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FORCE FIELD-SCF CALCULATIONS ON CYCLOPROPENE INTERMEDIATES IN CARBENE REARRANGEMENTS. COMPARISON WITH EXPERIMENT

CURT WENTRUP,*† CLAUDE MAYOR,‡ JÜRGEN BECKER§ and HANS JÖRG LINDNER*¶
Department of Chemistry, Philipps-University, D-3550 Marburg, West Germany
Institut für Organische Chemie und Biochemie, Technische Hochschule Darmstadt, Petersenstrasse 22, D-6100 Darmstadt, West Germany

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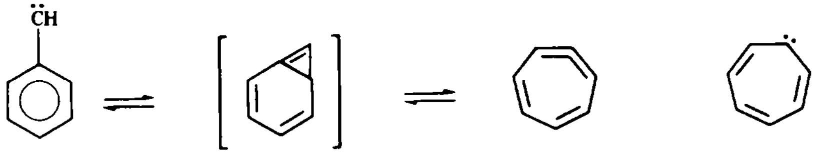
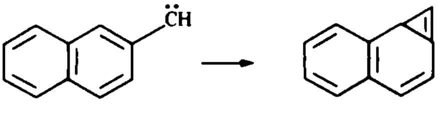
Abstract—Heats of formation and geometries of benzocyclopropene, cyclopropa[*b*]naphthalene, bicyclo[4.1.0]hepta-2,4,7-triene, and benzannelated derivatives have been calculated with a combined force field-SCF program. The bicycloheptatrienes are stabilized relative to the isomeric arylcarbenes by benzannelation, and destabilized by loss of aromaticity and/or increased strain. 1-Naphthylcarbene, 2-naphthylcarbene, 9-phenanthrylcarbene and 9-anthrylcarbene were generated by gas-phase pyrolysis of the corresponding arene aldehyde tosylhydrazone sodium salts, diazomethanes, or 5-aryltetrazoles, and rearranged to cyclobuta[*de*]naphthalene (**21**), cyclobuta[*jk*]phenanthrene (**33**), and cyclobuta[*de*]anthracene (**38**), respectively. 10,11-Dihydrodibenzo[*ad*]cyclohepten-5-ylidene (**15**), similarly generated from 5-diazo-10,11-dihydro-5*H*-dibenzo[*ad*]cycloheptene (**39**), rearranged to 5a,9b-dihydro-5*H*-benzo[3,4]cyclobut[1,2-*a*]indene (**40**), 5*H*-dibenzo[*ad*]cycloheptene (**41**), and 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**44**). **40** rearranged thermally to **41**. The mechanisms of the rearrangements are discussed.

The interconversion of phenylcarbene (**1**) with cycloheptatetraene (**3**) and/or cycloheptatrienylidene (**4**) has been reviewed.[1-3] The cycloheptatetraene (**3**) has been matrix-isolated and directly observed by IR and UV spectroscopy,[4] and the chirality test for cyclic allenes has demonstrated the non-planarity and hence allenic nature of the species (**3**) trapped in solution with diphenylisobenzofuran.[5] However, the possibility still remains that the carbene **4** may play a role in some reactions in solution.[5,6] MINDO/3 calculations indicate that **3** is the only true minimum of the seven membered ring system,[7] and *ab initio* calculations predict **3** to be more stable than **4** by about 18 kcal/mol.[8]



1 **2** **3** **4** (1)

There is much less information about the presumed bicyclo[4.1.0]hepta-2,4,7-triene intermediate (**2**) in this interconversion. Although it has repeatedly been stated that **2** had been directly observed by matrix IR spectroscopy,[9,10] this statement was withdrawn.[4,11] Yet, the annelated derivative **6**, derived from 2-naphthylcarbene (**5**) is, apparently, observed under such conditions.[9-11] From the MINDO/3 calculations already mentioned, it was concluded that **1** and **2** are roughly isoenthalpic, and that the activation energy for **1** → **2** is about 6.3 kcal/mol,[7] a surprisingly low number in view of the fact that this rearrangement has never been observed in solution.



5 **6**

In order to compare different cyclopropene intermediates of the type **2** it is desirable to know their heats of formation. To this end we have performed force field-SCF calculations on a series of fused cyclopropenes. The results are compared with experimental findings which demonstrate that drastic increases in the heats of formation of the cyclopropenes do not prevent the reactions from occurring.

RESULTS

1. *Force field-SCF calculations*

The heats of formation and geometries of benzocyclopropene, bicyclo[4.1.0]hepta-2,4,7-triene (**2**), and several annelated derivatives (Table 1 and Fig. 1) were calculated using a combined force field-SCF program[12] which had proven reliable for strained aromatic and polyenic molecules and radicals.[12,13] Due to the high degree of angle deformation in the fused cyclopropenes, the angle strain energy[12] was corrected

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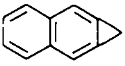
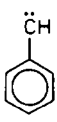
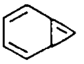
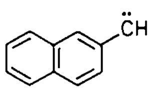
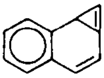
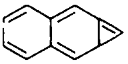
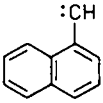
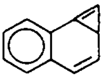
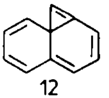
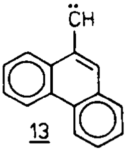
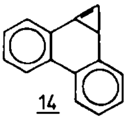
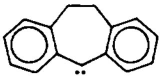
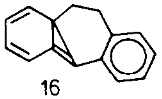
† University of Marburg.

‡ Ph.D. Dissertation, University of Lausanne, Switzerland, 1974.

§ Ph.D. Dissertation, University of Marburg, 1983.

¶ Technische Hochschule Darmstadt.

Table 1. Force field-SCF and thermochemical calculations

Carbene (triplet)	ΔH_f° (carbene)[a] (kcal/mol)	Cyclopropene derivative	ΔH_f° (kcal/mol)		
			exptl.[b]	FF[c]	FF_{corr}[d]
		 8	89 ± 1	81	89
		 9	104	97	105
 1	102	 2		104	112
 5	118	 6		107	115
		 7		125	133
 10	118	 11		115	123
		 12		142	150
 13	132	 14		120	128
 15	129 e)	 16		144	152

[a] Thermochemical estimate.

[b] Ref. 14*a*.

[c] Force field-SCF calculation.

[d] Corrected values, see text.

[e] A force field-SCF calculation on 10,11-dihydrodibenzo[*ad*]cyclohepten-5-yl gave $\Delta H_f^\circ = 72$ kcal/mol. From this value and group increments[17] $\Delta H_f^\circ(\mathbf{15}) \cong 129$ kcal/mol is obtained.

as follows:

$$E_\alpha = 1/2k_\alpha(\alpha-\alpha_0)^2 + 1/3d_\alpha|\alpha-\alpha_0|^3;$$

$$k_\alpha = 82.34 \text{ kcal/mol} \cdot \text{rad}^2;$$

$$d_\alpha = 84.93 \text{ kcal/mol} \cdot \text{rad}^3.$$

The geometries calculated for benzocyclopropene (**8**) and cyclopropa[*b*]naphthalene (**9**; Fig. 1) are in good agreement with experimental data.[14] The bicyclo-[4.1.0]hepta-2,4,7-triene moieties in **2**, **6**, **11**, **12**, **14** and **16** show highly distorted geometries at the bridgehead sp^2 C atoms. The intact benzene rings in **6**, **11**, **14** and **16** are nearly undistorted.

