (**1c**) was not obtained; it is probably too unstable to survive the reaction conditions.

+ Dedicated to Professor Dr. Hans Wijnberg, a stimulating friend for many years, on the occasion of his sixty-fifth birthday.

The formation of **1** from **2** can be rationalized by invoking the intermediacy of the diradical **3**, derived from **2** by homolytic cleavage of one of its spirobonds (Scheme 1). Recombination of the terminal radical sites of **3** by ring closure gives **1**. When the thermolysis of **2** was performed at a higher temperature, the yield of **1** dropped while the formation of β-methylcycloalkabenzenes **4** and *p*-alkylstyrenes **5** was observed.



Scheme 1

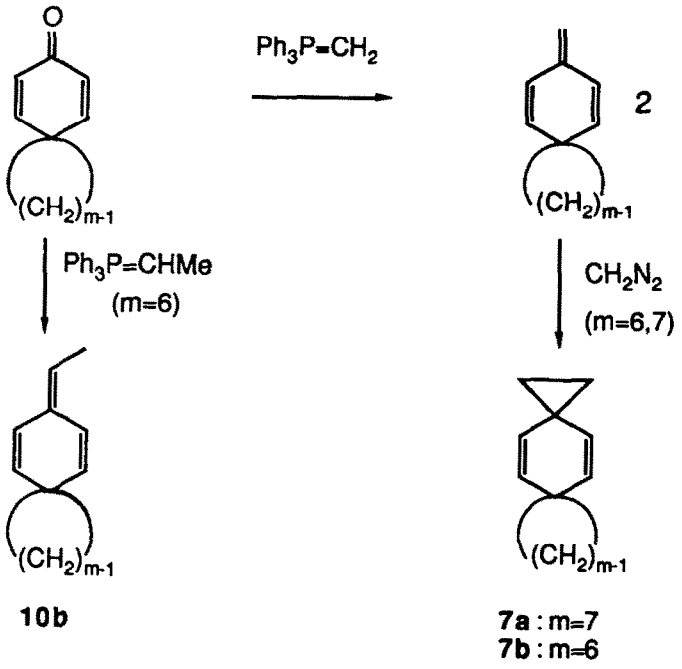
Compounds **4** are probably formed directly from **3** by attack of the alkyl radical at the meta-position of the benzylradical moiety, followed by hydrogen migration . The *p*-alkylstyrenes **5** are mechanistically the most puzzling products, because their formation from **2** requires the translocation of a carbon atom from one side of the six- membered ring to the other side. This can best be explained by intermediate formation of the paracyclophanes **1**[2] which react not only by cleavage of the benzylic bond (a, Scheme 1) and thus revert to **3**, but also by cleavage of the less susceptible homobenzylic bond (b) leading to diradical **6**. It is important to point out that contrary to **1** and **4**, the styrenes **5** were not isomeric with the starting materials (**2a** gave **5d** and **5e**, **2b** gave **5d**, and **2c** gave **5e**). This implies that the diradicals **6** fragment by extrusion of the elements of C_2H_4 or C_3H_6 from the aliphatic chain before attaining final stabilization.

In order to obtain support for this postulated mechanism, an independent and direct generation of the diradicals **6** and the products derived from them was considered desirable. The dispiro[2.2.m-1.2]cyclohexadienes **7** were expected to give directly the postulated diradical **6** because cleavage of the strained three-membered ring was likely to be their primary mode of thermal reaction.

It will be shown that our goal was reached in sofar as strong evidence for the intermediacy of **6** was obtained from the similarity in product formation patterns. On the other hand, new intriguing products were encountered which give rise to new intriguing questions.

RESULTS

The methylenespiroalkadienes **2** were obtained as previously described[1] from the corresponding spiroalkadienones[3] by Wittig reactions with methylenetriphenylphosphorane. The trienes **2b** and **2c** were treated with diazomethane in diethyl ether at 0 °C in the presence of a catalytic amount of palladium acetate; in a regiospecific cyclopropanation of the exocyclic double bond, [4] the dispiro[2.2m-1.2]alkadienes **7a** and **7b**, respectively, were obtained in 75-80% yield (Scheme 2). The lower homologue **7e**[5] was kindly given to us by Prof. T. Tsuji.



Scheme 2

The FVT reactions of **7** (and of its structural isomers **9** and **10**, *vide infra*) were carried out in the apparatus previously used for the pyrolysis of **2**.[1] At a pressure of approximately 0.01 mbar, the substrates were slowly evaporated into an alumina tube heated to temperatures ranging from 500 to 750 °C; at the exit of the tube, the pyrolysates were collected by condensation in a cold trap (-70 °C) and analyzed by ^{1}H NMR and GCMS.

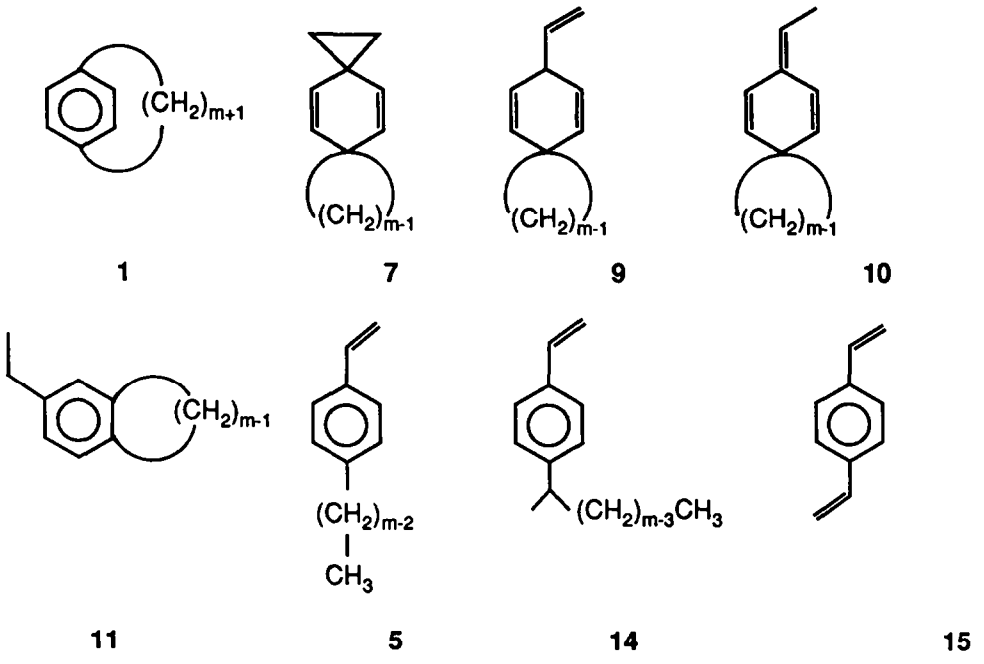
The product mixture from FVT was unexpectedly complex; it is shown in Scheme 3 and Table 1. The recoveries were good in the lower temperature range and decreased to about 60% at 750 °C. The loss of material is probably due to some polymerization and, in particular, to formation of volatile products of low molecular weight (*vide infra*) which have not been investigated.

