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The Azulene-to-Naphthalene Rearrangement Revisited: a DFT Study of Intramolecular and Radical-Promoted Mechanisms

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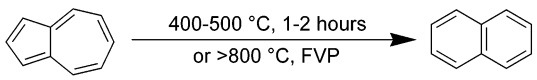
Abstract: Intramolecular and radical-promoted mechanisms for the rearrangement of azulene to naphthalene are assessed with the aid of density functional calculations. All intramolecular mechanisms have very high activation energies (≥350 kJ mol^{-1} from azulene) and so can only be competitive at temperatures above 1000 °C. Two radical-promoted mechanisms, the methylene walk and spiran pathways, dominate the reaction below this temperature. The activation energy for an orbital symmetry-allowed mechanism via a bicyclobutane intermediate is 382 kJ mol^{-1}. The norcaradiene−vinylidene mechanism that has been proposed in order to explain the formation of small amounts of 1-phenyl-1-buten-3-ynes from flash thermolysis of azulene has an activation energy of 360 kJ mol^{-1}; subtle features of the B3LYP/6-31G(d) energy surface for this mechanism are discussed. All intermediates and transition states on the spiran and methylene walk radical-promoted pathways have been located at the B3LYP/6-31G(d) level. Interconversion of all *n*-*H*-azulyl radicals via hydrogen shifts was also examined, and hydrogen shifts around the five-membered ring are competitive with the mechanisms leading to rearrangement to naphthalene, but those around the seven-membered ring are not. Conversion of a tricyclic radical to the 9-*H*-naphthyl radical is the rate-limiting transition state on the spiran pathway, and lies 164.0 kJ mol^{-1} above that of the 1-*H*-azulyl radical. The transition state for the degenerate hydrogen shift between the 9-*H*-azulyl and 10-*H*-azulyl radicals is 7.4 kJ mol^{-1} lower. Partial equilibration of the intermediates in the spiran pathway via this shift may therefore occur, and this can account for the surprising formation of 1-methylnaphthalene from 2-methylazulene. The rate-limiting transition state for the methylene walk pathway involves the concerted transfer of a methylene group from one ring to the other and lies 182.3 kJ mol^{-1} above that of the 1-*H*-azulyl radical. It is shown that rearrangement via a combination of 31% methylene walk and 69% spiran pathways can account semiquantitatively for all the products from 1-^{13}C-azulene, 9-^{13}C-azulene, and 4,7-$^{13}C_2$-azulene, in addition to accounting for the products from methylazulenes, and the formation of naphthalene-d_0 and -d_2 from azulene-4-*d*. It is also pointed out that a small extension to the spiran pathway could provide an alternative explanation for the formation of 1-phenyl-1-buten-3-ynes.

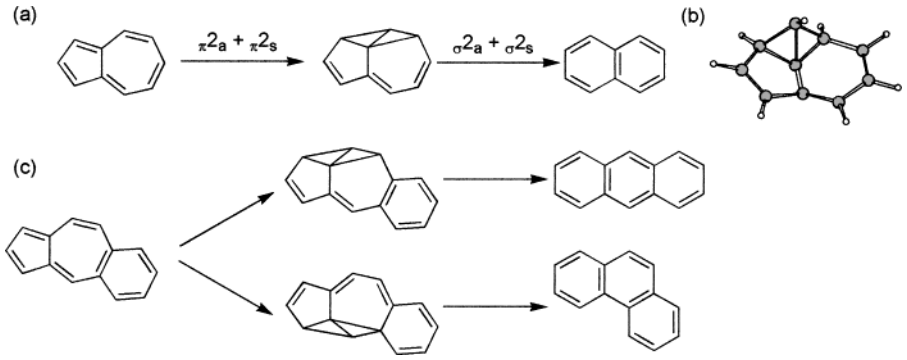
The thermal rearrangement of azulene **1** to naphthalene **2**, first reported in 1947,[1] is an example of a rare type of reaction: the conversion of one aromatic compound to another. The reaction can be carried out by static thermolysis above 400 °C or by flash vacuum thermolysis above 800 °C. While the reaction is preparatively useless, it poses very intriguing mechanistic questions and has been extensively investigated from this point of view.[2−7] Mechanisms that result in the conversion of one aromatic compound to another have gained fresh interest since the advent of fullerene chemistry (e.g., the Stone−Wales rearrangement).[8] We showed many years ago[9] that the conversion of bifluorenylidene to dibenz[*g*,*p*]chrysene, which is essentially a Stone−Wales rearrangement, was promoted by radicals and probably involved mechanisms closely related to those discussed in this paper. More recently, other groups[10,11] have considered hydrogen atom or other "elemental catalysis" mechanisms for the Stone−Wales rearrangement.



A variety of intramolecular and radical-promoted mechanisms have been proposed for the azulene-to-naphthalene rearrangement, and it has been asserted that one mechanism cannot

(1) Heilbronner, E.; Plattner, P. A.; Wieland, K. *Experientia* **1947**, *3*, 70−71.
(2) Scott, L. T. *Acc. Chem. Res.* **1982**, *15*, 52−58.
(3) Alder, R. W.; Whittaker, G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 714−723.
(4) Alder, R. W.; Wilshire, C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1464−1468.
(5) Alder, R. W.; Whiteside, R. W.; Whittaker, G.; Wilshire, C. *J. Am. Chem. Soc.* **1979**, *101*, 629−632.
(6) Becker, J.; Wentrup, C.; Katz, E.; Zeller, K. P. *J. Am. Chem. Soc.* **1980**, *102*, 5110−5112.
(7) Zeller, K. P.; Wentrup, C. *Z. Naturforsch., B*: *Anorg. Chem., Org. Chem.* **1981**, *36B*, 852−857.
(8) Fowler, P. W.; Manolopoulos, D. E.; Ryan, R. P. *Carbon* **1992**, *30*, 1235−1250.
(9) Alder, R. W.; Whittaker, G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 712−713.
(10) Eggen, B. R.; Heggie, M. I.; Jungnickel, G.; Latham, C. D.; Jones, R.; Briddon, P. R. *Science* **1996**, *272*, 87−89.
(11) Slanina, Z.; Zhao, X.; Uhlik, F.; Ozawa, M.; Osawa, E. *J. Organomet. Chem.* **2000**, *599*, 57−61.

Scheme 1. (a) Bicyclobutane Mechanism, (b) Structure of the Bicyclobutane, and (c) Alternative Products from Benz[*f*]azulene. The Upper Pathway Should Be Preferred, but Phenanthrene Is the Only Product Observed



explain all the data.[2] Scott[12] has pointed out that the concurrent operation of several mechanisms is quite likely at the high temperatures involved. In this paper, we set out to reassess all mechanisms that have received serious consideration with the aid of density functional theoretical methods.

Calculational Methods

All calculations were performed with Gaussian 98[13] using Becke's three-parameter exchange functional[14] with the correlation functional of Lee, Yang, and Parr (B3LYP).[15] All species were characterized by full geometry optimization followed by analytical frequency calculations using the B3LYP method with the 6-31G(d) basis set. For singlet species, restricted DFT methods were generally used, while unrestricted methods were used for all radicals and triplets. However, for several of the singlet species, unrestricted calculations were also carried out with mixing of the restricted orbitals so as to check for the existence of lower-lying open-shell solutions. Key transition states and intermediates were also optimized using HF/6-31G(d) and BP86/6-31G(d) and/or subjected to B3LYP, BP86, and MP2 single point energy calculations using the 6-311+G(3df,2p) basis set at the B3LYP/6-31G(d) geometry. Differences between these methods are noted later, but in general were not significant, although MP2 calculations produce poor results for open-shell species due to spin contamination.

Throughout this paper, the relative energies reported are differences in electronic energies; zero point corrections are given in the Supporting Information.

Results and Discussion

Naphthalene is 143 kJ mol^{-1} more stable than azulene and is the thermodynamic sink for all $C_{10}H_8$ hydrocarbons, and a variety of routes to such a stable product might be expected. Much effort has been put into finding simple intramolecular mechanisms that can explain the experimental results, and we examine the three principal proposals first. These are (1) a mechanism via orbital symmetry-allowed formation and reopening of a bicyclobutane; (2) a mechanism involving simple cleavage of the 9,10-bond in azulene, originally proposed by Scott;[12] and (3) the norcaradiene−vinylidene mechanism, originally proposed by Becker, Wentrup, Katz, and Zeller.[6]

Table 1. Bicyclobutane Mechanism[a]

azulene	TS	bicyclobutane	TS	naphthalene
0.0	382.4	265.2	375.9	−143.3

[a] B3LYP/6-31G(d) energies relative to azulene (kJ mol^{-1}).

We will then consider three radical-promoted pathways, again examining all the intermediates and transition states: (1) a simple mechanism involving hydrogen abstraction from the 4-position of azulene, which is the radical-promoted counterpart of Scott's 9,10-bond cleavage mechanism; (2) the methylene walk mechanism, first proposed by Alder et al.,[3] which involves radical addition to the seven-membered ring of azulene, followed by a sequence of homoallyl−cyclopropylcarbinyl radical rearrangements to move one carbon atom to the five-membered ring to create the naphthalene skeleton; and (3) the spiran pathway, also first proposed by Alder et al.,[4,5] which involves not only radical addition to the five-membered ring of azulene and another sequence of homoallyl−cyclopropylcarbinyl radical rearrangements but also a degenerate 9.10-hydrogen shift.

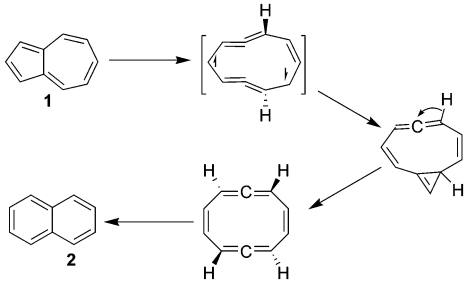
The methylene walk and spiran radical-promoted pathways may appear complex and even chaotic, but we will show that they can account well for product distributions in every case examined without predicting the formation of products that are not observed.