The computed heats of formation of the cyclopropa-renes **8** and **9** (Table 1) were *ca* 8 kcal/mol too low. This appears to be a systematic error which could be removed by appropriate reparametrization, but in order to maintain the program, which works well for less highly strained molecules,[12,13] an empirical correction of 8 kcal/mol was added to all computed values (Table 1).

The heats of formation thus obtained are internally

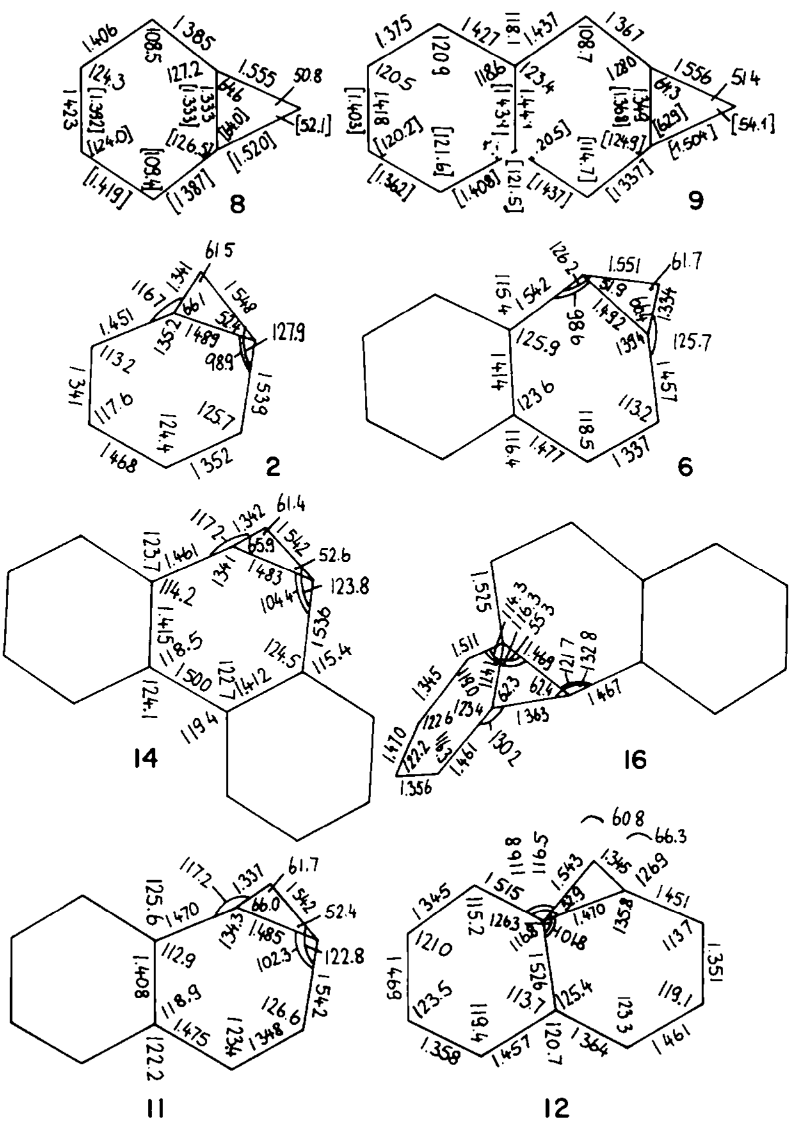


Fig. 1. Calculated geometries of benzocyclopropene (**8**), cyclopropa[*b*]naphthalene (**9**), and bicycloheptatrienes **2**, **6**, **11**, **12**, **14** and **16**. Values in brackets are the experimental data.[14]

consistent, since they satisfy the principle of group additivity.[15] For example, from the computed $\Delta H_f^\circ(\mathbf{2}) = 112$ kcal/mol one calculates with group increments[15] $\Delta H_f^\circ(\mathbf{6}) \cong 116$ kcal/mol and $\Delta H_f^\circ(\mathbf{14}) \cong 124$ kcal/mol.

If the thermochemical resonance energy of benzocyclopropene (**8**) is the same as that of benzene (20 kcal/mol[16]), it is seen that after correcting for the resonance energy, **2** is only about 3 kcal/mol more highly strained than **8**. The thermochemically derived heat of formation of **2** previously reported[17] was apparently too high due to the assumption of an "extra strain" energy[18] of 18.5 kcal/mol.

The heats of formation of the *triplet* carbenes given in Table 1 were obtained by group additivity as previously reported.[17] Although the absolute values may be in error, only their *differences* are of importance here, and these are expected to be quite accurate. The MINDO/3 values for triplet and singlet phenylcarbene (**1**) are 91.5 and 113.8 kcal/mol, respectively.[7] In view of the facts that the singlet–triplet splitting in diphenylcarbene is very small, about 3 kcal/mol,[19] and for methylene itself about 9 kcal/mol,[20] the MINDO/3 singlet–triplet splitting for **1** (22.3 kcal/mol) appears far too high. We believe that the heats of formation of the *singlet* carbenes are only a few kcal/mol higher than the values for the triplets given in Table 1. This assumption is in agreement with *ab initio* calculations on phenylcarbene.[8]

We now wish to report some experiments, and then to discuss the results in the light of the computed enthalpy data.

2. *Naphthylcarbenes*

The naphthylcarbenes **10** and **5** (Scheme 1) are best generated by piptopyrolysis† of the tosylhydrazone salts **17** and **22** at 400–800°. Under these conditions,

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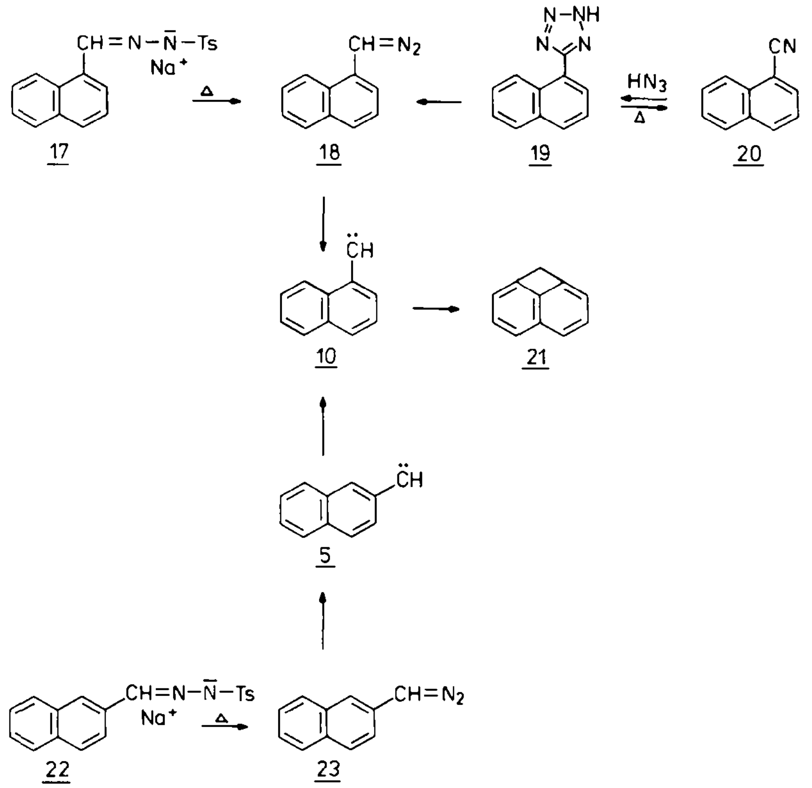
† In a piptopyrolysis (πιπτι = it is falling) the solid to be pyrolyzed is allowed to fall into a vertical pyrolysis tube maintained at an initial vacuum of 10^{-3} Torr. Vaporization takes place on a quartz wool plug placed inside the tube.