At 500 °C, starting materials **7a** and **7b** were recovered as the main components of the pyrolysate. In the high temperature region (700 - 750 °C), *p*-divinylbenzene (**15**) and various *p*-alkylstyrenes (**5**, **14**) were the main products. The region of 550 - 650 °C was a transition zone in the sense that it produced both starting materials and high temperature products, but, characteristically, gave the vinylspirocyclohexadienes **9** and the β-ethylcycloalkabenzenes **11** as the main products. The product mixture obtained from **7e** contained only three products, all of which were also formed from **7a** and **7b**: *p*-ethylstyrene (**5e**), *p*-isopropylstyrene (**14e**) and **15**.

Table 1. Product composition of the pyrolysates obtained from **7**, **9a** and **10b**

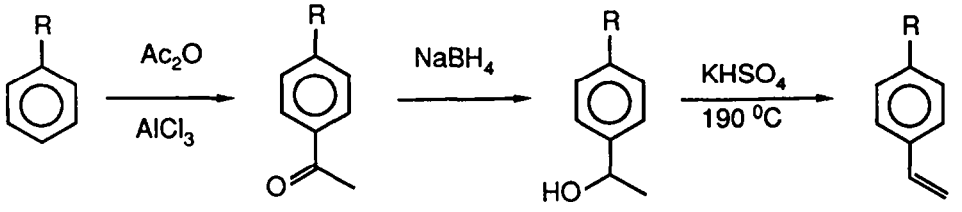
Educt		T	Products (%)													
Cpd	m	(°C)	**7**	**9**	**10**	**11**	**1**	**5a**	**5b**	**5d**	**5e**	**15**	**14c**	**14d**	**14e**	recovery
7a	7	500	52	22		22	2									98
		550	29	25		18	8									80
		600	12	32		13	17									78
		650		12		6	17	6		3	3	18		8	5	77
		700		3		5	8	6		3	5	21		4	4	58
		750				3	3	5		5	7	30		2	4	59
7b	6	500	66	10	4	5										85
		550	17	25	5	19			4							69
		600		32	1	15			6			6			6	65
		650		14		5			3		4	15	3	2	11	57
		700		6		4			3		5	25		2	14	59
		750				2			3		8	35		2	12	61
7e	3	500	77								7	2				87
		550	28								24	14				66
		600									32	22				62
		650									23	22			7	53
		700									23	24			6	53
		750									24	31			7	62
9a	7	700		25		12						19				100
10b	6	550			77				5			1			2	85
		600			19	12			10		3	7	5	2	12	70
		650				1			3		7	30	4	3	20	69
		700				4			3		8	32	3	3	22	74

The identification of the reaction products was based on their ^{1}H NMR and mass spectra. Compounds **5d**, **5e** and **15** were known; the spectra of **5b**, **9a** and **9b** were sufficiently characteristic. The identity of *p*-alkylstyrenes **5a**, **14d** and **14e** was established by acetylation of the corresponding alkylbenzenes at the *para*-position, followed by reduction with sodium borohydride and elimination of water (Scheme 4).



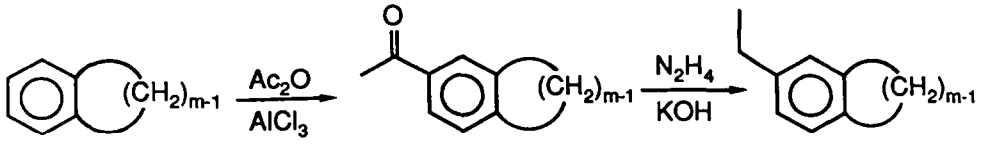
Scheme 3 **a** : m=7; **b** :m=6; **c** : m=5; **d** : m=4; **e** : m=3;

The structure of **10b** was corroborated by its independent synthesis from dispiro[5.5]undeca-1,4-dien-3-on and triphenylethylidenephosphorane (Scheme 2). The β-ethylcycloalkabenzenes **11a** and **11b** were independently synthesized by acetylation of cycloocta- and cycloheptabenzene, respectively, followed by Wolff-Kishner reduction (Scheme 5). The β-position of the ethyl groups followed unambiguously from the NMR spectra of their acetyl precursors: in the ^{1}H NMR spectrum, an isolated proton at low field and an AB quartet were observed, and the ^{13}C chemical shifts of **11a** could be simulated with shift increments only when β-substitution was assumed.



5a : R = n-C_6H_{13}
14d : R = s-C_4H_9
14e : R = i-C_3H_7

Scheme 4



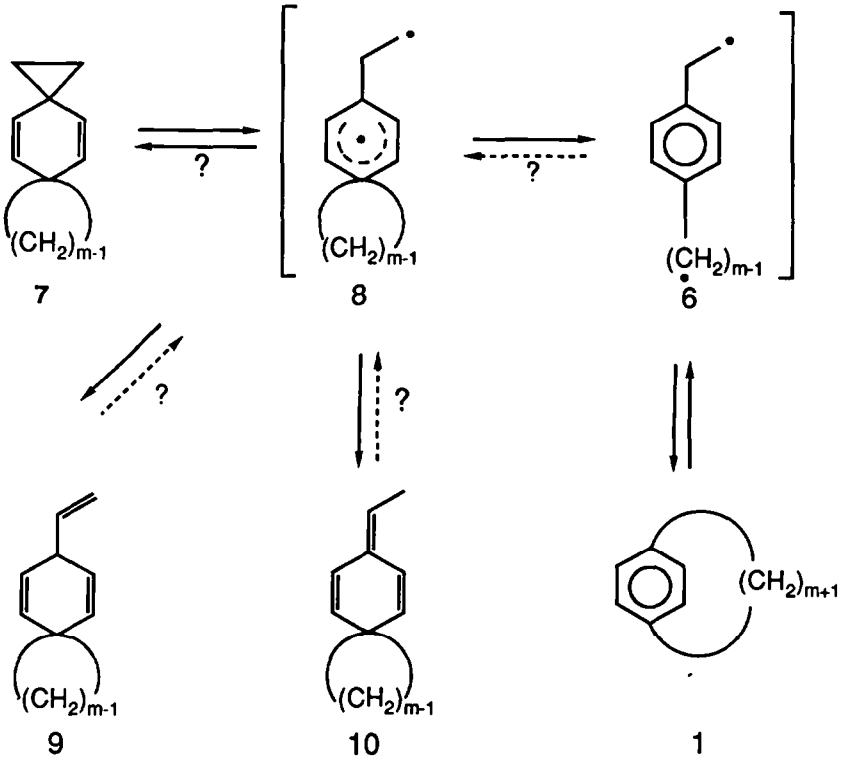
a : m = 7
b : m = 6

11

Scheme 5

DISCUSSION

The first step in the thermolysis of **7** undoubtedly is the homolytic cleavage of a spiro bond of the strained cyclopropane rings; it leads to the diradicals **8** (Scheme 6).