Intramolecular Mechanisms

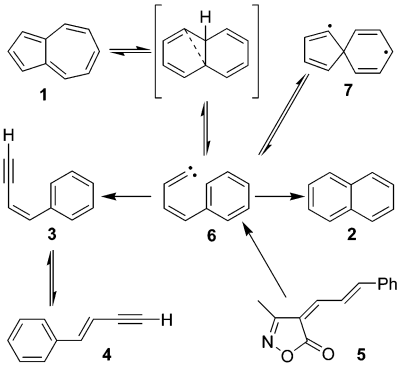
Bicyclobutane Mechanism. It was the seductive simplicity of the orbital symmetry-allowed mechanism via a bicyclobutane, Scheme 1a, that first attracted us to study the azulene/naphthalene rearrangement. Transition states for the formation of the bicyclobutane and for its subsequent rearrangement to naphthalene were readily located using AM1 semiempirical methods and were subsequently optimized at the B3LYP/6-31G(d) level (Table 1). The higher of the two transition states was found to have an energy of 360.5 kJ mol^{-1}above that of azulene at the MP2/6-311+G(3df,2p) level. The structure of the bicyclobutane intermediate is shown in Scheme 1b; note the "inverted" geometry at the two bridgehead carbon atoms. In view of the extremely high activation energy, this mechanism appears unlikely to contribute significantly even at the highest temperatures studied by flash thermolysis (1180 °C). Indeed, the rearrangement of benz[*f*]azulene to phenanthrene to the exclusion of anthracene under static thermolysis conditions is

(12) Scott, L. T.; Kirms, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 5875−5879.
(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
(14) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(15) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

Scheme 2. 9,10-Bond Cleavage Mechanism



Scheme 3. Norcaradiene−Vinylidene Mechanism



evidence against this process,[3] since it would surely be expected that the favored bicyclobutane intermediate would be the one which did not disrupt the aromaticity of the benzenoid ring, and this intermediate would yield anthracene (Scheme 1(c)).

9,10-Bond Cleavage Mechanism. Scott[12] proposed a mechanism involving simple cleavage of the 9,10-bond in azulene, followed by a hydrogen shift in the resulting biradical, leading to a diallene that can exist in *meso* and *dl* forms (the latter is shown in Scheme 2). The electrocyclic ring closure of each of these to naphthalene was discussed by Woodward and Hoffmann.[16] B3LYP/6-31G(d) calculations suggest that breaking the transannular C−C bond leads via a C_2 transition state (480 kJ mol^{-1} above azulene) to an allene−cyclopropene (see Scheme 2) rather than a diradical (a search for diradicals and transition states leading to them was conducted using unrestricted DFT, but none could be located). The allene−cyclopropene can undergo a 1,2-hydrogen shift to the *dl*-diallene, but the transition state for this lies >600 kJ mol^{-1} above that of azulene. This mechanism can therefore probably be discounted, but a related radical-promoted process will be discussed later.

Norcaradiene−Vinylidene Mechanism. The intramolecular mechanism that has received the most convincing experimental support is the norcaradiene−vinylidene mechanism, Scheme 3.

Flash vacuum thermolysis of azulene at 1100 °C (10^{-2} Torr) yields small amounts (up to 3%) of **3** and **4** in addition to naphthalene.[6] Becker, Wentrup, Katz, and Zeller also showed that flash thermolysis of 4-cinnamylideneisoxazol-5-(4H)-one **5** at 680−750 °C (10^{-1}−10^{-3} Torr) produced **3**, **4**, naphthalene and azulene in the ratio 27:15:36:1. They therefore proposed the norcaradiene−vinylidene mechanism, shown in Scheme 3. Dewar and Merz[17] proposed a variation on this mechanism on the basis of MNDO semiempirical calculations; they asserted that the vinylidene **6** played no part in the azulene/naphthalene rearrangement but provided no experimental support for their version. We first revisited the norcaradiene−vinylidene mechanism and the Dewar/Merz variant using the AM1 semiempirical method, and then applied B3LYP/6-31G(d) calculations to all the transition states and intermediates we could locate. It should be noted first of all that we found the potential energy surface in the vicinity of the *cis*-vinylidene **6** to be rather flat, which makes certain elements of its interpretation rather complex. However, **6** is clearly shown to exist as a minimum on the potential energy surface, and it rearranges via a low barrier to *cis*-1-phenyl-1-buten-3-yne **3** as expected. The remaining behavior of **6** is usefully viewed as arising from rotation around the aryl−vinyl bond. A small rotation from the ground state for **6** leads to a transition state for insertion into the *ortho* C−H bond to give naphthalene, another low barrier process (see Figure 1 and Scheme 4). Repeated attempts to locate an energy minimum resembling the proposed norcaradiene intermediate failed, but further rotation around the aryl−vinyl bond leads to a spiran structure **7** (see Schemes 3 and 4) arising from attack of the vinylidene at the *ipso*-carbon of the benzene ring. This is a pure biradical, with essentially equivalent energies for singlet and triplet states. The singlet state of **7** can subsequently rearrange to azulene, but the activation energies both for formation of biradical **7** and for its rearrangement to azulene are so high that the amount of azulene that could be formed in competition with rearrangement to naphthalene and *cis*- and *trans*-1-phenyl-1-buten-3-yne would be quite negligible.

However, there is another low-energy pathway from **6** to azulene, through a closed-shell singlet transition state (see Scheme 4c) that resembles the norcaradiene, but with the methylenecyclopropane in a stretched and highly distorted form. The vinylidene carbon is clearly bonded with one *ortho*-carbon (distance 1.618 Å) but only partially to the *ipso*-carbon (shown by the dotted bond in Scheme 3, distance 2.051 Å). This transition state can easily be shown to lead to azulene on one side, but its connectivity on the other side is less clear. Upon starting from this transition state, and carrying out a set of constrained optimizations in which the $C_{ipso}-C_{ortho}-C_{vinylidene}$ angle is progressively increased, one goes smoothly down to the vinylidene; the reverse of this path is the desired low-energy route from **6** to azulene, with a barrier of 47.7 kJ/mol. However, a second set of constrained optimizations, in which the $C_{ortho}-C_{vinylidene}$ bond length was varied, led instead directly to naphthalene, through structures resembling the insertion TS mentioned previously. Geometry optimization starting from slightly displaced geometries close to the TS also leads directly to naphthalene. Attempts to carry out an intrinsic reaction coordinate (IRC) calculation starting at the same TS encountered severe convergence problems, due to the flat nature of the surface in the region of this TS. One possible interpretation of these calculations is that the surface has an unconventional topology, such that the new transition state does not link directly to a minimum but to the TS for rearrangement of the vinylidene to naphthalene (see Figure 1). A number of such cases are described in the literature, where one transition state connects to a second transition state via a valley−ridge inflection point.[18] These considerations should not obscure the point of major chemical significance: as the whole potential energy surface is

(16) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.
(17) Dewar, M. J. S.; Merz, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 5142−5145.
(18) Zhou, C.; Birney, D. M. *Org. Lett.* **2002**, *4*, 3279−3282.

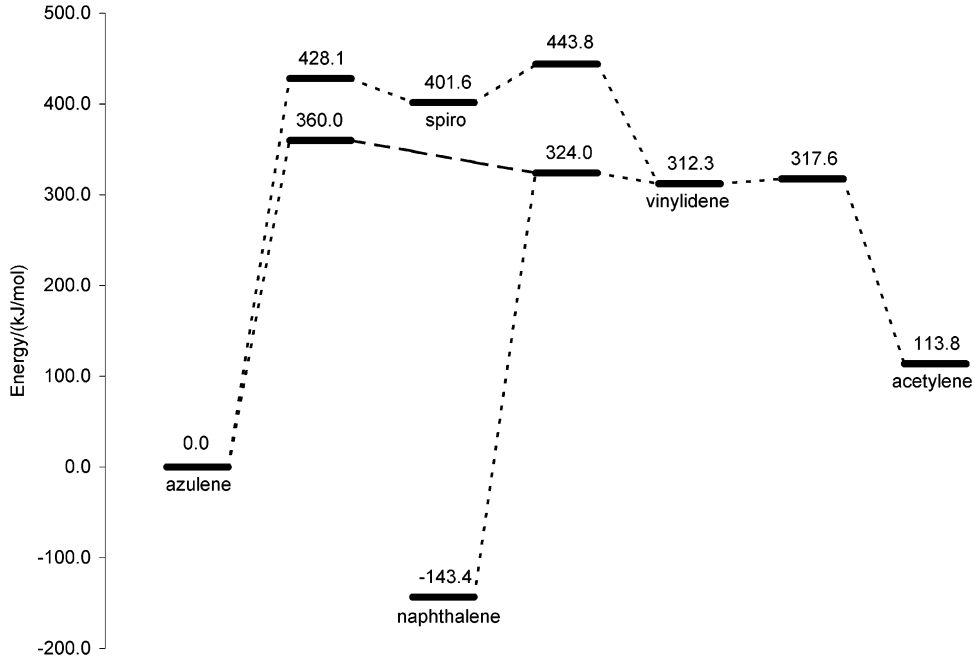
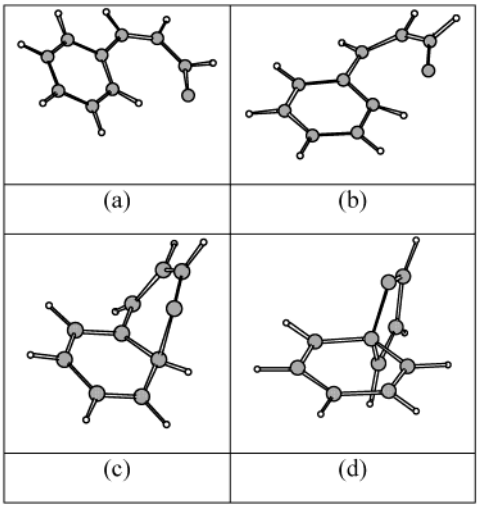


Figure 1. Vinylidine−Norcaradiene mechanism (B3LYP/6-31G(d)).