Scheme 1.

yields of up to 40% of cyclobuta[*de*]naphthalene (**21**) were obtained from *both* **17** and **22**.[21] The diazo compound **18** was obtained by the thermal decomposition of **17** at 130° and identified by its IR and ^{1}H-NMR spectra. A subsequent gas-phase pyrolysis of **18** at 600° (10^{-4}–10^{-3} Torr) confirmed the formation of **21**, but the overall yield was low due to the low volatility of **18** and resulting extensive decomposition in the solid state. Furthermore, **21** was also obtained in 26% yield by pyrolysis of the tetrazole **19** at 700°/10^{-3} Torr; in this case, the major product was the nitrile **20** (61%), formed by reversion of the 1,3-dipolar cycloaddition reaction used to prepare the tetrazole. The formation of diazo compounds and thence carbenes by pyrolysis of tetrazoles is well established.[1,22]

The formation of **21** from the two carbenes **10** and **5** suggests that these interconvert by a ring expansion–ring contraction cycle of the type given in Eq. (1).[21] Engler and Shechter[23] have described an alternative production of naphthylcarbenes by pyrolysis of [methoxy(naphthylmethyl)]trimethylsilanes and also reported yields of *ca* 40% of **21** as well as additional evidence for the interconversion of **10** and **5** (*vide infra*).

In the 600° piptopyrolysis of **17** and **22** small amounts of 1-vinylideneindene (**28**) and 1*H*-cyclopenta[*cd*]indene (**29**) were also identifiable by comparison of the ^{1}H-NMR spectra with those of the compounds previously obtained[24] from 1-(2-diazoethylidene)indene (**26**) via the carbene **27** (Scheme 2). There are at least three routes whereby these products may be formed from the naphthylcarbenes **5** and **10** (Scheme 2). Although these routes are entirely tentative, they are exact analogs of the mechanism of ring contraction in phenylcarbene.[25] Since cyclobuta[*de*]naphthalene (**21**) appears to be the thermochemical sink on this energy surface, it is not surprising that only traces of **28** and **29** are formed.

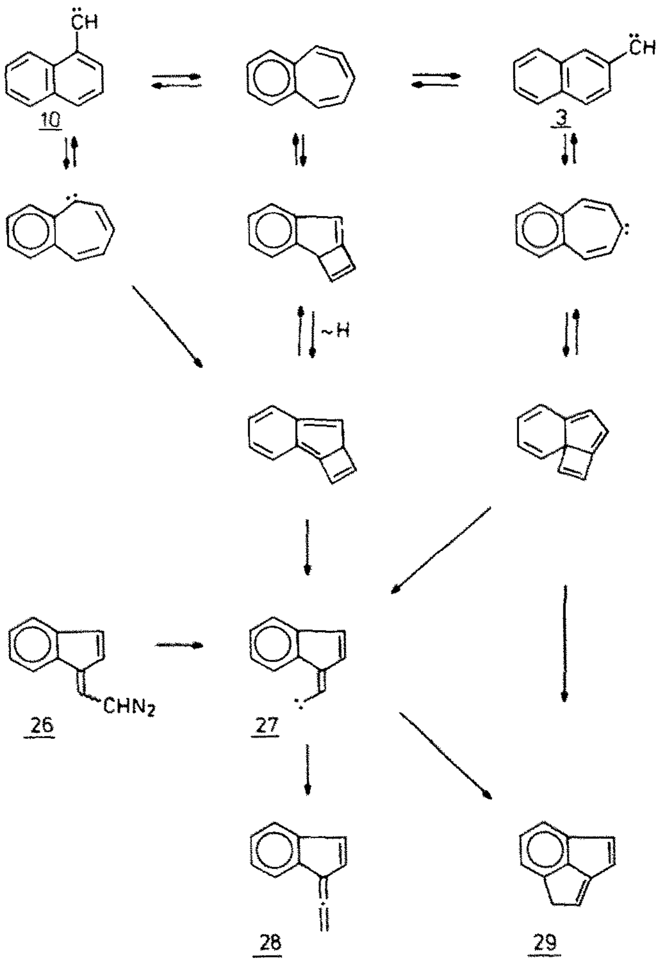
3. *9-Phenanthrylcarbene and 9-anthrylcarbene*

The piptopyrolyses of **30** and **32** at 600° gave a 7% yield of cyclobuta[*jk*]phenanthrene (**33**), isolated by preparative gas chromatography and identified by its spectroscopic properties (Experimental). The tetrazole **32** underwent 76% cycloreversion to 9-cyanophenanthrene under these conditions. A *ca* 1% yield of cyclopenta[*def*]phenanthrene (**35**) was obtained in both cases. This is explained in terms of the carbene–carbene rearrangement **13** → **34** (Scheme 3) as also proposed by Engler and Shechter[23] who obtained superior yields by pyrolysis of [methoxy(9-phenanthrylmethyl)]trimethylsilane at 590°/0.1 Torr (9 : 1 mixture of **33** and **35** with a combined yield of 72%).

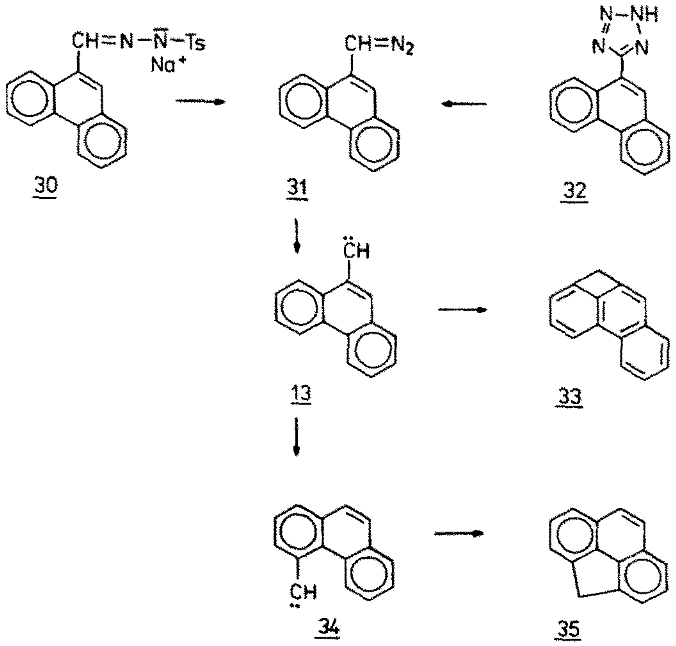
9-Anthrylcarbene (**37**) was generated by piptopyrolysis of the tetrazole **36** (Scheme 4). At 600° 11% of cyclobuta[*de*]anthracene (**38**) and 58% of 9-anthrylcarbonitrile were obtained. **38** has also been prepared (52% yield) by rearrangement of 1-anthrylcarbene, formed by pyrolysis of [methoxy(1-anthrylmethyl)]trimethylsilane.[23]