Scheme 6

However, at this stage, the reaction pattern becomes very complicated because **8** has several options for further reaction. The simplest one is reversion to **7**. Being unproductive, this mode of reaction is not directly detectable under our conditions, but it may be responsible for some of the recovered **7**. Tsuji et al. have demonstrated the principle feasibility of this retro reaction in the case of **7e** by observing CIDNP phenomena.[5]

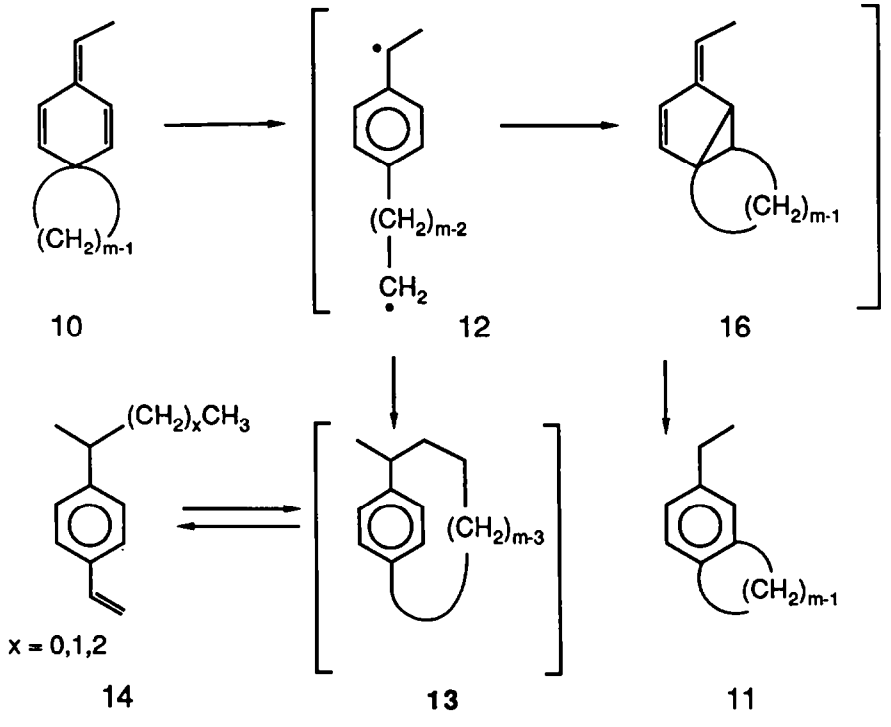
Somewhat contrary to our expectation, the next choice of **8a** and **8b** was not the opening of the second spiro-ring which leads to the desired intermediate, the diradical **6**. The most diagnostic evidence for the formation of **6** is its ring closure reaction to give **1**. As we will discuss later in detail, this reaction did occur, but especially at the lowest temperatures, it was only of minor importance. Instead, a third and fourth mode of reaction of **8** were more prominent, i.e. 1,2-hydrogen shifts leading to **9** and **10**, respectively (Scheme 6). This means that the 1,2-hydrogen shift must have a lower activation barrier than opening of the second spiro-ring !

Table 2. Heats of formation ΔH_f^o (kcal.mol^{-1}) [a]

compound	m	1[b]	6	7[c]	8[d]	9	10	11	12[e]
a	7	12.4	66.2[f]	35.4	76.4	15.6	25.0	-12.0	53.2
b	6	21.4	71.3[f]	33.8	74.9	14.0	23.4	- 7.7	58.2
c	3		86.0[g]	65.5	117.3				

[a] Estimated from group increments[6] unless otherwise stated. [b] See ref.19. [c] Obtained from MNDO calculations of 6,6-dimethylspiro[2.5]octa-4,7-diene in combination with group increments[a]. [d] Obtained from ΔH_f^o (3-ethylspiro[5.m-1]alka-1,4-diene)[a] + D(H-CH_2CH_3)[6] + D(H-cyclohexa-1,4-dien)[6] - 2 ΔH_f^o (H)[6]. [e] Obtained from ΔH_f^o (p-$H_3CCH_2C_6H_4(CH_2)_{m-2}CH_3$)[a] + D(H-$CH_2C_6H_5$)[6] + D(H-$C_3H_7$)[6] - 2 ΔH_f^o(H)[b]. [f] Obtained from ΔH_f^o (p-$H_3CCH_2C_6H_4(CH_2)_{m-2}CH_3$)[a] + D(H-$C_2H_5$)[6] + D(H-$C_3H_7$)[6] - 2 ΔH_f^d (H)[6]. [g] Obtained from MNDO calculation.

According to the calculational results presented in Table 2, the 1,2-hydrogen shift is quite exothermic. Literature reports on the behaviour of similar radicals[7] suggested that the isomers **9** and **10** should be formed in about equal amounts. This seemed to be contraindicated by the actual product composition (Table 1), as **9a** was the only isomer in the **a**-series (yield $\leq$ 32%), and **10b** was a minor component ($\leq$ 5%) compared to **9b** ($\leq$ 32%). We believe, however, that this is not so much a consequence of preferential formation of **9**, but rather of a lower kinetic stability of **10**. As a 1,4-dihydrobenzene, **9** is relatively stable and survives at lower temperatures. In contrast, **10** is a *para*-semibenzene and has a low activation energy pathway available by opening the second spiro-ring under formation of the stable, benzylic-aliphatic diradical **12** (Scheme 7).



Scheme 7

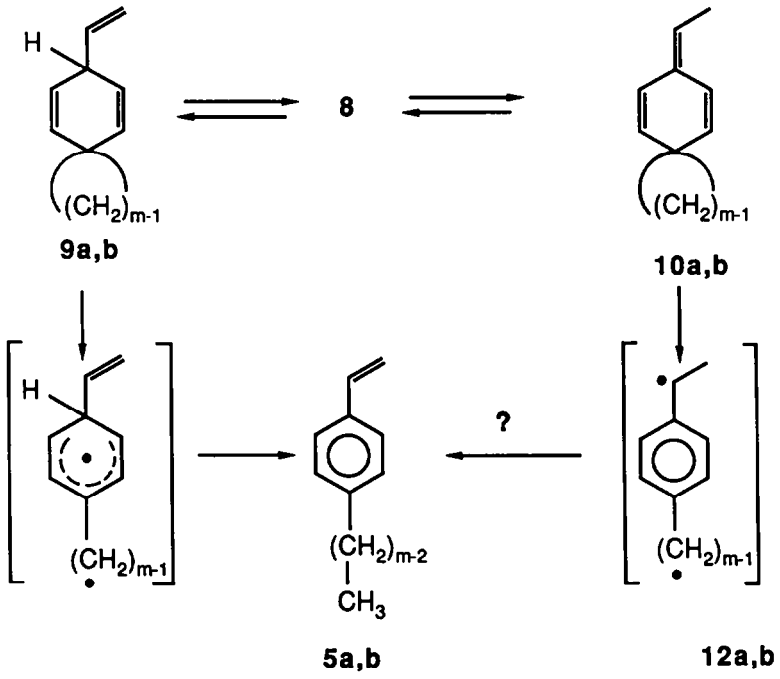
At lower temperatures, the preferred mode of stabilization of **12** is attack of its aliphatic radical at the *meta*-position of its benzylic radical moiety, leading to **16**; the latter aromatizes under hydrogen migration, to furnish **11**. Although, for reasons of spin density, the *meta*-position of a benzyl radical is not the most favourable one for radical attack, in this particular situation, it avoids the strain produced by spin pairing at the *ortho*- or the benzylic position; it may also be favoured by entropy (i.e. proximity) and, after all, **16** is a spin-paired and relatively stable product.[8] Incidentally, the formation of **11** from **12** is completely analogous to the previously postulated formation of the methyl analogues **4** from **3**[1] (Scheme 1).