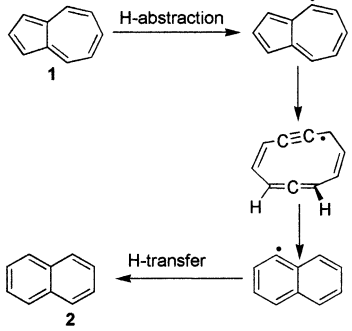
Scheme 4. (a) *cis*-Vinylidene Intermediate **6** (Aryl−Vinyl Torsion Angle −12.9°), (b) Transition State for C−H Insertion to Form Naphthalene (Torsion Angle −26.1°), (c) Transition State for the Rearrangement to Azulene (Torsion Angle −60.7°), and (d) Spiran Biradical **7** (Torsion Angle −90°)



quite flat, *cis*-vinylidene can rearrange by low-energy pathways to give any of three products: alkyne **3**, azulene **1**, and naphthalene **2**.

The overall activation energy for rearrangement of azulene to naphthalene by this pathway is 360 kJ mol^{-1} at the B3LYP/6-31G(d) level. Single point energies at the B3LYP/6-31G(d) transition state geometry were calculated with a larger basis set and using MP2: E(B3LYP/6-311+G(3df,2p)) = 351 kJ mol^{-1}, E(MP2/6-311+G(3df,2p)) = 333 kJ mol^{-1}. If the lowest of these estimates for E_a is assumed, this mechanism could only be competitive in flash thermolysis at temperatures above 1100 °C, assuming a contact time of a few seconds and a pre-exponential factor of 10^{12} s^{-1}. A possible alternative source for the 1-phenyl-1-buten-3-ynes via radicals generated in the spiran pathway will be discussed later.

Scheme 5. A Simple Radical-Promoted Mechanism



Summary - Intramolecular Mechanisms. All the intramolecular mechanisms that have been suggested have extremely high activation energies (approximately 350 kJ mol^{-1} or higher) according to the calculations. That should occasion no surprise, since the formation of any intermediate involves loss of the aromatic stabilization of azulene and also the introduction of extreme levels of strain in σ-bonds, unless a simple σ-bond cleavage occurs. The bicyclobutane intermediate and the norcaradiene-like transition state both suffer from very high σ-bond strain. It seems certain that no unimolecular mechanism can contribute significantly to the rearrangements observed in static thermolyses at 400−500 °C. We will argue later that the contribution of unimolecular mechanisms may be small even under high-temperature flash thermolysis conditions.

Radical-Promoted Mechanisms

A Simple Radical-Promoted Mechanism. The mechanism in Scheme 5 is probably the simplest radical-promoted pathway from azulene to naphthalene. It is essentially a radical analogue of the 9,10-bond cleavage mechanism described previously and might, with appropriate isotope effects, account for the deuterium scrambling observed by Becker et al.[6] discussed later. The calculated energetics (Table 2) illustrate the advantages and

Table 2. Simple Radical Mechanism[a]

4-azulenyl	TS	monocyclic radical intermediate	TS	1-naphthalenyl
0.0	160.3	157.7	159.6	−123.9

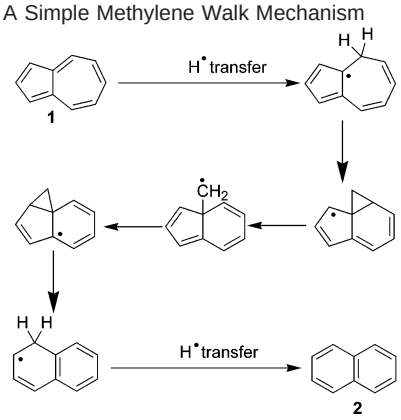
[a] B3LYP/6-31G(d) energies relative to 4-azulene (kJ mol^{-1}).

disadvantages of radical-promoted processes nicely. Cleavage of the 9,10-bond in the 4-azulenyl radical is (relatively) much more favorable that in azulene itself, since a new π-bond is being created. The disadvantage is that initial bimolecular abstraction of a hydrogen from a strong C(sp^2)−H bond is required. In the (more complex) radical pathways discussed later, initiation is provided by transfer of a hydrogen atom (or other radical) *to* azulene, producing a more stable delocalized radical. The simple mechanism shown in Scheme 5 fails to account for any of the detailed labeling studies described in the following.

Evidence for the Involvement of Radicals. In an important experiment, Becker, Wentrup, Katz, and Zeller[6] showed that thermolysis of 4-^{2}H-azulene in an ampule at 400 ± 5 °C gives about 13% naphthalene-d_0, 13% naphthalene-d_2, and the remainder being naphthalene-d_1. Thus, a minimum 26% of the reaction is intermolecular under these conditions. If the intermolecular mechanisms responsible for the deuterium transfer are the methylene walk and spiran pathways discussed later, then the proportion of the reaction that is intermolecular can be significantly higher. Remarkably, these authors found an almost identical degree of deuterium scrambling (12% naphthalene-d_0 and 12% naphthalene-d_2) under flash thermolysis conditions at 1180 °C. Thus, even under conditions that favor intramolecular mechanisms, intermolecular mechanisms are probably very important. We return to this question at the end of the paper.

Several other lines of evidence point to significant involvement of intermolecular reactions in the rearrangement, at least under static thermolysis conditions. Thus, (a) radical initiators such as azomethane and di-*tert*-butyl peroxide promote the rearrangement,[3] and (b) an induction period can be observed in the rearrangement of carefully purified azulene in sealed ampules.[5] Heilbronner and Kallen[19,20] made a detailed kinetic study of the rearrangement and showed that it obeys first-order kinetics (data extrapolated to infinite dilution), and this led Heilbronner to conclude that "the reaction is essentially homogeneous and intramolecular..." However, Scott[21] re-examined the kinetic data in the light of our own work[3−5] and concluded that they are equally compatible with a radical chain mechanism, with appropriate initiation steps. Recently, Keller, Beckhaus, and Rüchardt[22] have shown that transfer hydrogenation of azulene at 340−375 °C using hydrogen donors such as 9,10-dihydroanthracene can promote the rearrangement with the formation of both naphthalene and tetralin. They proposed a radical mechanism involving many of the intermediates in the methylene walk and spiran pathways described later but suggested that this was not a chain reaction under their transfer hydrogenation conditions.

Scheme 6. A Simple Methylene Walk Mechanism



Two related intermolecular pathways have received substantial experimental support. Thermolyses of a set of methyl- and dimethylazulenes, especially those with substituents in the seven-membered ring, led to the proposal of a methylene walk pathway, shown at its simplest in Scheme 6, which transposes one carbon with its substituent from the seven- to the five-membered ring.[4] This mechanism consists of a series of homoallyl−cyclopropylcarbinyl radical rearrangements, and it explains the product distribution very satisfactorily in most cases when account is taken of all the possibilities for (a) starting the rearrangement by radical addition to any of the CH-carbons in the seven-membered ring and (b) the addition and/or loss of methyl radicals in the case of methyl-substituted azulenes (N.B. for simplicity, we only discuss hydrogen atom additions throughout the remainder of this paper).

However, one early observation[20] poses significant extra problems: 2-methylazulene yields appreciable amounts of 1-methylnaphthalene in addition to the 2-isomer that most mechanisms would predict. Neither the methylene walk nor any of the intramolecular mechanisms discussed previously can account for the formation of the 1-isomer. The 1-methyl-/2-methylnaphthalene ratio is typically about 1:2.4. This feature of the rearrangement was shown[4,5] (a) to be general for a variety of 2-substituents and (b) to involve migration of C-2 of the azulene, not just the substituent, as shown by study of 2-^{13}C-methyl-^{13}C-azulene. Although rearrangements of 1-substituted azulenes to 2-substituted azulenes are known,[23] they cannot account in themselves for the formation of the 1-substituted naphthalene product. These results led to the proposal of a second radical-promoted mechanism, called the spiran pathway.[4,5] This pathway again consists mainly of a series of homoallyl−cyclopropylcarbinyl radical rearrangements but involves radical adducts to the 9-position of azulene, which can ring close and then ring open to a spiro-radical. This spiro-radical can reclose to a cyclopropylcarbinyl radical in four ways, permitting some scrambling of labels. This is not enough, in itself, to explain the 2-methylazulene to 1-methylnaphthalene rearrangement, and it was necessary to postulate a hydrogen shift between the bridgehead carbons in the radical adduct to the 9-position of azulene. Scheme 7 shows the simplest route from 2-methylazulene to 1-methylnaphthalene. The hydrogen shift step is without any close precedent, although it was pointed out that there was a formal similarity with hydrogen shifts in cyclopentadienes.

(19) Heilbronner, E. *Non-benzenoid Aromatic Compounds*; Wiley-Interscience: New York, 1959.
(20) Kallen, H. J. Ph.D. Thesis No. 2856, Eidgenossischen Technischen Hochschule, Zurich, 1958.
(21) Scott, L. T. *J. Org. Chem.* **1984**, *49*, 3021−3022.
(22) Keller, F.; Beckhaus, H. D.; Ruchardt, C. *Liebigs Ann.-Recl.* **1997**, 2055−2063.
(23) Wetzel, A.; Zeller, K. P. *Z. Naturforsch., B* **1987**, *42*, 903−906.