4. *10,11-Dihydrodibenzo*[ad]*cyclohepten-5-ylidene*

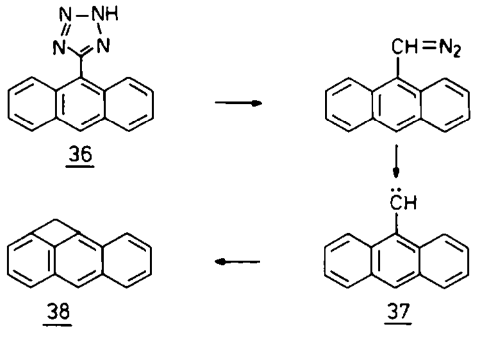
Gas-phase pyrolysis of 5-diazo-10,11-dihydro-5*H*-dibenzo[*ad*]cycloheptene (**39**) produced three $C_{15}H_{12}$ hydrocarbons, 5a,9b-dihydro-5*H*-benzo[3,4]-cyclobut[1,2-*a*]indene (**40**), 5*H*-dibenzo[*ad*]-cycloheptene (**41**), and 8,9-dihydro-4*H*-cyclopenta-[*def*]phenanthrene (**44**). A mechanism for their formation is presented in Scheme 5, and the yields and reaction conditions in Table 2. **41** and **44** were identified by comparison with authentic samples. The structure of



Scheme 2.



Scheme 3.



Scheme 4.

Table 2. Pyrolysis of 5-diazo-10,11-dihydro-5*H*-dibenzo[*ad*]-cycloheptene (**39**) and benzocyclobut[1,2-*a*]indene (**40**)[a]

Starting material	T°C	Products, rel. yields		
		40	**41**	**44**
39	300	53	43	4
39	385	20.6	73.0	6.3
39	490	1.8	87.5	10.7
39	580	0	84.5	15.5
39	685	0	80	20
39	750	0	78.5	21.5
39	815	0	74	26
40	385	80	20	0
40	580	0	100	0

[a] Samples were sublimed into the horizontal pyrolysis tube at 40°/10^{-2} Torr. Relative yields were determined by GC. The total yields were 77–100%.

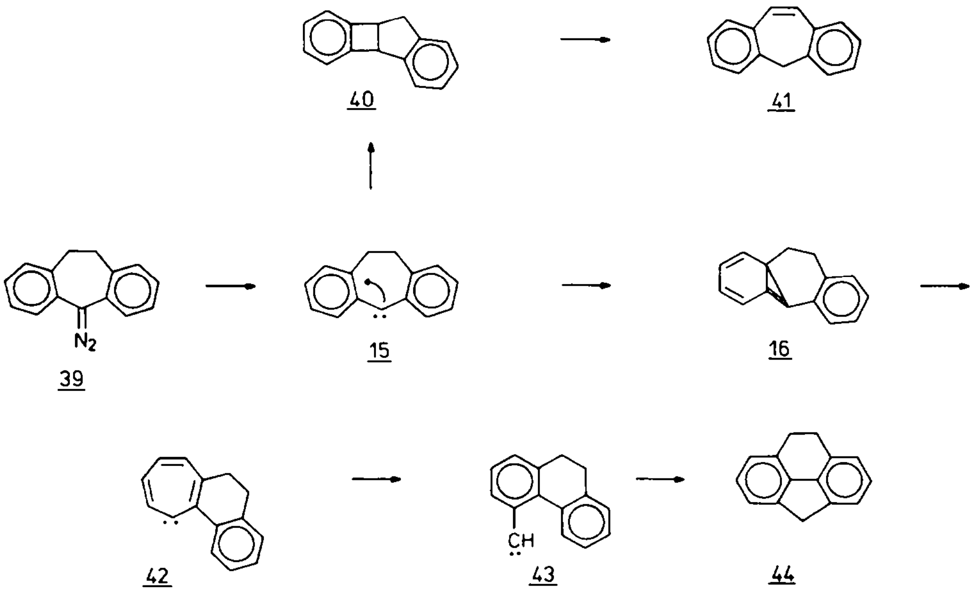
40 was ascertained by ^{1}H-NMR spectroscopy with the aid of spin decoupling (Experimental), and by the circumstance that **40** itself rearranged to **41** upon gas-phase pyrolysis (Table 2). The NMR data and thermal behavior of **40** are in complete agreement with the properties of the related 2a,7a-dihydro-7*H*-cyclobut[*a*]indene.[26]

It is known that thermolysis and photolysis of **39** in solution gives the carbene **15**.[27] The transannular insertion reaction **15** → **40** finds precedence in *o*-alkylphenylcarbenes,[28] although cycloheptylidene itself does not undergo such a reaction to give bicyclo[3.2.0]heptane.[29] The transformation **15** → **44** is depicted in Scheme 5 as a carbene–carbene rearrangement in analogy with the formation of fluorene from diphenylcarbene and numerous other such rearrangements.[1–3]

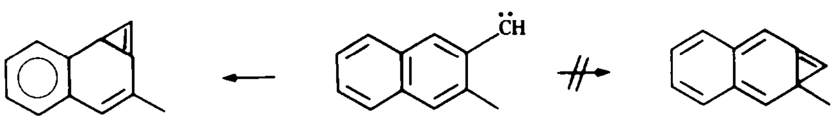
Assuming that the Arrhenius equation is applicable, and that the *A*-factors for the reactions **15** → **40** and **15** → **44** have similar temperature dependencies, the data given in Table 2 permit an estimation of the difference in activation energies for the two processes. This will probably not be strictly correct under the low-pressure conditions of the experiments.[30] Nevertheless, a plot of the logarithm of the ratio of yields (**40** + **41**)/(**44**) versus T^{-1} gives a straight line from which E_a(**15** → **44**) − E_a(**15** → **40**) ≃ 5 kcal/mol is obtained.

DISCUSSION

It was shown previously[31] that Me-substituted naphthylcarbenes undergo carbene–carbene rearrangement in a manner corresponding to addition of the carbenic carbon to the bond of highest bond order (the 1,2-bond in naphthalene). Thus, for example, 3-methyl-2-naphthylcarbene (**45**) gave 2-vinylnaphthalene, but 1-methyl-2-naphthylcarbene did not give 1-vinylnaphthalene. This implies that **45** reacts via **46**, but not via **47**.[31] Furthermore, evidence for the existence of the cyclopropene **6**, formed by rearrangement of the carbene **48** in solution, was obtained by the isolation in 16% yield of the adduct **49** with cyclopentadiene.[32] At higher temperatures, **6** rearranged further to 2-naphthylcarbene (**5**), and this was shown to be formed in the singlet state.[33]



Scheme 5.

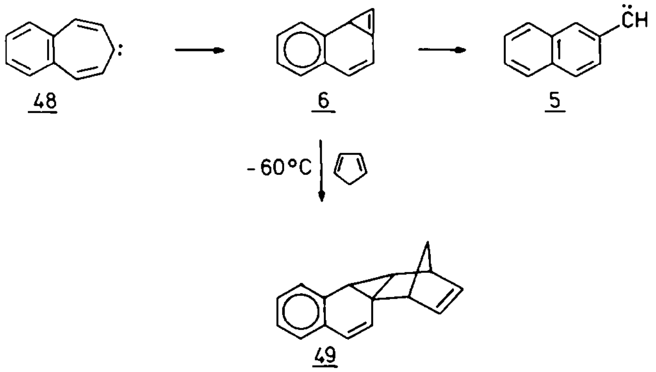

46 **45** **47**

The computational data given in Table 1 confirm that 2-naphthylcarbene should indeed undergo preferential ring closure with the 1,2-bond, i.e. **5** → **6** or **45** → **46**. This data also implies that the reaction **5** → **6** be exothermic, but due to the difficulty of estimating the heats of formation of the carbenes with precision, this result should be used with caution. The chemistry summarized in Scheme 6 suggests that the reaction **5** → **6** may be endothermic, although it may equally well be roughly thermoneutral with the carbene **5** being more reactive than the cyclopropene **6**.