Thus, when comparing yields, one should compare that of **9** with the combined yields of **10** + **11**. Especially at lower temperatures, this ratio is indeed close to unity, and we consider this to be strong support for the suggestion that **9** and **10** are originally formed from **8**. Another experimental justification for this rationalization was found in the independent FVT of **9a** and **10b** (Table 1). While the latter was completely consumed at temperatures as low as 650 °C, 25% of **9a** survived even at 700 °C. The yield of **11b** from **7b** and from **10b** was comparable (at 600 °C: 15% and 12%, respectively). The rest of the product spectrum was also qualitatively similar; absolute yields at a given temperature showed some discrepancies, but the trends with increasing temperature were analogous. It should be pointed out that the formation of some **11a** (13%) from **9a** indicates a certain degree of reversibility of 1,2-hydrogen shifts from and to **8** (Scheme 6).

We now return to the previously mentioned second mode of reaction of **8**, i.e. its conversion to **6**, which is an aliphatic diradical with a fully aromatized benzene ring (Scheme 6). Not only was **6** the primary goal of this investigation, but it was also a potentially useful intermediate in the synthesis of the paracyclophanes **1** from **7**. The results of Table 1 show that the synthetic goal was not realized. No [7]paracyclophane **1b** was isolated from **7b**; this is not too surprising in view of the low yield of **1b** in the FVT of **2b** (Scheme 1). But even the highest yield of **1a** was only 17% which does not compare favourably with the attractive 80% obtained from **2a**. Still, the formation of **1a** from **7a** is of mechanistic interest, as it proves the basic correctness of our expectation that **6** should be able to cyclize to **1**. It is not a priori obvious why the yields of **1** from **6** are much lower than those from **3**. Two factors may be responsible. First, the energy content of **6**, an aliphatic diradical, is higher than that of its benzylic-aliphatic isomer **3** (cf. **6a** (Table 2): ΔH^0_f = 66.2 kcal·mol^{-1}; **3a**[1]: ΔH^0_f = 53.6 kcal·mol^{-1}); thus, **6** will undergo faster and less selective side reactions, one of which might be a 1,2-hydrogen shift to form **12**, as this is an exothermic reaction (Table 2). Secondly, ring closure of **6** to **1** will produce the latter in a higher energetic state; under the conditions of FVT (vacuum of 0.01 mbar), **1** cannot easily dispose of this excess energy by collisions, and so it will tend to yield fragmentation products. Thirdly, in **6**, both radical ends can adopt conformations which are unsuitable for ring closure, whereas in **3**, the benzylic radical position is much more restrained as part of a rigid skeleton.

Next, we discuss the formation of the unbranched *p*-alkylstyrenes **5**. As briefly pointed out in the Introduction, their formation in the FVT of both **2** and **1**, and the postulated intermediacy of **6** had been one of the starting points for this work. We notice interesting similarities and differences in the FVT behaviour of **1** and **2** on the one hand and of **7** on the other. The similarity lies in the formation of fragmentation products, **5d** and **5e** in both series. The analogy is closest for **1a**, **2a**, and **7a**; in all cases, both **5d** (loss of C_3H_6) and **5e** (loss of 2 times C_2H_4) are observed. At 750 °C, the yield of **5d** (27%) and **5e** (14%) is much higher from **2a**[1] than from **7a** (5% and 7%, respectively), in agreement with our earlier

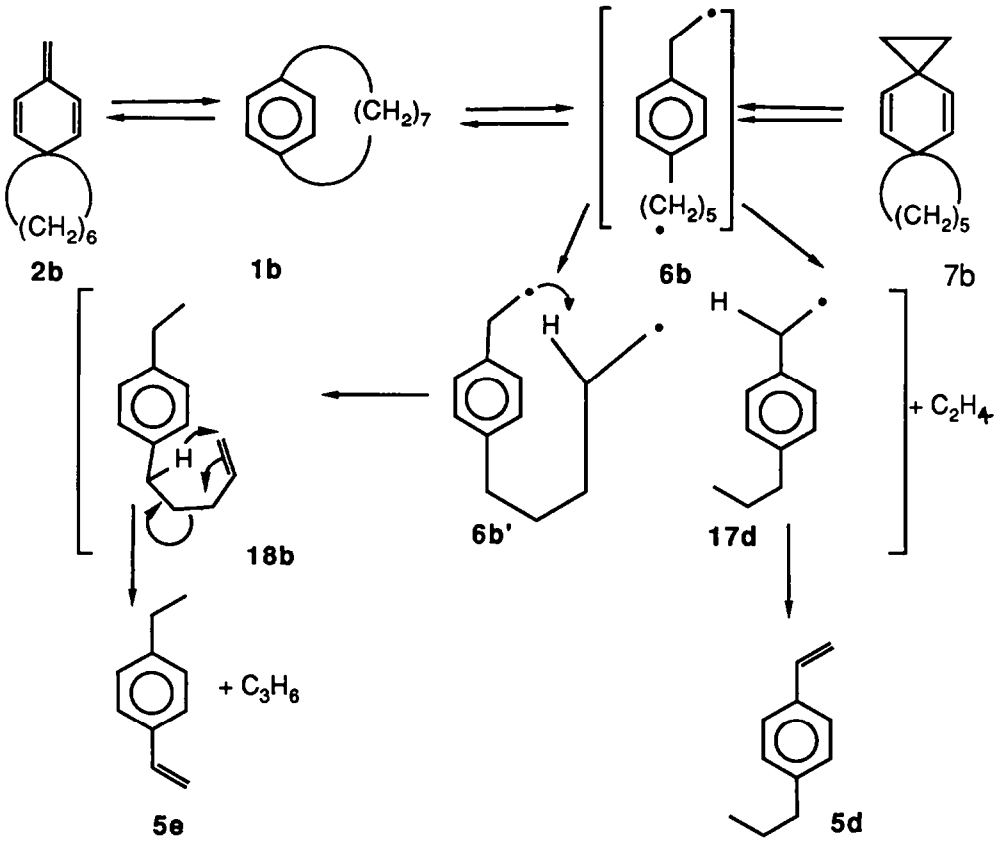
conclusion that the yield of **1a** from **2a** is much higher than from **7a**. It is therefore reasonable to postulate the fragmentation of **6a** as the mode of generation of **5d** and **5e** in all cases (Schemes 1, 6 and 9). In contrast, the unfragmented **5a** is obtained only from **7a**, but not from **1a** and **2a**. The appearance of **5a** at higher temperatures, where the yield of **9a** decreases, suggests that **9a** may be an intermediate; this is corroborated by the high yield of **5a** (44%) from direct FVT of **9a**. The most likely course of events is shown in Scheme 8. After opening of the spiro-ring of **9a**, the intermediate diradical gives **5a** by intramolecular abstraction of the doubly activated hydrogen of the cyclohexadienyl radical.