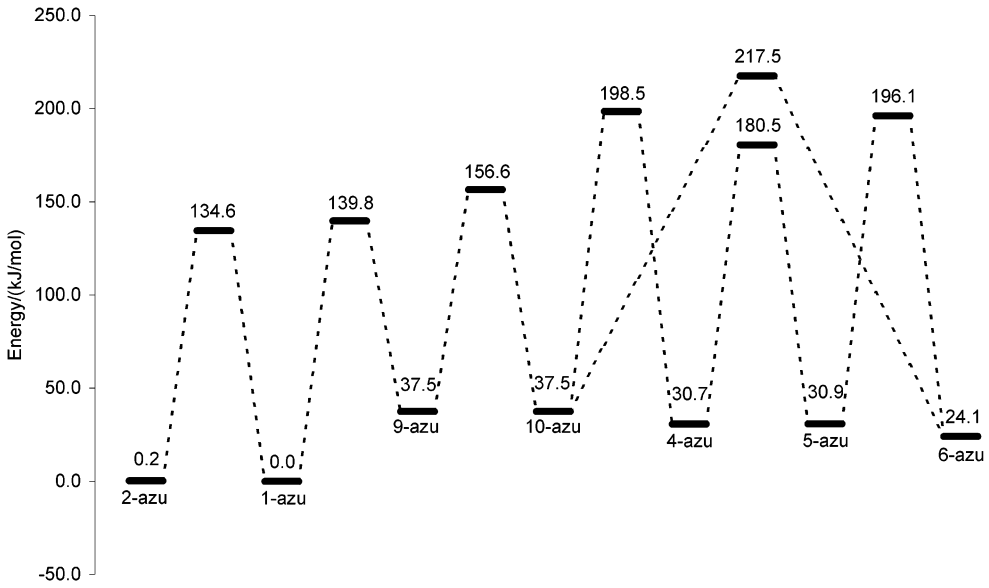
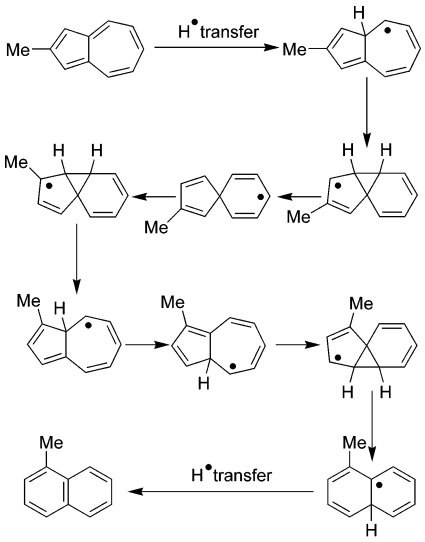
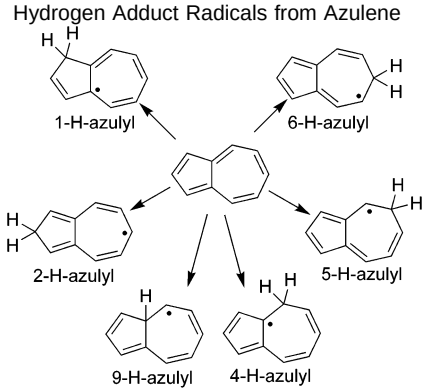


Figure 2. 1,*n*-shifts in $C_{10}H_9$: B3LYP/6-31G(d) energies in kJ mol^{-1} relative to the 1-*H*-azulyl radical.

Scheme 7. A Route to 1-Methylnaphthalene from 2-Methylazulene



Scheme 8. Hydrogen Adduct Radicals from Azulene



A combination of the methylene walk and spiran pathways can explain essentially all the results for the rearrangement of methyl-substituted azulenes without predicting products that are not found, but we have always been conscious that this proposal poses problems that must be taken seriously. In particular, the concurrent operation of two mechanisms is always hard to accept in the light of Occam's razor. So it is desirable to establish whether the two pathways can have comparable activation energies, and it was with this in mind that the current theoretical study was initiated. We also wished to establish whether the crucial 9,10-hydrogen shift was really a viable possibility.

Hydrogen Adducts and Hydrogen Shifts. Hydrogen atom transfer to azulene can produce six different $C_{10}H_9$ radicals (see Scheme 8). Systematic nomenclature for these is cumbersome, and so we refer to these as adduct radicals as 1-*H*-azulyl, and so forth.

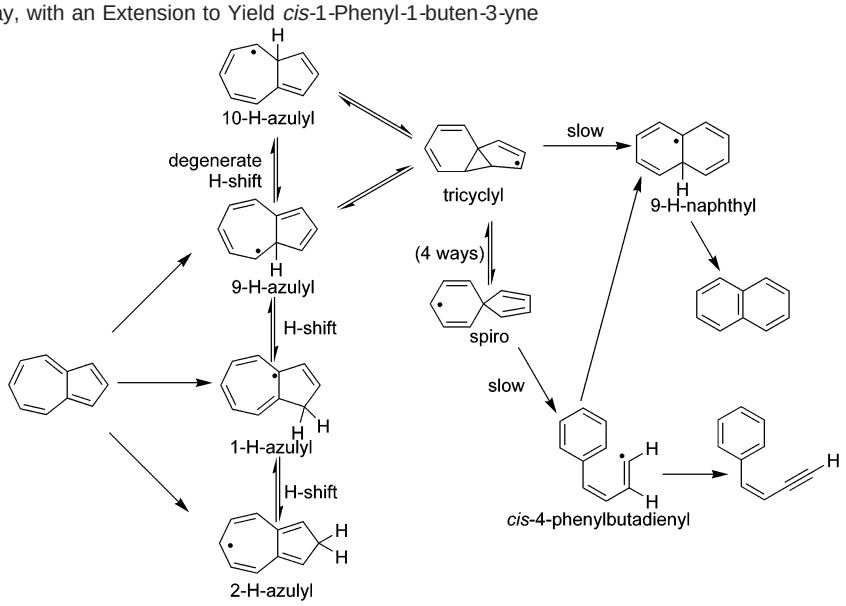
We examined the relative stability of these and the barriers to the hydrogen shifts that could interconvert them (see Figure 2). Keller, Beckhaus, and Rüchardt[22] have reported calculation of the heats of formation of the radical adducts by the AM1 semiempirical method, and we find that the B3LYP/6-31G(d) order of stability is rather similar. The 1-*H*-azulyl and 2-*H*-azulyl radicals are of almost equal stability, with the 4-, 5-, and 6-*H*-azulyl radicals lying 24−31 kJ mol^{-1} higher. This agrees qualitatively with the observation that radical substitutions in azulene generally occur in the five-membered ring. Waters and Tilney-Bassett[24] found that attack of a benzyl radical gives mainly 1- and 2-benzylazulene, while we reported[3] that methylation of azulene by di-*t*-butylperoxide at 165 °C gave all five monomethylazulenes in the following relative amounts: 1-, 35.9; 2-, 51.1; 4-, 7.7; 5-, 2.2; 6-, 3.2%. These ratios will be determined by the relative rates of radical attack rather than the thermodynamic stability of the radicals formed, but there is at least qualitative agreement with calculated values for the latter.

In addition to the 1,2-shifts, one example of a transannular (1,5-type) hydrogen shift (from the 6- to the 10-*H*-azulyl radical) is included in Figure 2, but this proved to have a high barrier. Although we have not examined other possible 1,5-shifts, it seems unlikely that these will be important.

We suggested earlier that hydrogen shifts around the five-membered ring in the *n*-*H*-azulyl radicals could resemble the well-known[25] 1,5-hydrogen shift in cyclopentadiene. The B3LYP/

(24) Waters, W. A.; Tilney-Bassett, J. F. *J. Chem. Soc* **1959**, 3123.

Scheme 9. Spiran Pathway, with an Extension to Yield *cis*-1-Phenyl-1-buten-3-yne



6-31G(d) calculated ΔH values for the latter (112.5 kJ mol^{-1}) are indeed similar and in good agreement with experiment (101.7 kJ mol^{-1}). Okajima and Imafuku[26] have recently used B3LYP methods to study 1,5- and 1,7-shifts in cyclopentadiene and cycloheptatriene; our results are in satisfactory agreement with theirs for cyclopentadiene 1,5-shifts. However, while our calculated barriers for 1,2-shifts around the seven-membered ring in the *n*-*H*-azulyl radicals are considerably lower than that reported[26] for a 1,7-shift in cycloheptatriene (288.0 kJ mol^{-1} at B3LYP/6-311G(d,p)), the barrier we calculate for the 6- to 10-*H*-azulyl 1,5-type shift is significantly higher than that reported for cycloheptatriene (166.8 kJ mol^{-1} at B3LYP/6-311G-(d,p)).

The spiran pathway starts from the 9-*H*-azulyl radical, while the methylene walk pathway begins from the 4-, 5-, or 6-*H*-azulyl radicals. Transition states for hydrogen shifts around the five-membered ring are calculated to be lower in energy than those for the rate-limiting steps in both the spiran and methylene walk pathways (164.0 and 182.3 kJ mol^{-1} relative to the 1-*H*-azulyl radical, respectively). On the other hand, transition states for 1,7-hydrogen shifts around the seven-membered ring are calculated to be at significantly higher energy. This suggests that the readily formed 1- and 2-*H*-azulyl radicals could enter the spiran pathway by first undergoing 1,5-hydrogen shifts to generate the 9-*H*-azulyl radical (Rüchardt et al.[22] assumed that this species was only formed by direct hydrogen transfer). The 4-, 5-, and 6-*H*-azulyl radicals lead into the methylene walk pathway, and leakage from the 9-*H*-azulyl radical into this pathway seems unlikely to be important. We return to this question of competition between these pathways later.

Spiran Pathway. The spiran pathway was introduced in Scheme 7, but Scheme 9 shows a more complete version with the names we will use for all the intermediates. The energies of intermediates and transition states on this pathway are shown in Figure 3.