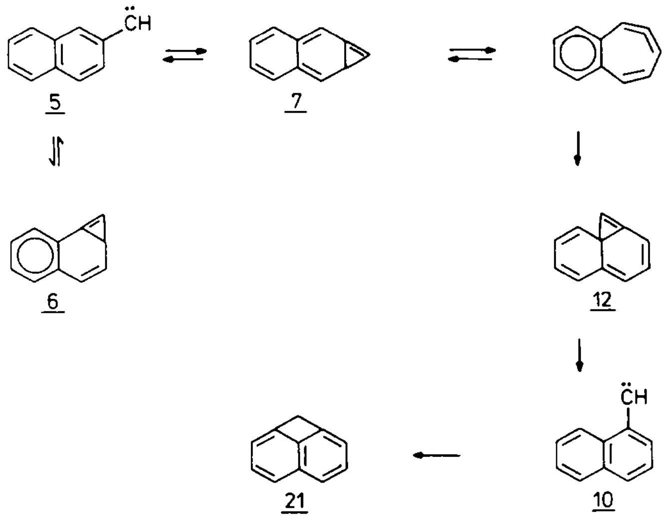
From Table 1 it is clear, however, that the reaction **5** → **7** is endothermic, and **7** is significantly less stable than **6** due to the loss of the entire aromatic resonance energy. Yet, a reaction of this kind is required to explain the ready rearrangement of 2-naphthylcarbene to 1-naphthylcarbene and thence cyclobuta[*de*]naphthalene (Schemes 1 and 7). Furthermore, if cyclopropenes are involved all the way, the highly endothermic **12**, some 30 kcal/mol above the naphthylcarbenes, is also indicated. Carbene **5** will presumably rapidly interconvert with cyclopropene **6** under the reaction conditions, but in the absence of an internal trap such as the methyl group in **46**, this reaction is unproductive.

Similarly, 1-naphthylcarbene (**10**) should easily cyclize to **11** (Table 1), which it may well do in a reversible manner enroute to cyclobuta[*de*]naphthalene (**21**). However, the observation by Engler and Shechter[23] that the methyl-substituted 1-naphthylcarbene **50** gives a mixture of the two cyclobutanaphthalenes **51** and **53** implies the occurrence of the steeply endothermic reaction **50** → **52** (**10** → **12**).

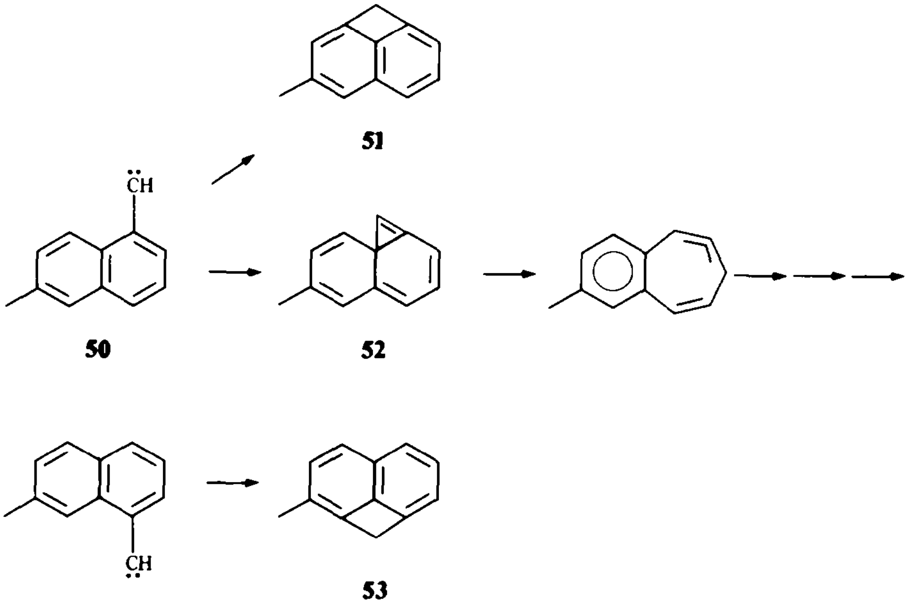
Again, 9-phenanthylcarbene (**13**) should readily cyclize to the cyclopropene **14** (Table 1) which has been generated in different ways and trapped in solution.[32,34,35] Here, the isolation of cyclopenta[*def*]phenanthrene (**35**) implies a multiple carbene–carbene rearrangement to **34** via the cyclopropenes **14** and **54** (Scheme 8). We have not attempted a calculation of the heat of formation of **54**, but it is seen that this compound



Scheme 6.



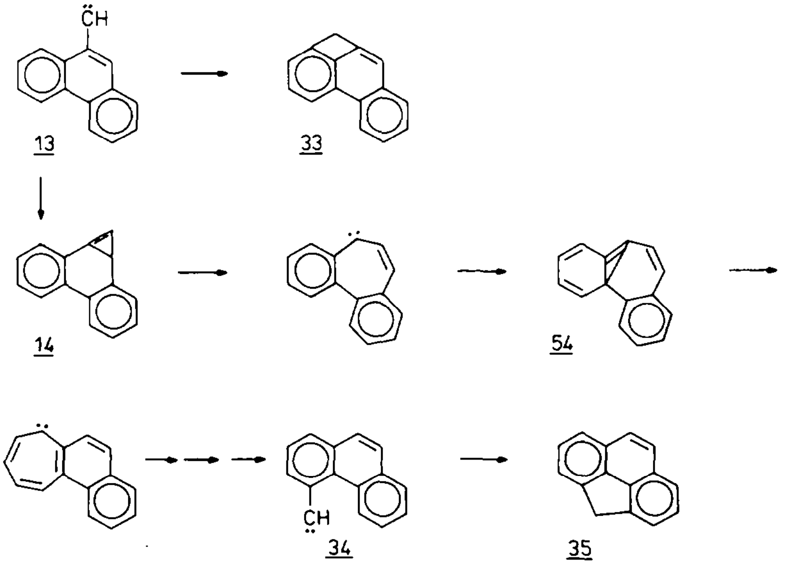
Scheme 7.



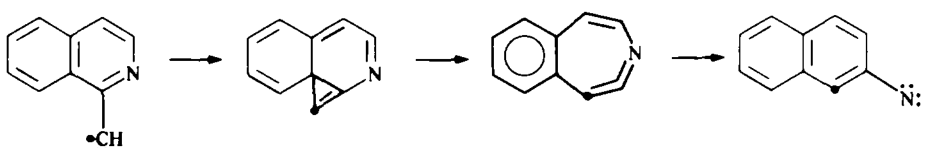
has a structure similar to that of **16** (Table 1); if other things are equal, the additional double bond in **54** would raise the heat of formation to a phenomenal ~ 180 kcal/mol.