Scheme 8

The formation of **5b** from **7b**, but not from **1b** and **2b**[1], may be explained in a similar fashion. The yield of **5b** is similar from **7b** and from **10b**. We explain this by rearrangement of **10b** to **9b**. The alternative pathway from **10b** via **12b** to **5b** is considered less likely, but **12a** may be an intermediate in the formation of **11a** from **9a** (Scheme 8). This again confirms the postulated reversible interconversion between **7**, **9**, and **10** via **8** (vide supra).

However, in the **b**-series, we notice a remarkable difference in fragmentation patterns: **1b** and **2b** yield **5d** under extrusion of C_2H_4, whereas **7b**, like **10b**, loses C_3H_6 to give **5e**. The difficulty is not so much to devise a reasonable mechanism for these reactions (and the analogous behaviour in the **a**-series fragmentations). As shown in Scheme 9, the intermediate diradical **6b** may either fragment by the wellknown β-cleavage which is also part of the generally accepted Rice-mechanism of alkane thermolysis;[9] this leads to diradical **17d** which (in an as yet unknown fashion) transports one hydrogen from the benzylic position of the two-carbon side chain to the end of the three-carbon chain to furnish **5d**. Regarding the unknown pathway of this hydrogen migration, it should be pointed out that the conversion of **7e** via **6e** to **5e** requires an analogous transannular hydrogen shift. Alternatively, **6b** may rearrange via the transition state conformation **6b'** (Scheme 9) to **18b** which, being an α-olefine, can cleave off propene by a thermally allowed ene reaction[10] to furnish **5e**.

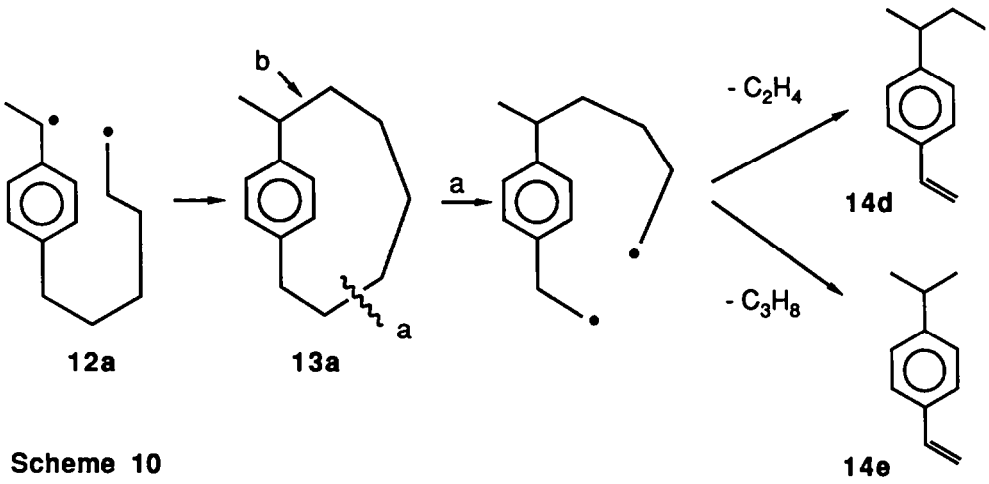


Scheme 9

Thus, reasonable pathways can be proposed, but so far, we were not able to explain why different starting materials (e.g. **2b** and **7b**), apparently via identical intermediates (**6b**), give rise to different products (i.e. **5d** and **5e**, respectively). Obviously, the content and/or distribution of energy in **6** must depend on its mode of formation, and for this reason we believe that the results presented here may open a unique experimental access to improving our understanding of simple and fundamental aspects of thermal hydrocarbon chemistry. We have to refrain from speculative interpretations until a complete material balance and labelling studies have been performed; note, e.g., that according to Scheme 9, the vinyl groups of **5d** and **5e** would originate from different carbon atoms of the respective starting materials.

Another interesting group of products which were obtained from **7** and **10**, but not from **1** and **2**, are the branched, *p-sec*-alkylstyrenes **14**. Their formation may be explained by invoking the intermediacy of diradical **12** which results from opening of the spiro-ring of **10** (Scheme 7) . In fact, **10** is a methyl derivative of **2**, and thus, a similar product pattern may be expected. One parallelity in behaviour has already been pointed out, i.e. the transformation **2** → **4** (Scheme 1) and **10** → **11** (Scheme 7). Another parallel to be expected is cyclophane formation: **2** → **3** → **1** (Scheme 1) and **10** → **12** → **13** (Scheme 7). As **13a** and **13b** are (methyl) derivatives of the strained cyclophanes **1b** and **1c**, respectively, one would expect them not to survive under the reaction conditions, but to cleave a homobenzylic bond of the bridge. In analogy to the formation of **5** from **1**[1], **13** is expected to yield **14**. This analogy holds also for the fragmentation processes reported for **1**; [1] most of the ring opened products from **13** have lost two or three carbon atoms. At closer inspection of Table 1, **13** appears to exhibit a reactivity pattern which is a

hybrid of the two mutually exclusive modes discussed above for the fragmentation of the corresponding [n]cyclophane with the same number of bridging carbon atoms. Thus, [7]paracyclophane (**1b**), either directly or from **2b**,[1] loses C_2H_4 only to give **5d**, whereas from **7b**, **1b** loses C_3H_6 only to give **5e**; while **13a**, which is 1-methyl[7]paracyclophane, loses both C_2H_4 and C_3H_6 and yields **14d** and **14e**, respectively. An analogy between **1c** ([6]paracyclophane)[1] and **13b** (1-methyl[6]paracyclophane) can be found in the loss of C_2H_4 from both of them to yield **5e** and **14e**, respectively. On the other hand, **13b** also produces **14c** and **14d** which implies loss of no or even one (!) methylene group, respectively. Again, it seems not advisable to speculate on the mechanism of these fragmentations; labelling experiments must help to trace the origin of the different carbon atoms in **14**. However, it is evident that remarkably specific processes must be involved. This can be concluded from the observation that only products of the structural type of **14** are formed having an unsubstituted vinyl group and a methyl-branched, saturated alkyl substituent, whereas the opposite combination, i.e. a substituted vinyl group and a straight chain saturated alkyl substituent, are not observed. If one accepts the intermediacy of **13** in these reactions, this implies probably cleavage of the homobenzylic bond a which is opposite to the benzylic carbon-carbon bond b closed in the formation of **13** from **12** as shown for **13a** in Scheme 10.