Calculated structures for the several critical intermediates and transition states are shown in Scheme 10. The tricyclyl radical can open in three ways. Ring opening to the more stable 9-*H*-naphthyl radical has a higher barrier than that to the spiro-radical, in line with known stereoelectronic effects on these reactions (see the following for a fuller discussion).[27−29] Ring opening of the tricyclic radical to the 9-*H*-azulyl radical is found to have virtually no activation energy by B3LYP/6-31G(d) calculation. The tricyclyl radical actually becomes higher in energy than the tricyclyl/9-*H*-azulyl transition state (see Scheme 10b) after zero point energies are added; furthermore the tricyclyl radical is not a stationary point in BP86 calculations). This process can be viewed as a norcaradiene/cycloheptatriene rearrangement, but this is also true of several steps in the methylene walk mechanism which show "normal" barriers. We can therefore offer no simple explanation of the low barrier in this case. Nevertheless, according to the B3LYP calculations, the 9-*H*-azulyl radical would cycle to the spiro-radical (which can reclose in four ways) many times before opening to the 9-*H*-naphthyl radical.

The transition state for the degenerate hydrogen shift between the 9-*H*- and 10-*H*-azulyl radicals is calculated to lie 7.4 kJ mol^{-1} below that for the ring opening of the tricyclic radical to the 9-*H*-naphthyl radical. Taken at its face value, one would assume this would indicate that the 9,10-hydrogen shift would compete with the rate-limiting ring opening, but there would not be a complete scrambling of intermediates before the irreversible formation of the 9-*H*-naphthyl radical as we assumed in our earlier work. It is of course dangerous to read too much into the exact difference between two calculated activation energies, but we will argue later that many of the results from labeled azulenes can be explained by assuming that the probability of one of the intermediates in the spiran pathway undergoing *at least* one 9,10-hydrogen shift lies between 0 and 1 and is in fact about 0.67 at 725 °C. This corresponds to a $\Delta\Delta G^{\ddagger}$ of 6 kJ mol^{-1}, in astonishingly good agreement with the calculations. This degree of involvement of the 9-/10-hydrogen shift is quite sufficient to account for the formation of 1- as

(25) Roth, W. R. *Tetrahedron Lett.* **1964**, 1009−1013.
(26) Okajima, T.; Imafuku, K. *J. Org. Chem.* **2002**, *67*, 625−632.
(27) Friedrich, E. C.; Holmstead, R. L. *J. Org. Chem.* **1971**, *36*, 971−975.
(28) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073−3100.
(29) Ingold, K. U.; Walton, J. C. *Acc. Chem. Res.* **1986**, *19*, 72−77.

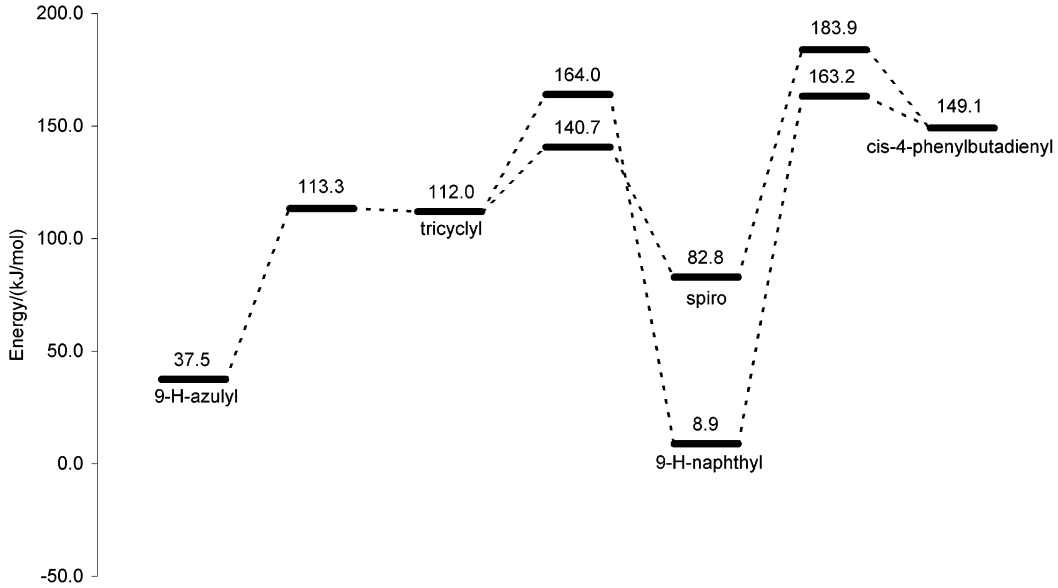
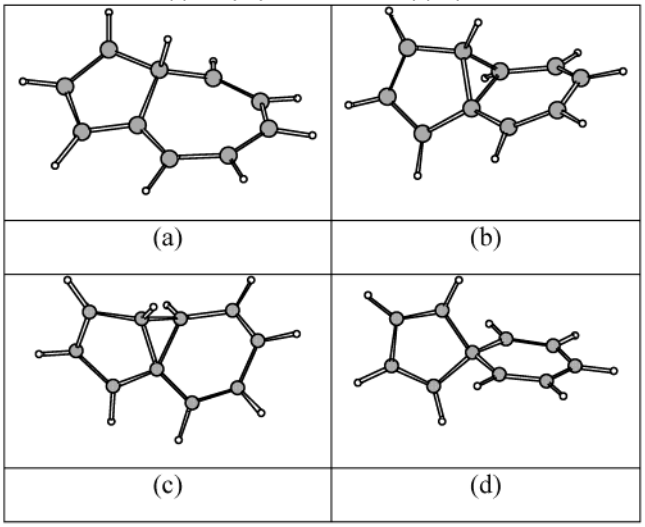


Figure 3. Spiran pathway: B3LYP/6-31G(d) energies in kJ mol^{-1} relative to the 1-*H*-azulyl radical.

Scheme 10. (a) 9-*H*-azulyl Radical, (b) 9-*H*-Azulyl/Tricyclyl Transition State, (c) Tricyclyl Radical, and (d) Spiro Radical



well as 2-methylnaphthalene from 2-methylazulene as will be discussed later.

A simple extension from the spiran pathway (see Scheme 9 and Figure 3) provides a possible explanation for the formation of minor amounts of *cis*- and *trans*-1-phenyl-1-buten-3-ynes in the flash thermolysis of azulene. The spiro-radical can undergo a C−C bond cleavage to generate a benzene ring and produce the *cis*-4-phenylbutadienyl radical that could produce 1-phenyl-1-buten-3-ynes by a subsequent hydrogen abstraction, in addition to providing an alternative route to naphthalene. As shown in Figure 3, the activation energy for the required bond cleavage is 43.2 kJ mol^{-1} higher than that of the ring closure back to the tricyclic radical, but this process could certainly be competitive enough at higher temperatures to yield a few percent of the alkyne products. Zimmermann et al.[30,31] have indeed proposed the involvement of this vinyl radical in flow thermolyses of 1-phenyl-1-buten-3-ynes, although strangely they did not invoke its direct ring closure to the 9-*H*-naphthyl radical or mention the spiro-radical.

We note that the spiran pathway as proposed previously would result in naphthalene-d_0:-d_1:-d_2 ratios of 25:50:25 from 4-^{2}H-azulene. We have considered the possibility that hydrogen shift in the 9-*H*-naphthyl radical to give the much more stable 1-*H*-naphthyl radical might compete with bimolecular hydrogen abstraction to give naphthalene. This would substantially alter the expected degree of deuterium scrambling from 4-^{2}H-azulene. However, all our attempts to find a transition state for this hydrogen shift by B3LYP/6-31G(d) calculations met with failure. We do not understand why this is so, since a transition state for hydrogen shift between the 1-*H*-naphthyl and 2-*H*-naphthyl radicals with an energy 197.6 kJ mol^{-1} above that of 1-*H*-naphthyl could be readily located.

Methylene Walk Pathway. The methylene walk pathway was introduced in Scheme 6. A more complete version including names for all the intermediates is shown in Scheme 11. It is built entirely from cyclopropylcarbinyl−homoallyl rearrangements. The energies of all intermediates and transition states are shown in Figure 4.

Several different types of intermediate are to be found in this pathway. As might be expected, the 1- and 2-*H*-naphthyl radicals are the most stable, since they contain an intact aromatic ring. At the other extreme, nonconjugated radicals such as 4-methylyl are the least stable intermediates, as expected, but note that the 1-methylyl (but not 2-methylyl) radical is much more stable, again due to the presence of an intact aromatic ring (also present in 1,2-cyp).

With one important exception, the calculations predict that each ring closure and ring opening is a normal stepwise homoallyl/cyclopropylcarbinyl rearrangement. The activation energies for these processes are discussed in the next section. The exceptional case is the crucial transfer of the methyl from one ring to the other (conversion of 4,9-cyp to 1,9-cyp) which B3LYP/6-31G(d) calculations predict to be a concerted process. The 9-methylyl radical (see Scheme 12) is found to have one

(30) Schulz, K.; Hofmann, J.; Findeisen, M.; Zimmermann, G. *Eur. J. Org. Chem.* **1998**, 2135−2142.
(31) Zimmermann, G. *Eur. J. Org. Chem.* **2001**, 457−471.