The situation is not quite so dramatic in the case of the reaction **15** → **16** (Table 1), but this process, too, clearly requires a high activation energy. If the enthalpy difference between **16** and **15** (~ 23 kcal/mol) is taken as a lower limit for the activation energy for the reaction **15** → **44** (Scheme 5), it follows that the activation energy for the transannular reaction **15** → **40** is ~ 18 kcal/mol (Section 4).

From the results discussed so far it appears that even a dramatic instability of the fused cyclopropenes is no serious obstacle to carbene–carbene rearrangements formally proceeding through them. There are many other examples of this phenomenon. Thus, 1-isoquinolylcarbene (**55**) has been shown by ^{13}C-labeling to rearrange cleanly to 2-naphthylnitrene (**57**) under mild gas-phase conditions;[36] formally, this implies the intermediacy of the cyclopropene **56**. Moreover, the related and ^{15}N-labeled 1-isoquinolylnitrene **58** cleanly rearranges to the carbodiimide **60** in the gas-phase at 380°/10^{-4} Torr.[37,38] Hypothetically, this reaction will pass through the azirine **59**. In the corresponding rearrangement of 9-phenanthridylnitrene (**61**) to the observed carbodiimide **63**,[37] an azirine (**62**) in which the entire aromatic resonance energy has been sacrificed, can be formulated. Most strikingly of all, the nitrene **64** rearranges thermally to the carbodiimide **66** in the gas-phase at ≥ 300°/10^{-3} Torr, *in solution* at 160–180° or—very slowly—in refluxing benzene at 90°, and photochemically in Ar matrix at 10 K.[39] In the solution reactions, this

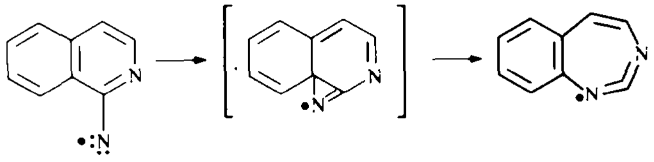


Scheme 8.



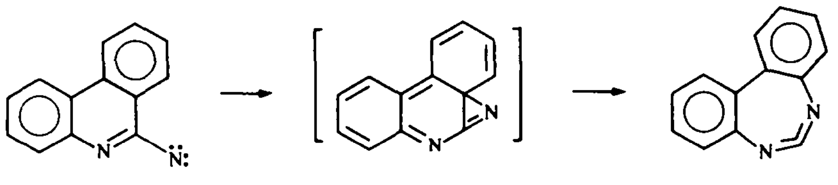
55 **56** **57**

• = ^{13}C

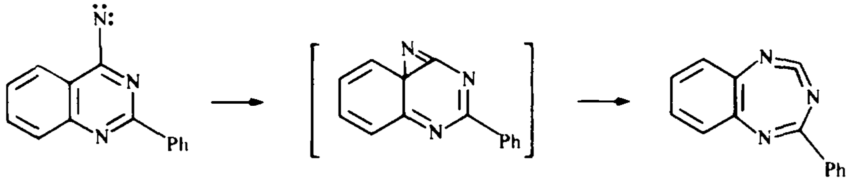


58 **59** **60**

• = ^{15}N



61 **62** **63**

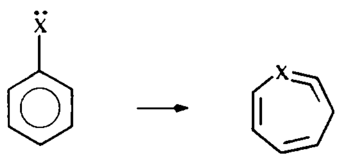


64 **65** **66**

rearrangement competes successfully with intermolecular H-abstraction from added octanethiol by the nitrene. It would thus appear that the activation energy cannot be very high, and that **65** is not a likely intermediate. No evidence for the formation of **65** was seen in the matrix photolysis experiments, but we did observe fused azirines in other systems where their formation would be thermochemically advantageous.[40]

CONCLUSION

There is no doubt that fused cyclopropenes such as **6**, **11** and **14** are involved in many carbene–carbene rearrangements. The interconversion between these cyclopropenes and the corresponding arylcarbenes are roughly thermoneutral. Corresponding azirines can also be formed from arylnitrenes. However, there is a large body of experimental data on carbene and nitrene rearrangements *formally* proceeding *via* highly endothermic intermediates such as **12**, **16**, **54**, **56**, **59**, **62** and **65**. Some of these may be real, but their high energies often do not seem to impair the efficiency of the reactions. Consequently, many such reactions may be concerted processes of the type shown below.



EXPERIMENTAL

M.ps are uncorrected. NMR spectra were recorded on Bruker HX-90, Varian XL 100, or Bruker WH-400 instruments. Chemical shifts are expressed on the δ-scale in ppm relative to Me_4Si. Mass spectra were recorded on CEC 21-490, AEI MS 902, Varian MAT CH 7a or 711 instruments at 70 eV, using direct inlet and a source temperature of 200°. Gas chromatography was carried out on Hewlett–Packard 5750 using H_2 as carrier gas (analytical and preparative), and preparatively also on a Varian Aerograph A-90.

Gas-phase pyrolyses were carried out by subliming the material through a horizontal 30 × 2 cm heated quartz tube at 10^{-4}–10^{-2} Torr. The products were collected in a U-tube, on a cold finger, or for IR purposes on a KBr disk, at −196°. In a piptopyrolysis (Section 2) the same type of apparatus is used except that the pyrolysis tube is vertical, and the finely divided solid starting material is continuously added from the top of the tube at an operating pressure of 10^{-3}–10^{-1} Torr. The tube is fitted with a loose plug of quartz wool 10 cm below the top of the heated zone. Products are collected in two consecutive U-tubes at −196°.

1-*Naphthaldehyde tosylhydrazone* was prepared from equimolar amounts of 1-naphthaldehyde and tosylhydrazine in ether (250 ml per 0.03 mol). After stirring for 1 hr at room temp the product was filtered to give white crystals (100%), m.p. 128–130°. (Found: C, 67.01; H, 4.88; N, 8.35. Calc for $C_{18}H_{16}N_2SO_2$: C, 66.56; H, 4.97; N, 8.64%) which were used without further purification.[41]

Preparation and pyrolysis of the sodium salt of 1-*naphthaldehyde tosylhydrazone.* 9.0 g (27.7 mmol) of the hydrazone in 250 ml of a 1:1 mixture of dry ether and methanol was stirred with 665 mg (27.7 mmol) of NaH for 10 hr at room temp. The precipitated salt was filtered under N_2 and dried in a high vacuum at 40° for 8 hr. The salt slowly decomposed between 120 and 300°.

(i) 200 mg of the Na salt was decomposed at 120°/10^{-3} Torr and the vapors so produced condensed as a red solid on a −196° cold finger. After 10 hr a *ca* 10% yield of 1-*naphthyldiazomethane* was obtained; IR: 2080 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 100 MHz): δ 5.55 (s, 1H), 7.03–8.20 (m, 7H).