Scheme 10

Even though they do not help to clarify this aspect, the FVT results of **7e** must be mentioned at this point. This compound had been included in our programme because its chemistry has been extensively studied in solution.[5] Good evidence has been obtained under these conditions for the intermediacy of **8e**. Contrary to **8a** and **8b**, **8e** never showed any tendency towards a 1,2-hydrogen shift which would have furnished **9e** and **10e**. This is not too surprising if one considers the high exothermicity (and presumably low activation barrier) of the opening of the second cyclopropane ring to give **6e** (Scheme 6 and Table 2). In solution at 160 °C, **6e** abstracts two hydrogens from the solvent or from other hydrogen donors to give *p*-diethylbenzene or corresponding addition products.[5] Under our conditions, this possibility does not exist, as other reaction partners are (practically) not available at the relatively high vacuum of ca. 0.01 mbar. Consequently, **6e** stabilizes itself by two major routes, i.e. isomerization to **5e** by (successive) hydrogen shifts, or by dehydrogenation to **15** (*vide infra*).

However, a certain complication arises from the observation of a third product from **7e**. The formation of ca. 7% **14e** is in conflict with one of the essential premises of our discussion so far, namely that all the gas phase reactions described are unimolecular. In general, unimolecular reactions seem to be strongly

prevailing under FVT conditions.[11] As **14e** possesses one carbon atom more than **7e**, clearly, an intermolecular step must have occurred either in the gas phase, at the wall, or after condensation in the cold trap. When the FVT of **7e** was repeated at approximately 0.1 mbar, i.e. a pressure about ten times higher than usual, the yield of **14e** was not essentially different (9% at 600°C). Moreover, the yield of **14e** from **7e** is lower (6-7%) than from **7b** (11-14%) or **10b** (12-22%). Therefore, we feel that the large majority of the products described here are resulting from monomolecular reactions. Nevertheless, the formation of **14e** from **7e** remains an interesting puzzle.

Finally, *p*-divinylbenzene (**15**) is an interesting product. It is increasingly formed at higher temperatures, and at 750 °C, it accounts for about one half of the recovered material. Although its mode of formation has not been investigated, some comments can be made. It is unlikely that **15** is formed by direct thermal dehydrogenation of the ethyl group of **5e** for two reasons. In our apparatus, ethylbenzene was unchanged under the normal conditions; only at 900 °C, it was dehydrogenated to styrene, but not more than 5%.[12] Furthermore, the formation of **15** occurs hardly at the expence of **5e** (Table 1); this is particularly evident in the case of **7e**.

CONCLUSION

The Flash Vacuum Thermolysis (FVT) of the title compounds **7** has essentially confirmed the interpretation of product formation connected with the thermal approach to small [n]paracyclophanes **1**.[1] In particular, the ring closure to cyclophanes **1** from diradicals **3** finds its parallel in the formation of **1** from **6** and of **13** from **12**. Similarly, the formation of β-alkylsubstituted *ortho*-isomers proceeds in an analogous fashion from **3** to **4** and from **12** to **11**. Finally, the previously postulated homobenzylic carbon-carbon bond cleavage in **1** has been strongly supported by the complementary independent generation of diradical **6** from **1** and **7**, and the ensuing fragmentation in both cases which leads to **5**.

On the other hand, novel and interesting chemistry has been encountered. The low activation barrier 1,2-hydrogen shift from **8** to **9** or **10**, an apparently reversible reaction, is an illustration. Also, the unexpected and rather specific formation of *p-sec*- alkylsubstituted styrenes **14** poses new problems for mechanistic interpretation. We feel that further investigation of these rather specific and simple reactions will be of value in deepening our understanding of the thermal chemistry of aliphatic and aromatic hydrocarbons, an area which inspite of intensive study is still not free from ambiguities and controversies.[9b,10,12,13]

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker WH-90 spectrometer at a frequency of 90 MHz or on a Bruker WM-250 spectrometer at a frequency of 250.1 MHz. Chemical shifts are reported in δ units relative to tetramethylsilane. ^{13}C NMR spectra were recorded on a Bruker WM-250 spectrometer at a frequency of 62.9 MHz, chemical shifts are reported in δ units relative to tetramethylsilane. All compounds were analyzed by GCMS using a Hewlett-Packard 5970/5890 mass-spectrometer, high resolution mass spectra were measured on a Varian CH-5 DF mass spectrometer at an ionization potential of 70 eV. Preparative GLC was performed with a Intersmat 120 gas chromatograph with a 10% SE-30/Chromosorb W column (1.5 m) and H_2 as carrier gas (60 ml.min^{-1}).

Dispirocycloalkadienes (**7a,b**). An etheral solution of CH_2N_2 was prepared from 2,7 g (26 mmol) N-nitroso-N-methyl- ureum, 17.5 ml 50% aqueous KOH solution and 50 ml ether. After stirring for one hour, the ether layer was decanted , dried over KOH pellets and added to 4.4 mmol of **2b**[1,3] (0.77 g) or **2c**[1,3] (0.70 g), followed by addition of 18 mg $Pd(OAc)_2$. After the vigorous gas evolution had ended, the mixture was stirred for another 10 min. , filtered and the filtrate concentrated under reduced pressure. In the case of **7b**, this procedure had to be performed twice to obtain a good conversion. Further purification was achieved by column chromatography (silicagel 60, 35-70 Mesh, PE 40-60 as eluens) and by preparative GLC.

Dispiro [2.2.6.2]tetradeca-4,13-diene (**7a**). Yield 0.66 g (80%). Colourless crystals. M.p. 34.0 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 5.67 and 4.95 (AA'BB' system, J(AB) = 10.0 Hz, 4H), 1.56 (bs, 12H), 0.74 (s, 4H); MS *m/z* (rel. intensity) 188 (10)**7a**$^{+\cdot}$,160 (31), 131 (49), 118 (54), 117 (100), 104 (46), 91 (55); HRMS 188.1564; calcd. for $C_{14}H_{20}$, 188.1565; Anal. found: C, 89.10; H, 10.90%. Calcd. for $C_{14}H_{20}$: C, 89.30; H, 10.70%.