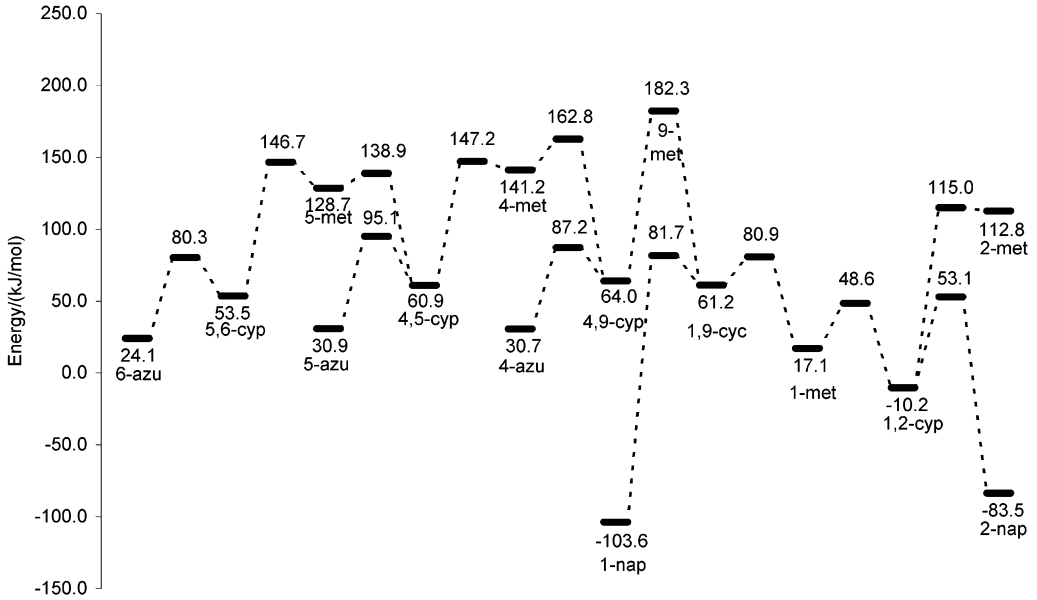
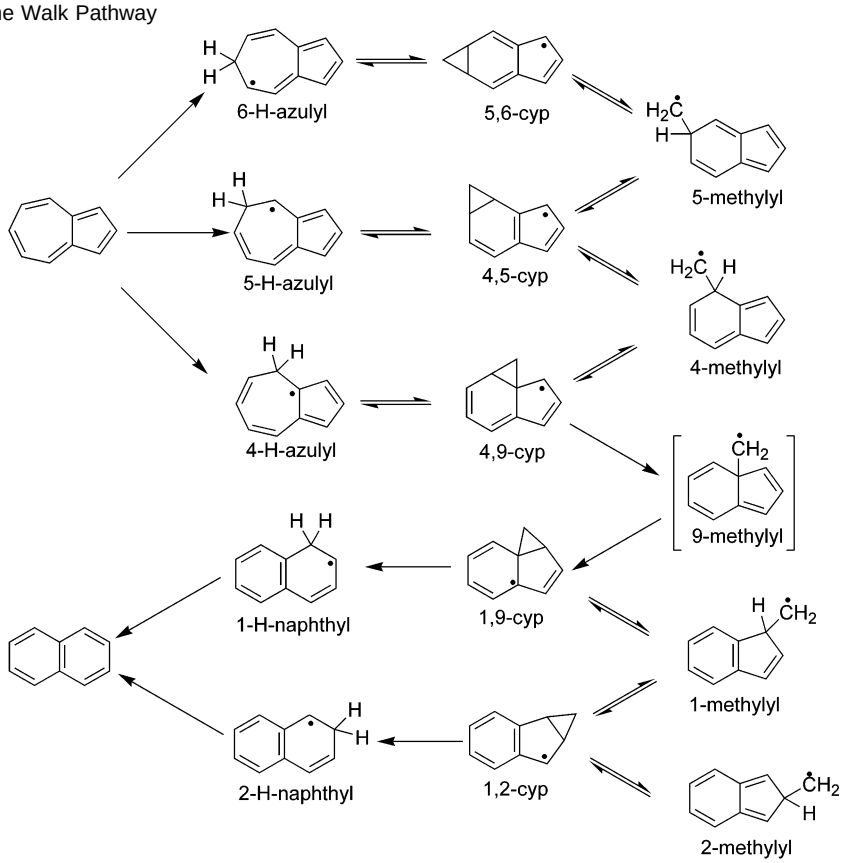


Figure 4. Methylene walk pathway: B3LYP/6-31G(d) energies in kJ mol^{-1} relative to the 1-*H*-azulyl radical (the names of radical intermediates have been abbreviated; thus, 6-azu = 6-*H*-azulyl, 5-me = 5-methylyl, and 1-nap = 1-*H*-naphthyl).

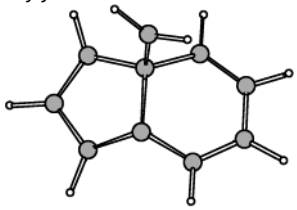
Scheme 11. Full Methylene Walk Pathway



imaginary frequency and so is a transition state for interconversion of 4,9-cyp to 1,9-cyp. This process appears to proceed with retention of configuration.

It is interesting to examine the label scrambling from 4-^{2}H-azulene in terms of the methylene walk mechanism. According to this pathway, loss of deuterium would only occur for those molecules that entered the methylene walk mechanism by addition to the labeled carbon (C-4). Since addition to C-8 is equally likely (ignoring a secondary isotope effect), and

Scheme 12. 9-Methylyl Radical Transition State



methylene walks starting from additions to C-5, C-6, and C-7 are also likely to be occurring, less than 50% of the 4-^{2}H-azulene

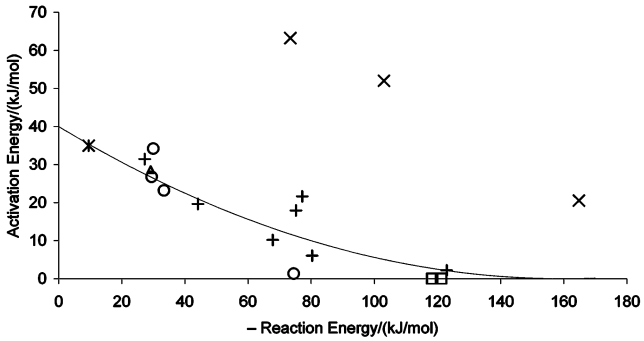


Figure 5. Graph of activation energy ($\Delta E^{\ddagger}$) vs reaction energy ($-\Delta E$) for exothermic rearrangement of cyclopropylcarbinly/homoallyl radicals. Key: (+) methylyl/cyclopropyl, (○) seven-membered ring/cyclopropyl, (×) six-membered ring/bicyclo[3.1.0]hexenyl radical, (△) tricylclyl/spiro, (□) 9-methylyl/cyclopropyl, and (*) Radom's cyclopropylcarbinyl/homoallyl.

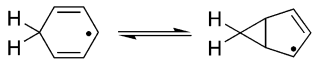
would show any scrambling. In other words, >50% of the reaction must be proceeding by intermolecular reactions if this interpretation is correct. We return to this question later.

Activation Energies for the Homoallyl/Cyclopropylcarbinyl Rearrangement Steps. Homoallyl/cyclopropylcarbinyl rearrangements have been thoroughly studied experimentally, with absolute rates established for the parent and other simple examples.[32,33] Radom[34] and co-workers have shown that B3LYP/6-31G(d) calculations perform well in reproducing the energetics of these processes, and the energies calculated for the various homoallyl/cyclopropylcarbinyl rearrangement steps in the spiran and methylene walk pathways fit in well with what can be expected. In the case of the unstabilized 2-methylyl, 4-methylyl, and 5-methylyl radicals in the methylene walk pathway, ring closure is the favorable process (the extreme case is cyclization of 4-methylyl to 4,5-cyp, which is exothermic by 80.3 kJ mol^{-1}). In other cases, ring opening can be very favorable (1,9-cyp opening to 1-*H*-naphthyl is exothermic by 164.8 kJ mol^{-1}). Both of these extreme examples have relatively low barriers, but that for the latter is notably larger than that for the former (20.5 vs 6.0 kJ mol^{-1}). In an attempt to explore this further, we have plotted the activation energy for the favorable process (which may be ring opening or closing), against the reaction enthalpy, (Figure 5). It is interesting to analyze the wide range of activation energies in terms of a Marcus-like equation:

$$\Delta E^{\ddagger} = \frac{\Delta E_0^{\ddagger}}{(1 - \Delta E/4\Delta E_0^{\ddagger})^2}$$

The curve in Figure 3 assumes an intrinsic barrier ($\Delta E_0^{\ddagger}$) of 40 kJ mol^{-1}.

Those rearrangements that involve ring closure within a seven-membered ring generally fit the curve well, but the opening of the tricyclyl radical to the 9-*H*-azulyl radical, as has been noted already, has a very low activation energy and lies 10 kJ mol^{-1} below the Marcus equation curve. Rearrangements that involve an exocyclic radical closing onto a five- or six-membered ring also fit the curve satisfactorily. Note that ring closures of the spiran radical are of this type. The three points which lie well above the curve all involve the closure of a six-membered ring to form a bicyclo[3.1.0]hexenyl radical:



There is little doubt that this type of ring closure is subject to a stereoelectronic disadvantage. In ring opening the bicyclo-[3.1.0]hexenyl radical, there is very poor overlap of the allyl orbitals with the cleaving C–C bond.[28,29,35,36] Thus, there is good experimental evidence that the 1,2-cyp radical opens more rapidly to the 1-methylyl radical than to the much more stable 2-*H*-naphthyl radical. Freidrich and Holmstead[27] found that reduction of mixtures of *exo* and *endo*-l-bromocycloprop[2,3]-indenes with various tin hydrides led to the formation of 1-methylindene and 1,2-dihydronaphthalene in ratios of ~10:1. The difference in energies between the two calculated transition states would predict a kinetically controlled product ratio of 7:1 if ΔE (4.5kJ mol^{-1}) is used or 17:1 if ΔH (6.9 kJ mol^{-1}) is taken, in excellent agreement with experiment.