(ii) 1 g portions of the tosylhydrazone Na salt were piptopyrolyzed at 400, 600 and 800°/10^{-3}–10^{-1} Torr in the course of 1 hr. The products were analysed and separated by gas chromatography using SE 30 and SE 52 columns at 110 and 130°, respectively. The yields of naphthalene, 1-methylnaphthalene and cyclobuta[*de*]naphthalene (**21**) were, at 400°: 3, 0 and 3%; at 600°: 21, 15 and 39%; at 800°: 18, 8.3 and 22%. These products were identified by comparison of ^{1}H-NMR, mass spectra, and GC retention times with authentic materials or, in the case of **21**, literature values.[42] The following data were recorded for **21**: ^{1}H-NMR ($CDCl_3$, 100 MHz): δ 4.78 (s, 2H), 7.08 (dd, J = 5.6 and 1 Hz, 2H), 7.6–7.3 (m, 4H); ^{13}C-NMR ($CDCl_3$, 25.16 MHz): δ 146.2 (s), 141.5 (s), 130.5 (d, J = 156 Hz), 125.3 (s), 121.3 (d, J = 160 Hz), 117.1 (d, J = 165 Hz), 47.4 (t, J = 145 Hz); mass spectrum: *m/z* 141 (11), 140 (100), 139 (76), 138 (4), 114 (4), 113 (5), 89 (4), 84 (5), 70 (7), 69.5 (6), 63 (9), 27.5 (7); IR (KBr): ν 3090 (sh), 3080, 3070 (sh), 3000, 2960, 1490, 1355, 1015, 800, 775 cm^{-1}.

In addition to the above products, the ^{1}H-NMR spectrum of the crude pyrolyzate from the 600° reaction showed peaks at δ 3.96 and 6.62 ppm, identical in shape with those of 1*H*-cyclopent[*cd*]indene (**29**).[24] A further signal at δ 5.43 ppm and an IR absorption at 1935 cm^{-1} were identical with those of 1-vinylideneindene (**28**) prepared in a different manner.[24]

(iii) The diazo-compound from (i) above was pyrolyzed at 800°/10^{-3} Torr in the horizontal pyrolysis tube. Naphthalene (19%), 1-methylnaphthalene (3%), and **21** (24%) were identified by ^{1}H-NMR and GC retention times. At 600°/10^{-3} Torr the composition of the product mixture was very similar to that described for the same temperature under (ii).

2-*Naphthaldehyde tosylhydrazone* was prepared in the same way as the 1-isomer but in the absence of light. The light-sensitive product was obtained in 95% yield as white crystals, m.p. 172–173° (lit.[31] 175°), decomposing at 174°. (Found: C, 66.95; H, 5.01; N, 8.34. Calc for $C_{18}H_{16}N_2SO_2$: C, 66.65; H, 4.97; N, 8.64%.)

Preparation and pyrolysis of the sodium salt of 2-*naphthaldehyde tosylhydrazone* were carried out as described above for the 1-isomer. The salt, prepared in the absence of light, decomposed at 120–300°. The piptopyrolyses, carried out under the same conditions as described for the 1-isomer, gave naphthalene, 2-methylnaphthalene, and cyclobuta[*de*]naphthalene (**21**) in yields similar to those reported under (ii) above, and identified by ^{1}H-NMR, ^{13}C-NMR, MS, IR and GC retention times.

Using a pyrolysis temperature of 250°/10^{-4} Torr and condensing the product on a KBr disk at 80 K, a strong absorption for 2-diazomethylnaphthalene was observed at 2040 cm^{-1}.

5-(1-*Naphthyl*)*tetrazole.* A mixture of 4.6 g (0.03 mol) of sublimed naphthalene-1-carbonitrile, 1.59 g (0.03 mol) NH_4Cl and 1.95 g (0.03 mol) NaN_3 in 50 ml dry and distilled dimethylformamide was stirred under N_2 at 120° for 12 days. After cooling, the solvent was removed *in vacuo*, and 100 ml of water was added to the residue. The precipitated naphthalene-1-carbonitrile was filtered, the filtrate was acidified with conc HCl, and the now precipitated tetrazole was filtered, dried at room temperature for 4 hr at 10^{-2} Torr, and then sublimed at 180°/10^{-3} Torr to give white crystals, 1.25 g (21%), m.p. 217–218° (dec). (Found: C, 67.04; H, 4.02; N, 28.40. Calc for $C_{11}H_8N_4$: C, 67.34; H, 4.11; N, 28.55%.)

^{1}H-NMR (DMSO-d_6, 400 MHz): δ 8.56 (d, J = 8 Hz, 1H), 8.18 (d, J = 8 Hz, 1H), 8.08 (d, J = 8 Hz, 1H), 7.99 (d, J = 7 Hz, 1H), 7.72–7.62 (m, 3H), 3.5 (very broad, 1H, exchangeable with D_2O); ^{13}C-NMR (DMSO-d_6, 100.6 MHz): δ 155.1 (m, broad), 133.3 (t), 131.3 (td), 129.9 (t), 128.6 (td), 128.3 (dd), 127.6 (dd), 126.6 (dd), 125.2 (d), 125.0 (dd), 121.4 (m); mass spectrum: *m/z* 196 (9), 168 (17), 153 (5), 143 (5), 140 (4), 127 (6), 92 (6), 91 (100), 77 (5), 64 (24), 63 (10), 51 (7), 39 (9), 31 (6).

Pyrolysis of 5-(1-*naphthyl*)*tetrazole.* 4 g of the tetrazole was piptopyrolyzed at 700°/10^{-3} − 5 × 10^{-1} Torr in the course of 4 hr. The pyrolyzate was dissolved in EtOH and analyzed and separated by gas chromatography (SE 30, 180°) to give naphthalene (6%), **21** (26%), and naphthalene-1-carbonitrile (61%). The identity of the products was verified by ^{1}H-NMR and mass spectrometry.

5-(9-*Phenanthryl*)*tetrazole* was prepared from phenanthrene-9-carbonitrile (2 g; 10 mmol), NH_4Cl (580 mg; 11 mmol) and NaN_3 (720 mg; 11 mmol) in 100 ml dry dimethylformamide as described for 5-(1-naphthyl)tetrazole above. 2.1 g (85%) colorless crystals were obtained, m.p. 244–246° (lit.[43] 243–244°; ^{1}H-NMR (DMSO-d_6, 400 MHz): δ 8.95 (d, J = 8 Hz, 1H), 8.89 (d, J = 8 Hz, 1H), 8.54 (d, J = 8 Hz, 1H), 8.42 (s, 1H), 8.10 (d, J = 7 Hz, 1H), 7.82–7.72 (m, 4H), *ca* 5 (very broad, NH); mass spectrum (field desorption): *m/z* 246 [$M^{+\cdot}$].