Dispiro[2.2.5.2]trideca-4,12-diene (**7b**). Yield 0.57 g (75%). Colourless liquid. Spectral data were in agreement with reported data. [4b]

Flash Vacuum Thermolysis (FVT). The FVT equipment has been described earlier.[1] In our experiments, an Al_2O_3 tube (28 cm long, 1.5 cm wide) was used, heated externally by a Heraeus B 1.8/25 Furnace. In a typical run, **7** (50 mg) was sublimed into the hot zone at a rate of of 100 mg·h^{-1} using a sublimation furnace (Büchi GKR-50) to heat the sample bulb (50-70 °C). At the end of the hot zone, the pyrolysate was condensed in a cold trap (dry ice, acetone, -70 °C). By washing with diethyl ether or methylbutane, the pyrolysate was collected, the solvent was removed under reduced pressure and the recovery determined by ^{1}H NMR and GCMS. Full spectroscopic analysis was performed by isolation of the products by preparative GLC followed by ^{1}H NMR, GCMS and exact mass measurements. In the case of **5a**, **10b**,**11**, **14d** and **14e**, an independent synthesis provided an unambiguous proof for their structure.

[8]Paracyclophane (**1a**). Spectral data were in agreement with those reported. [14]

p-n-Hexylstyrene (**5a**). Colourless liquid. ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.35 and 7.14 (AA'BB' system, J(AB) = 8.2 Hz, 4H) 6.72, 5.70 and 5.19 (CDE system, J(CD) = 17.6 Hz, J(CE) = 10.9 Hz, J(DE) = 1.1 Hz, 3H), 2.60 (t, J = 7.2 Hz, 2H), 1.80 - 1.05 (m, 8H), 0.88 (m, 3H); MS *m/z* (rel. intensity) 188 (25) **5a**$^{+\cdot}$, 118 (24), 117 (100), 115 (23), 91 (18); HRMS 188.1580, calcd. for $C_{14}H_{20}$: 188.1565. The spectral data were identical with those of a sample of **5a** obtained by independent synthesis according to Scheme 4.

p-n-Pentylstyrene (**5b**). Colourless liquid. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.34 and 7.15 (AA'BB' system, J(AB) = 8.1 Hz, 4H), 6.71, 5.71 and 5.20 (CDE system, J(CD) = 17.9 Hz, J(CE) = 10.6 Hz, J(DE) = 0.5 Hz, 3H), 2.62 (t, J = 7.5 Hz, 2H), 1.70 - 1.04 (m, 4H), 1.04 - 0.80 (m, 5H); MS *m/z* (rel. intensity) 174 (27) **5b**$^{+\cdot}$, 118 (16), 117 (100) [**5b**-Bu]$^+$, 115 (17), 91 (13); HRMS 174.1398, calc. for $C_{13}H_{18}$, 174.1409.

p-n-Propylstyrene (**5d**) and *p*-ethylstyrene (**5e**). Spectral data were in agreement with those reported.[1]

3-Vinylspiro[5.6]dodeca-1,4-diene (**9a**). Colourless liquid. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.75 and 5.52 (AA'BB' part of AA'BB'X system, J(AB) = 10.2 Hz, J(BX) = 3.5 Hz, J(AX) = 1.8 Hz, 4H), 5.70, 5.03, 4.99 and 3.28 (DEFX system, J(DE) = 17.0 Hz, J(DF) = 9.9 Hz, J(DX) = 7.4 Hz, J(EF) = 1.7 Hz, J(FX) = 1.7 Hz, J(EX) = 1.2 Hz, 4H), 1.55 (m, 12H); MS *m/z* (rel. intensity) 188 (11) **9a**$^{+\cdot}$, 131 (10), 118 (27), 117 (100); HRMS 188.1556, calcd. for $C_{14}H_{20}$, 188.1565.

3-Vinylspiro[5.5]undeca-1,4-diene (**9b**). Colourless liquid. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.80 and 5.58 (AA'BB' part of AA'BB' X system, J(AB) = 10.4 Hz, J(BX) = 3.5 Hz, J(AX) = 1.9 Hz, 4H), 5.71, 5.06, 4.99 and 3.33 (DEFX system, J(DE) = 17.1 Hz, J(DF) = 9.8 Hz, J(DX) = 7.4 Hz, J(EF) = 1.6 Hz, J(FX) = 1.2 Hz, J(EX) = 0.9 Hz, 4H), 1.58 (m, 10H); MS *m/z* (rel. intensity) 174 (16) **9b**$^{+\cdot}$, 131 (16), 118 (32), 117 (100); HRMS 174.1406, calcd. for $C_{13}H_{18}$, 174.1409.

3-Ethylidenespiro[5.5]undeca-1,4-diene (**10b**). Colourless liquid. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.44 and 5.92 (AB system, J(AB) = 10.2 Hz, 2H), 6.05 and 5.75 (AB system, J(AB) = 10.0 Hz, 2H), 5.30 (q, J = 7.0 Hz, 1H), 1.83 (d, J = 7.0 Hz, 3H), 1.52 (m, 10H); MS *m/z* (rel. intensity) 174 (35), **10b**$^{+\cdot}$, 159 (18), 145 (38), 131 (61), 118 (100), 117 (75), 115 (30), 91 (61); HRMS 174.1408, calcd. for $C_{13}H_{18}$, 174.1409.

8-Ethylcyclooctabenzene (**11a**). Colourless liquid. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.13 - 6.95 (m, 3H), 2.77 - 2.71 (m, 4H), 2.61(q, J = 7.6 Hz, 2H), 1.68 - 1.58 (m, 4H), 1.39 - 1.34 (m, 4H), 1.24 (t, J = 7.6 Hz, 3H); MS *m/z* (rel. intensity) 188 (62,)**11a**$^{+\cdot}$, 173 (16), 159 (100), 145 (47), 131 (47), 117 (61), 91 (50); HRMS 188.1586, calcd. for $C_{14}H_{20}$, 188.1565.

7-Ethylcycloheptabenzene (**11b**). Colourless liquid. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.04 - 6.92 (m, 3H), 2.80 - 2.76 (m, 4H), 2.61 (q, J = 7.6 Hz, 2H), 1.86 - 1.80 (m, 4H), 1.70 - 1.60 (m, 2H), 1.24 (t, J = 7.6 Hz, 3H); MS *m/z* (rel. intensity) 174 (68) **11b**$^{+\cdot}$, 159 (27), 145 (100), 117 (40), 91 (37); HRMS 174.1421, calcd. for $C_{13}H_{18}$, 174.1409.

p-Isopropylstyrene (**14e**). Colourless liquid. ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.34 and 7.17 (AA'BB' system, J(AB) = 8.2 Hz, 4H), 6.72, 5.73 and 5.21 (CDE system, J(CD) = 17.5 Hz, J(CE) = 10.9 Hz, J(DE) = 0.8 Hz, 3H), 2.92 (septet , J = 6.9 Hz, 1H), 1.27 (d, J = 6.9 Hz, 6H); MS *m/z* (rel. intensity) 146 (40) **14e**$^{+\cdot}$, 131 (100), 91 (45); HRMS 146.1088, calcd. for $C_{11}H_{14}$, 146.1096.