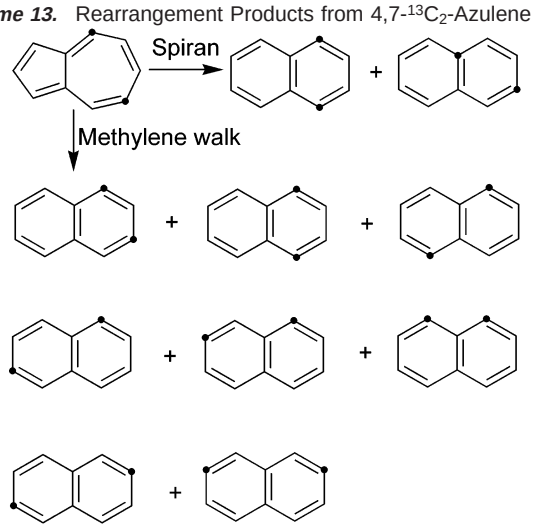
Competition between the Spiran and Methylene Walk Pathways. Concurrent operation of both spiran and methylene walk pathways appears to be required to account for the products from methyl-substituted and labeled azulenes. The spiran pathway begins from the 9-*H*-azulyl radical, although it seems likely that this can arise not only by direct hydrogen atom transfer but also by hydrogen shift from the 1- and 2-*H*-azulyl radicals. The relative rates of cyclopropylcarbinyl/homoallyl rearrangements and hydrogen shifts, as estimated from calculated barriers, suggest that these two pathways will proceed concurrently but separately. Thus 1-, 2-, and 9-*H*-azulyl radicals will rearrange to naphthalene via the spiran pathway, while 4-, 5-, or 6-*H*-azulyl radicals will go via the methylene walk. In static thermolyses at relatively high pressures and relatively low temperatures, these two groups of radicals might be interconverted via bimolecular hydrogen transfers faster than the subsequent rearrangement steps. However, this would imply the formation of substantial amounts of rearranged *azulenes* during thermolysis of compounds substituted with methyl groups in the seven-membered ring, which was not observed. We therefore suggest that competition between the two pathways is governed by the ratio of 1- + 2- + 9-*H*-azulyl to 4- + 5- + 6-*H*-azulyl radicals formed rather than by the difference in activation energies for the rate-limiting intramolecular rearrangement steps (164.0 vs 182.3 kJ mol^{-1}in favor of the spiran pathway). If the rates of hydrogen transfer to produce the *n*-*H*-azulyl radicals parallel those for methylation, the proportion of radicals capable of rearrangement by the spiran and methylene walk pathways would be about 87:13 at 165 °C. This translates to a $\Delta\Delta G^{\ddagger}$ between radical addition to the five- and seven-membered rings of about 7 kJ mol^{-1} and a spiran:methylene walk ratio of 78:22 at 400 °C, 70:30 at 700 °C, or 66:34 at 1000 °C, assuming that $\Delta\Delta G^{\ddagger}$ is independent of temperature (i.e., that $\Delta S^{\ddagger}$ for the two competing pathways are identical or nearly so). We shall now argue that competitive rearrangement between the spiran and methylene walk pathways at these ratios can account semiquantitatively for the products from ^{13}C-labeled azulenes.

(32) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151–1176.
(33) Beckwith, A. L. J.; Bowry, V. W. *J. Am. Chem. Soc.* **1994**, *116*, 2710–2716.
(34) Smith, D. M.; Nicolaides, A.; Golding, B. T.; Radom, L. *J. Am. Chem. Soc.* **1998**, *120*, 10223–10233.
(35) Olivella, S.; Sole, A. *J. Am. Chem. Soc.* **1991**, *113*, 8628–8633.
(36) Batey, R. A.; Grice, P.; Harling, J. D.; Motherwell, W. B.; Rzepa, H. S. *J. Chem. Soc., Chem. Commun.* **1992**, 942–944.

Accounting for the Products from Labeled Azulenes by a Combination of the Radical-promoted Pathways. No static thermolyses of ^{13}C-labeled azulenes have been reported. However, Zeller and Wentrup[7] passed 4,7-$^{13}C_2$-azulene through a flash thermolysis tube at 950 °C and an estimated pressure of 10^{-2} to 10^{-3} Torr. These authors analyzed the outcome of this elegant double-labeling experiment in terms of their norcaradiene−vinylidene mechanism, although at least three of the products they identified (1,3-, 1,6-, and 1,7-$^{13}C_2$-naphthalene) could not arise via this mechanism.

It is interesting to reanalyze their data in terms of the spiran and methylene walk mechanisms, which can account for *all* their labeled naphthalene products, while not predicting the formation of other isomers that are not observed. The ^{13}C NMR spectrum of their naphthalene product shows doublets for labeled carbon atoms coupled to nonequivalent labeled carbons elsewhere in the same molecule (e.g., 1,7-$^{13}C_2$-naphthalene) and singlets due to the carbon atoms of symmetrical doubly labeled naphthalenes (e.g., 1,5-$^{13}C_2$-naphthalene). The presence of small amounts of singly labeled azulene in the starting material may also give rise to singlets. The naphthalene product shows unsplit peaks at both 125.7 and 133.4 ppm in addition to doublets centered at these positions due to the expected 2,10-$^{13}C_2$-naphthalene. The 133.4 ppm singlet is reasonably assigned to the presence of 9-^{13}C-naphthalene arising via the spiran pathway from some singly labeled azulene. However, the unsplit peak at 125.7 ppm, due to labeled carbons at β-positions in naphthalene, is about 3 times stronger relative to the doublet due to 2,10-$^{13}C_2$-naphthalene than the central 133.4 ppm peak is relative to the other doublet for 2,10-$^{13}C_2$-naphthalene. We propose that 2,6- and 2,7-$^{13}C_2$-naphthalene, products of the methylene walk pathway in which the labeled 4-^{13}C becomes transposed into the other ring, can explain the extra intensity in the 125.7 ppm peak. The large unsplit peak at 127.8 ppm can be assigned to 1,4-, 1,5-, and 1,8-$^{13}C_2$-naphthalene. The norcaradiene−vinylidene mechanism can only account for 1,4-$^{13}C_2$-naphthalene, although Zeller and Wentrup acknowledged the potential presence of the other isomers. Thus, all the observed products can be accounted for by a combination of the spiran and methylene walk pathways. One product which can only be explained by the spiran pathway (2,10-$^{13}C_2$-naphthalene) is clearly present, and we suggest that there are several products present which can only arise via the methylene walk: 1,3-$^{13}C_2$-naphthalene resulting from migration of the 5- or 6-carbon in 4,7-$^{13}C_2$-azulene into the other ring, and 1,5-, 1,6-, 1,7-, 1,8-, 2,6- and 2,7-$^{13}C_2$-naphthalenes arising by migration of one or other of the labeled carbons (Scheme 13). A semiquantitative interpretation can be attempted on the assumption that 69% of the reaction is proceeding via the spiran pathway, and 31%, by the methylene walk mechanism. The spiran pathway will then produce 35% 1,4-$^{13}C_2$- and 35% 2,10-$^{13}C_2$-naphthalene. As a first approximation, the methylene walk mechanism might result in equal migration from each of the 4-, 5-, 6-, 7-, and 8-positions of azulene, with the "walked" carbon appearing with equal probability at any of the positions in the other ring. Simple statistics then leads to 12% 1,3-$^{13}C_2$-, 6% 1,4-$^{13}C_2$-, 3% each of 1,6-$^{13}C_2$- and 1,7-$^{13}C_2$-, and 1.5% each of 1,5-, 1,8-, 2,6-, and 2,7-$^{13}C_2$-naphthalene from this pathway. The sum of these percentages from the two pathways fits the published NMR data rather well.

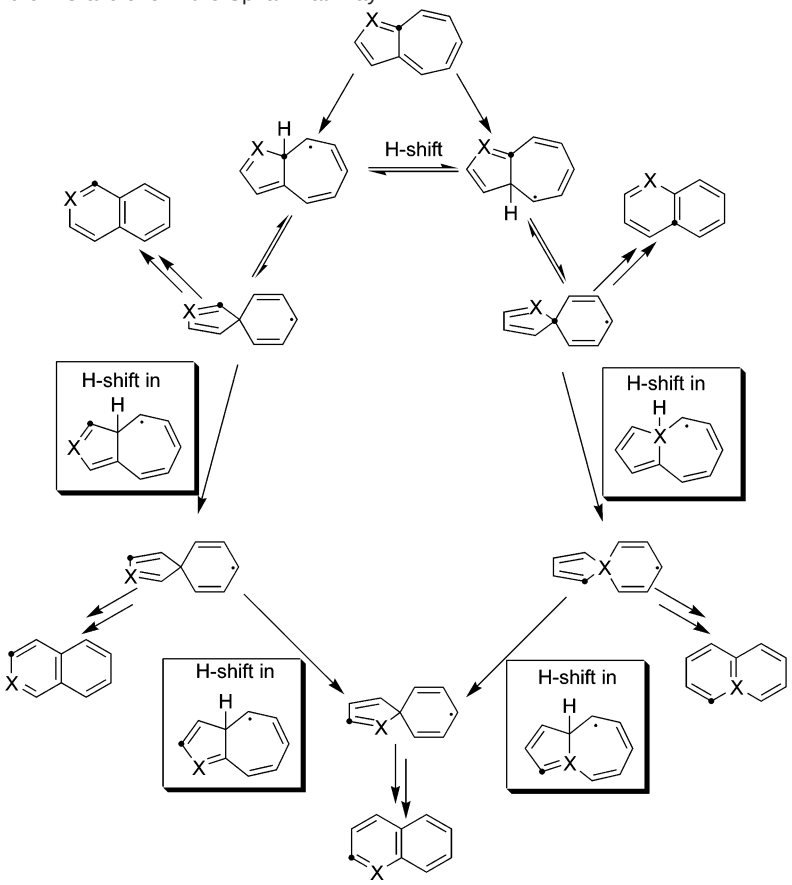
Scheme 13. Rearrangement Products from 4,7-$^{13}C_2$-Azulene