Pyrolysis of 5-(9-*phenanthryl*)*tetrazole.* The tetrazole was piptopyrolyzed at 400–700°/10^{-3}–10^{-1} Torr at a rate of 4 g per hr. The change in temp did not result in a significant change in product composition. The pyrolyzates were dissolved in CCl_4 and chromatographed on silicagel (Merck) on a 30 × 3 cm column. Elution with CCl_4 gave a product mixture which was examined by gas chromatography (see below). This procedure served to free the products of phenanthrene-9-carbonitrile, which remained on the column under these conditions and could be subsequently eluted with a 1:1 mixture of CCl_4 and $CHCl_3$. The CCl_4 eluate was concentrated, analysed, and preparatively separated by gas chromatography on a SE 52 column at 160°. In order to break the persistent aerosols emanating from the gas chromatograph, an electrostatic separator operating at 6–8 kV was constructed, and the products were then readily isolated in tubes cooled in liquid N_2. The products of the 600° pyrolysis were phenanthrene (4.7%), 9-methylphenanthrene (6.5%), 6*H*-cyclobuta[*jk*]-phenanthrene (7.0%), and 9*H*-cyclopenta[*def*]phenanthrene (1%). The yield of phenanthrene-9-carbonitrile from the column chromatography was 76%. Phenanthrene, 9-methylphenanthrene, 9*H*-cyclobuta[*def*]phenanthrene, and phenanthrene-9-carbonitrile were identified by comparison of ^{1}H-NMR and mass spectra with those of authentic samples. 6*H*-Cyclobuta[*jk*]phenanthrene had m.p. 88–90° (lit.[23] 87.5–88.5°); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.42–7.31 (m, 8H), 4.82 (s, 2H); ^{13}C-NMR ($CDCl_3$, 100.60 MHz): δ 145.0 (s), 141.1 (s), 139.1 (s), 137.4 (s), 130.2 (d), 129.9 (d), 129.5 (d), 126.2 (d), 125.4 (d), 124.0 (d), 122.7 (d), 119.5 (d), 119.2 (d), 117.6 (d), 46.6 (t, J = 143 Hz); mass spectrum: *m/z* 191 (11), 190 (71), 189 (100), 188 (15), 187 (17), 163 (9), 95 (10), 94 (27), 81 (12); mass spectrum, high resolution: found: 190.0782; IR (KBr): ν 3050 (w), 2970 (w), 2935 (w), 1440 (m), 1360 (m), 1270 (m), 1195 (m), 880 (s), 860 (m), 970 (m), 965 (s), 945 (s) cm^{-1}. (Calc for $^{12}C_{15}H_{10}$: 190.0782.)

Pyrolysis of the Na *salt of the tosylhydrazone of* *phenanthrene-9-carboxaldehyde.* The hydrazone had properties in agreement with those previously reported.[32] The Na salt, prepared as described for the naphthalene analogs above, was piptopyrolyzed at 650°/10^{-3}–10^{-1} Torr at the rate of 1.3 g/hr. The gas chromatogram and ^{1}H-NMR spectrum of the pyrolyzate showed a product composition similar to that reported from 5-(9-phenanthryl)tetrazole above, except that phenanthrene-9-carbonitrile was absent.

When the salt was decomposed *in vacuo* at 100–130°, and the vapors condensed on a KBr disk at − 196°, an absorption at 2040 cm^{-1} was observed and ascribed to 9-diazomethylphenanthrene. When the same vapor was led into a mass spectrometer, the parent peak was observed at *m/z* 218.

5-(9-Anthryl)tetrazole. A mixture of 4 g (20 mmol) anthracene-9-carbonitrile, 1.16 g (22 mmol) NH_4Cl, and 1.44 g (22 mmol) NaN_3 in 400 ml dimethylformamide was stirred under N_2 at 90° for 15 days. After removal of the solvent, addition of 100 ml 10 N KOH, filtering from the precipitated nitrile, acidifying the filtrate with conc HCl, extracting with ether, drying the extract over $MgSO_4$, evaporating, and recrystallizing from 50% aqueous EtOH, 580 mg of yellow crystals (12%), m.p. 268–270° (dec) was obtained. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ 8.95 (s, 1H), 8.25 (d, J = 8 Hz, 2H), 7.64–7.57 (m, 4H), 7.45 (d, J = 8 Hz, 2H), *ca* 3.4 (very broad, NH); ^{13}C-NMR (DMSO-d_6, 25.16 MHz): δ 152.6 (s), 130.5 (s), 130.4 (s), 130.3 (dt), 128.7 (dt), 127.6 (dd), 125.8 (ddd), 124.4 (dd), 118.1 (s); mass spectrum: *m/z* 247 (10), 246 (65), 219 (19), 218 (100), 204 (10), 203 (31), 191 (10), 190 (36), 189 (19), 187 (13), 176 (8), 165 (5), 164 (6), 163 (7), 109 (15), 102 (9), 96 (6), 95 (9), 94 (6), 88 (9), 82 (10), 63 (5). (Found: C, 73.18; H, 3.90; N, 22.57. Calc for $C_{15}H_{10}N_4$: C, 73.16; H, 4.10; N, 22.75%.)

Pyrolysis of 5-(9-anthryl)tetrazole. A total of 10 g of the tetrazole was piptopyrolyzed at 600°/10^{-3}–10^{-1} Torr. The product mixture was filtered through a short silicagel column and separated by gas chromatography (SE 52, 240°) to give anthracene (9%), 9-methylanthracene (11%), 1*H*-cyclobuta[*de*]anthracene (11%), and anthracene-9-carbonitrile (58%). 1*H*-cyclobuta[*de*]anthrene had ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.5–7.5 (m, 8H), 4.64 (s, 2H); *m/z* 190 [$M^{+\cdot}$].

Pyrolysis of 5-diazo-10,11-dihydrodibenzo[ad]*cycloheptene.* The diazo-compound[27] (500 mg) was pyrolyzed at 400°, being sublimed into the horizontal pyrolysis tube at 65° in the course of 24 hr. The oven pressure was 10^{-2} Torr. The product (365.4 mg; 83.7%), collected in a liquid N_2 trap, was taken up in $CHCl_3$ and subjected to gas chromatography (SE 30; 220°). Three products were isolated: **40**, **41** and **44**, with retention times 3.9, 5.1 and 6.4 min, respectively. **41** and **44** had retention times, ^{1}H-NMR and mass spectra identical with those of authentic samples prepared according to the literature.[44,45] **41**: ^{1}H-NMR (CCl_4): δ 7.07 (m, 8H), 6.93 (s, 2H), 3.60 (s, 2H). **44**: ^{1}H-NMR (CCl_4): δ 6.9–7.3 (m, 6H), 3.82 (s, 2H), 3.12 (s, 4H). **40** was isolated as a colorless oil which crystallized at room temp: m.p. 46–48°; ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 6.9–7.4 (m, 8H), 4.92 (d, J = 4 Hz, 1H (H4b)), 4.17 (quintet, 1H (H9a)), 2.8–3.5 (m, 2H (H9, 9′)). Spin decoupling of the doublet at δ 4.92 changed the multiplet at δ 4.17 into a 1:1:1:1 quartet with coupling constants $J_{H9a,H9'} = 4$ Hz and $J_{H9a,H9} = 8.4$ Hz. Irradiation of the center of the quintuplet at δ 4.17 changed the doublet at δ 4.92 into a singlet; at the same time the multiplet at δ 2.8–3.4 became an AB-system (δ 2.75 (H9) and 3.43 (H9′)) with $J_{H9,H9'} = 17.2$ Hz. UV spectrum (EtOH): $\lambda_{max}(\varepsilon)$ 274.9 (2400), 267.8 (2460), 262.3 (1600) nm; mass spectrum: *m/z* 192 (100), 191 (72), 189 (26), 165 (24), 139 (47), 115 (8); mass spectrum, high resolution, *m/z* 192.0939 (calc for $^{12}C_{15}H_{12}$: 192.0939), 192.0895 (calc for $^{12}C_{14}{}^{13}CH_{11}$: 192.0894), 191.0860 (calc for $^{12}C_{15}H_{11}$ ($[M-1]^{+\cdot}$): 191.0861).

The yields (by GC) and reaction conditions for further pyrolyses are given in Table 2. A plot of the logarithm of the ratio of yields, **40** + **41**/**44** against T^{-1} gave an activation energy difference, $\Delta E_a = 5.2 \pm 0.3$ kcal/mol.

Similar pyrolyses of **40** result in rearrangement to **41**. The data are given in Table 2. No other products were detectable by gas chromatography.

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