1,4-Divinylbenzene (**15**). Colourless liquid. ^{1}H NMR ($CDCl_3$, 90 MHz) 7.38 (s, 4H), 6.72, 5.75 and 5.25 (ABC system, J(AB) = 17.6 Hz, J(AC) = 10.7 Hz, J(BC) = 1.0 Hz, 6H); MS *m/z* (rel. intensity) 130 (100) **15**$^{+\cdot}$, 129 (41), 128 (41), 115 (34); HRMS 130.0772, calcd. for $C_{10}H_{10}$, 130.0783.

p-(2-Butyl)styrene (**14d**). Colourless liquid. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.35 and 7.15 (AA'BB' system, J(AB) = 8.1 Hz, 4H), 6.71, 5.71 and 5.19 (CDE system, J(CD) = 17.6 Hz, J(CE) = 10.8 Hz, J(DE) = 0.7 Hz, 3H), 2.60 (m, 1H), 1.27 (m, 2H), 1.24 (d, J = 7.0 Hz, 3H) 0.83 (t, J = 7.5 Hz, 3H); MS *m/z* (rel. intensity) 160 (23) **14d**$^{+\cdot}$, 131 (100), 129 (12), 117 (12), 116 (10), 91 (29); HRMS 160.1259, calcd. for $C_{12}H_{16}$, 160.1252.

p-(2-Pentyl)styrene (**14c**). Colourless liquid. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.35 and 7.15 (AA'BB' system, J(AB) = 8.0 Hz, 4H), 6.71, 5.71 and 5.19 (CDE system, J(CD) = 17.6 Hz, J(CE) = 10.9 Hz, J(DE) = 0.8 Hz, 3H), 2.69 (m, 1H), 1.28 (m, 4H), 1.23 (d, J = 7.5 Hz, 3H) 0.83 (t, J = 7.5 Hz, 3H); MS *m/z* (rel. intensity) 174 (24) **14c**$^{+\cdot}$, 131 (100), 129 (10), 117 (17), 116 (11), 115 (13), 91 (28).

Independent synthesis of **11a**. 1.01 g (6.3 mmol) cyclooctabenzene was treated with 0.69 g (6.8 mmol) acetic anhydride and 2.05 g (15.4 mmol) $AlCl_3$ in 10 ml CS_2 according to the procedure of Bergmann et al. [15] to give 8-acetylcyclooctabenzene.

8-Acetylcyclooctabenzene. Colourless liquid. Yield 1.1 g (80%). ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.73 - 7.72 and 7.19 (ABC system, J(AB) = 2.0 Hz, J(AC) = 8.4 Hz, J(BC) unresolved, 3H), 2.82 (m, 4H), 2.59 (s, 3H), 1.72 - 1.67 (m, 4H), 1.38 - 1.33 (m, 4H); ^{13}C NMR[16] ($CDCl_3$, 62.9 MHz) δ 198.4 (s, C=O), 147.5 (s, C10a), 141.9 (s, C6a), 135.6 (s, C8), 129.4 (d, J(CH) = 151 Hz, C7), 129.1 (d, J(CH) = 151 Hz, C9), 126.6 (d, J(CH) = 160 Hz, C10), 32.4 (t, J(CH) = 129 Hz), 32.3 (t, J(CH) = 129 Hz), 33.2 (t, J (CH) = 129 Hz), 32.0 (t, J(CH) = 129 Hz), 26.6 (q, J(CH) = 127 Hz, -CH_3), 25.9 (t, J(CH) = 124 Hz), 25.8 (t, J(CH) = 124 Hz); MS *m/z* (rel. intensity) 202 (28) M$^{+\cdot}$, 187 (100), 115 (21), 91 (16); HRMS 202.1377, calcd for $C_{14}H_{18}O$, 202.1358. 0.53 g (2.4 mmol) 8-Acetylcyclooctabenzene was treated with 0.28 ml (5.8 mmol) of 98% hydrazine monohydrate and 0.70 g (12.5 mmol) of KOH in 7.0 ml diethylene- glycol according to the procedure of Huang-Minlon.[17] The yield of **11a** was 0.29 g (64%); the product was identical with that obtained from pyrolysis of **7a**, according to ^{1}H NMR and GCMS.

Independent synthesis of **11b**. 7-Acetylcycloheptabenzene was obtained from cycloheptabenzene in an analogous fashion as described for 8-acetylcyclooctabenzene. Colourless liquid. Yield 0.32 g (30%). ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.70, 7.69 and 7.18 (ABC system, J(AB) = 2.0 Hz, J(AC) = 7.6 Hz, J(BC) unresolved), 2.89 - 2.83 (m, 4H), 2.58 (s, 3H), 1.97 - 1.80 (m, 2H), 1.74 - 1.61 (m, 4H); MS *m/z* (rel. intensity) 188 (23) M$^{+\cdot}$, 173 (100), 115 (18), 84 (23); HRMS 188.1218, calcd. for $C_{13}H_{16}O$; 188.1201. **11b** Was obtained from 7-acetycycloheptabenzene in a fashion analogous to that described for **11a**. Yield 0.23 g (60%). The product was identical with that obtained from pyrolysis of **7b** according to ^{1}H NMR and GCMS.

Independent synthesis of **14e**. 12.0 g (0.10 mol) isopropylbenzene was treated with 10.2 g (0.10 mol) of acetic anhydride and 30.5 g (0.23 mol) of $AlCl_3$ in 45 ml of CS_2 according to the procedure of Bergmann et al.[15], yielding *p*-acetylpropylbenzene.

p-Acetylisopropylbenzene. Colourless liquid. Yield 3.28 g (20%). ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.91 and 7.32 (AA'BB' system, J(AB) = 9.0 Hz, 4H), 2.91 (septet, J = 7.0 Hz, 1H), 2.58 (s, 3H), 1.30 (d, J = 7.0 Hz, 6H); MS *m/z* (rel. intensity) 162 (26) M$^{+\cdot}$, 147 (100), 91 (21). 3.28 g (20.2 mmol) *p*-Acetylpropylbenzene was treated with 3.00 g (80 mmol) $NaBH_4$ in 10 ml MeOH according to the procedure described in reference 18, yielding 2-(4-isopropylphenyl)ethanol.

2-(4-Isopropylphenyl)ethanol. Colourless liquid. Yield 2.7 g (83%). ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.32 and 7.22 (AA'BB' system, J(AB) = 9.0 Hz, 4H), 4.89 (m, 1H), 2.92 (septet, J = 7.0 Hz, 1H), 188 (m, 1H), 1.50 (d, J = 6.0 Hz, 3H), 1.26 (d, J = 7.0 Hz, 6H); MS *m/z* (rel. intensity) 164 (28) M$^{+\cdot}$, 149 (100), 79 (56). 2.7 g (16.5 mmol) of 1-(*p*-isopropylphenyl)ethanol was treated with a catalytic amount of $KHSO_4$ in a Claisen flask at 190 °C under reduced pressure (50 mm Hg). During the reaction a colourless liquid distilled. The distillate contained almost pure **14e**. Yield 2.2 g (90%). The product was identical with that obtained from pyrolysis of **7a, b, e** and **10c** according to ^{1}H NMR and GCMS.

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