Scott and Kirms[12] subjected 1-^{13}C-azulene to flow thermolysis at temperatures between 725 and 900 °C and found the labeled carbon to be distributed between the 1-, 2-, and 9-positions of naphthalene in the ratio 55:39:6%, with an estimated error in determination of the ratios of ±3%. They also thermolyzed 9-^{13}C-azulene at 835 °C and found the label distributed in the naphthalene product at the 1-:2-:9-positions in the ratio 32:15:53%, again ±3%. The methylene walk pathway predicts a 0:0:100% distribution in the latter case, while the spiran pathway with full equilibration via hydrogen shifts predicts 40:40:20%. As Scott and Kirms point out, no simple linear combination of these two can reproduce the observed ratios. On the other hand, if ring opening to the 9-*H*-naphthyl radical competes with the degenerate hydrogen shift between the 9-*H*- and 10-*H*-azulyl radicals, as discussed earlier, then the outcome of both the thermolyses can be accounted for. We assume a 69:31 ratio between the spiran and methylene walk pathways as discussed above, but also that a fraction x of the intermediates on the spiran pathway undergo *at least* one degenerate hydrogen shift before exiting to the 9-*H*-naphthyl radical. Note that a smaller fraction (x^2) will undergo *at least* two hydrogen shifts, x^3, *at least* three, and so forth; the required hydrogen shifts are highlighted in Scheme 14. Empirically, if $x = 0.67$, and 69% of the reaction proceeds by the spiran pathway (i.e., 31% methylene walk), the ratios predicted are 31:16:53% for 9-^{13}C-azulene and 52:39:9% for 1-^{13}C-azulene, in very satisfactory agreement with experiment. The assumption that $x = 0.67$ corresponds to $\Delta\Delta G^{\ddagger}$ 6 kJ mol^{-1} between ring opening to the 9-*H*-naphthyl radical and the degenerate hydrogen shift, and this compares very favorably with the calculated $\Delta\Delta G^{\ddagger}$ of 7.4 kJ mol^{-1} (see Scheme 9 and Figure 3). It is encouraging too that we can fit the results using the same 69% spiran pathway as was required to explain the result from 4,7-$^{13}C_2$-azulene. Note that, in the latter case, the fraction of intermediates on the spiran pathway that undergo hydrogen shift is immaterial, since the only possible products from the spiran pathway are [1,4-$^{13}C_2$]- and [2,10-$^{13}C_2$]-naphthalene.

Becker et al.[6] studied the naphthalenes produced from 4-^{13}C-azulene by photolysis and by thermolysis at temperatures ranging from 1000 to 1180 °C. Flash thermolysis at 1000 °C led to distribution of the label at the 1-:2-:9-positions in the ratio 57:10:32%. The assumptions used previously do not

Scheme 14. Fate of 1-^{13}C- and 9-^{13}C-azulene in the Spiran Pathway



perform so well in this case, predicting ratios of 62:3:35%. In particular, it is hard to see how the amount of 2-^{13}C-naphthalene could be greater than 5%, since the only route (intramolecular *or* radical-promoted) that leads to this product is methylene walk (of the labeled carbon). However, some scrambling of the label in recovered azulene was observed (92% 4-^{13}C-azulene, 5.4% 5-^{13}C-azulene, and 2.7% 1-^{13}C-azulene), and rearrangement of the 5- and 1-labeled azulenes could provide more 2-^{13}C-naphthalene.

There can be little doubt that competition between the two pathways would be influenced by the presence of substituents. Thus, most of the evidence for the methylene walk mechanism was gathered from thermolysis of dimethylazulenes in which both methyl groups were in the seven-membered ring. These would probably make radical addition to the 4-, 5-, and 6-positions of that ring more favorable and thus favor the methylene walk. On the other hand, the spiran pathway may contribute more to the rearrangement of 1- and 2-substituted azulenes because initial radical attack in the five-membered ring would be favored in these cases. Nevertheless, it is worth applying the simple assumptions used previously to predict the products from 2-substituted azulenes. At the lower temperatures used in these experiments, the fraction x of intermediates undergoing the hydrogen shift will increase, so that x should now be about 0.79, and the spiran:methylene walk ratio will increase to about 79:21. This leads to a predicted product ratio from 2-^{13}C-azulene of 1-^{13}C-:2-^{13}C-:9-^{13}C-naphthalene of 22:71:7. We reported a 1-:2- ratio of about 1:2, based on the small amount of labeled naphthalene from thermolysis of 2-^{13}C-2-methylazulene accompanied by demethylation. We also reported that thermolysis of 2-D-azulene at 440 °C gives 1-D- and 2-naphthalene in the ratio of ~1:2.4 (determined by Raman spectroscopy), and similar ratios (1:2.32 and 1:2.29) were observed for 2-methyl- and 2-cyanoazulene, respectively. If it is assumed that the substituents (other than deuterium) do not undergo the 9,10-shift, so that the predicted amount of 9-substituted naphthalene product should be added to the 1-substituted product, then the 1-:2- ratio should be 1:2.5, in good agreement with the experiment data for 2-methyl- and 2-cyanoazulene.

If the spiran and methylene walk mechanisms are the only pathways operating, at least in low-temperature static thermolyses, it should be possible to give a semiquantitative account of the extent of deuterium scrambling in the thermolysis of 4-^{2}H-azulene. It is worth noting that the naphthalene-d_0:-d_1:-d_2 observed ratios 13:74:13 at 400 ± 5 °C and 12:76:12 under flash thermolysis conditions at 1180 °C are quite close to that expected from the statistical loss of label from a $C_{10}H_8D$ radical (11:78:11). However, we argued previously that extensive *intermolecular* hydrogen atom scrambling between intermediates in the rearrangement is unlikely. As noted before, the spiran pathway should result in naphthalene-d_0:-d_1:-d_2 ratios of 25:50:25 from 4-^{2}H-azulene. Loss of deuterium would only occur for those molecules that entered the methylene walk mechanism by addition to the labeled carbon (C-4), so the amount of scrambling to be expected from this pathway is less. In static thermolyses at 400−500 °C, we assumed previously a spiran:methylene walk ratio of 79:21, and this leads to naphthalene-d_0:-d_1:-d_2 ratios of about 20:60:20, that is, rather more scrambling than was observed. In high temperature flash thermolyses, the spiran:methylene walk ratio would drop to about 64:36,

leading to the prediction of *less* scrambling, although our prediction, based on the assumptions used previously, is still above that observed. Thus, the room for incursion of intramolecular mechanisms seems to be very limited.

Radical-Promoted versus Intramolecular Pathways. We believe that the evidence for the operation of the spiran and methylene walk radical-promoted pathways in the rearrangement is very strong. These pathways surely operate more or less exclusively during static thermolyses at 400−500 °C. Flash thermolysis conditions should favor intramolecular processes, but we suggest that it is appropriate at this point to ask to what extent extra (intramolecular) mechanisms actually contribute even at the highest temperatures. Unimolecular mechanisms with free energies of activation $\approx$ 350 kJ mol^{-1} can only be competitive in flash thermolysis at temperatures above 1100 °C, assuming a contact time of a few seconds and a pre-exponential factor of 10^{12} s^{-1}. Alternatively, our calculated activation energies for the proposed intramolecular mechanisms would have to be in error by >80 kJ mol^{-1} to permit these mechanisms to operate even at 700−900 °C.

The evidence that the degree of deuterium scrambling in thermolyses of 4-^{2}H-azulene is the same within experimental error at 1180 °C under flash thermolysis conditions as that at 400−500 °C during static thermolysis also superficially suggests that radical-promoted pathways dominate even under these apparently "unimolecular" conditions. Our ability to account semiquantitatively for all the products from flash thermolyses of 1-^{13}C-azulene, 9-^{13}C-azulene, and 4,7-$^{13}C_2$-azulene by a plausible combination of 31% the methylene walk and 69% spiran pathways further strengthens the case that these really are the major mechanisms for rearrangement of azulene to naphthalene under almost all conditions.

The formation of 1-phenyl-1-buten-3-ynes **3** and **4** (about 3%) during flash thermolysis of azulene at 1100 °C remains the major piece of evidence for the incursion of the norcaradiene−vinylidene mechanism. There is now quite extensive evidence that intermolecular processes can be important under flash thermolysis conditions, and we have suggested that **3** and **4** could arise from a simple extension of the spiran pathway in which the spiro-radical opens to a vinyl radical (Figure 3 and Scheme 8). Indeed, Zimmermann et al.[30,37−39] have studied the formation of azulene, naphthalene, and 1-methylene-1*H*-indene from 1-phenyl-1-buten-3-yne under flash and flow thermolysis conditions at temperatures between 550 and 1000 °C and demonstrated the involvement of vinylidenes but also of vinyl type radicals. In his review,[31] Zimmermann states "**48** (1-methylene-1*H*-indene) and **49** (azulene) were proven to rearrange into **47** (naphthalene) exclusively by radical-drive steps". This refers to studies in the temperature range up to 800 °C, and Zimmermann et al.[38] also noted that the operation of radical-promoted pathways should decrease at higher temperatures, because of the decreasing probability of radical addition at these temperatures. On the basis of current evidence, the norcaradiene−vinylidene mechanism may operate to a limited extent in the azulene−naphthalene rearrangement at the highest temperatures (above 1000 °C); even here our judgment is that the radical-promoted pathways probably still dominate.

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Supporting Information Available: Cartesian coordinates, SCF energies, zero point corrections for all species, imaginary frequencies for transition states, and values of S^2 for all radicals and potential biradicals. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) Hopf, H.; Berger, H.; Zimmermann, G.; Nuchter, U.; Jones, P. G.; Dix, I. *Angew. Chem., Int. Edit. Engl.* **1997**, *36*, 1187−1190.
(38) Schulz, K.; Hofmann, J.; Zimmermann, G. *Liebigs Ann.-Recl.* **1997**, 2535−2539.
(39) Schulz, K.; Hofmann, J.; Zimmermann, G. *Eur. J. Org. Chem.* **1999**, 3407−3412.