Thermolysis of [1-^{13}C]-2-Methylazulene and Mechanism of the Azulene to Naphthalene Rearrangement

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Abstract: Thermolysis of [1-^{13}C]-2-methylazulene gives 1-methylnaphthalene (1-MN) labeled at C-2, C-3, C-9, and C-10 and 2-methylnaphthalene (2-MN) labeled at C-1, C-3, and C-4. To account for these and previous results, it is proposed that the rearrangement of azulene to naphthalene at 440 °C proceeds by two competing mechanisms (the methylene walk and spiran pathways), both of them sequences of homoallyl–cyclopropylcarbinyl steps in azulene radical adducts. The spiran pathway, however, also involves hydrogen shifts.

We report a study of the thermolysis of [1-^{13}C]-2-methylazulene which clarifies our understanding of the formation of 1-substituted naphthalenes from 2-substituted azulenes, and we propose a working hypothesis for the mechanism of the azulene to naphthalene rearrangement in the light of these and earlier[1,2] results.

Experimental Section

Ethyl [2-^{13}C]Cyanoacetate. Sodium [2-^{13}C]acetate (500 mg, 97.2% ^{13}C, from Prochem), fresh red phosphorus (50 mg), bromine (3 mL), and carbon tetrachloride (20 mL) were refluxed together for ca. 48 h under N_2. Ground glass joints were sealed with PTFE sleeves. Excess bromine was always present; no $-CHBr_2$ products are formed under these conditions. The reaction was monitored by ^{1}H NMR. Products containing $^{13}CH_2Br$ groups have $J_{^{13}C-H}$ = 150–155 Hz ($BrCH_2COBr$, $(BrCH_2CO)_2O$, and possibly $BrCH_2COOH$ are observed); products without CH_2Br groups (CH_3COBr, $(CH_3CO)_2O$) have $J_{^{13}C-H}$ = 130–135 Hz. When the reaction was complete, ethanol (10 mL) was added and refluxing continued for 5 min. The cooled solution was poured into aqueous $NaHCO_3$ solution and $Na_2S_2O_4$ added with stirring to destroy excess bromine. The organic layer was separated and dried (Na_2SO_4) and solvent was removed. The residue was dissolved in dry acetonitrile (5 mL), excess powdered potassium cyanide added, and the solution stirred for 48 h at room temperature under a drying tube. The solution was filtered, the solvent removed, and the residue distilled at water pump vacuum. The yield of ethyl cyanoacetate on this scale was about 30%.

[1-^{13}C]-2-Methylazulene. 3-Acetylcyclohepta[*b*]furan-2-one (270 mg, prepared as described previously[2]) and ethyl [2-^{13}C]cyanoacetate (130 mg) in ethanol (10 mL) were stirred at 0 °C and treated with a solution of sodium (150 mg) in ethanol (15 mL). The mixture was stirred at room temperature for 3 days and then poured into water and acidified with dilute HCl. The pink precipitate ([3-^{13}C]-3-cyano-2-methylazulene-1-carboxylic acid) was dried, mixed with 90% H_3PO_4 (20 mL), and heated at 130 °C for 3 h under N_2. The reaction mixture was poured into water, and the azulene extracted into petrol and chromatographed on alumina (elution with petrol). [1-^{13}C]-2-Methylazulene was sublimed before use (70 mg). The ^{13}C NMR showed a peak for the C-1 labeled carbon at −118.3 ppm from Me_4Si with side bands at −119.4 and −117.1 ppm.

Thermolysis Procedure. This was essentially the same as used earlier.[1] The labeled azulene (70 mg) was thermolyzed in three batches in a 250-mL ampule, thus ensuring comparable azulene pressure to that in earlier work, but thermolysis was continued for 5.5 h at 440 °C, to ensure a high conversion to naphthalenes. GLC analysis under conditions described earlier[1] showed that the product was mainly 1- and 2-methylnaphthalene (0.45:1 ratio), but also contained naphthalene (0.11), azulene (0.008), 1,3-dimethylnaphthalene (0.041), 2-methylazulene (0.075), and 1-methylazulene or 1,2-dimethylnaphthalene (0.011) together with five unidentified peaks (0.09, figures in parentheses are peak areas relative to 2-methylnaphthalene). ^{13}C NMR showed intense peaks for C-1, C-3, and C-4 of 2-MN and for C-2 of 1-MN together with at least two peaks in the region where the quaternary carbons of these compounds absorb, but assignment was uncertain. The $^1H\{^{13}C\}$ NMR spectrum is discussed in the Results section.

Preparative GLC. The 1- and 2-methylnaphthalenes in the thermolysis product were separated on a 4 m × 1 cm column with Carbowax 20M stationary phase (30% loading) in a Varian Aerograph 712 operated manually. Total N_2 pressure was 85 psi, back pressure 40 psi (reduced to 20 psi for injection); this represented about 300 mL/min. Column temperature was 200 °C, with the injector/detector block at 240 °C. A base line separation of 1- and 2-methylnaphthalene was achieved under these conditions.

Results

The 1-MN product gave peaks at −133.6 (12%), −132.7 (8%), −126.5 (100%), and −125.6 ppm (11%, intensity reported relative to −126.5-ppm peak) in the proton-decoupled ^{13}C spectrum. Comparison with spectra of nonenriched material and literature assignments[3] suggested that these peaks were due to C-10 (and/or C-1), C-9, C-2 (and/or C-4), and C-3 (and/or C-6 and C-7), respectively. Because of the symmetry of 2-methylazulene, some labeling at C-2 in 1-MN is almost inevitable. When the ^{13}C spectrum was run with the aromatic but not the CH_3 protons decoupled, the −126.5-ppm peak became a tight quartet, confirming that this peak was mainly due to C-2 ($J_{^{13}C-C-C-H} \sim 4$ Hz). No sign of a singlet due to C-4 label could be seen but small amounts would go undetected. None of the mechanisms discussed later predicts C-4 labeling. We assume that the −125.6-ppm peak is due to C-3 labeling; the amount of label here is notably small (see the Discussion section).

The important result is that 1-MN is labeled at the bridgehead carbon (or carbons). From comparison with intensities in natural abundance spectra there appears to be as much label in the −133.6- and −132.7-ppm peaks together as in the −126.5-ppm peak, as required by the symmetry of the 2-methylazulene. Two arguments can be advanced that the −133.6-ppm peak is due to C-10 and not C-1 labeling. (a) C-1 labeling would contradict our earlier observation[2] that the methyl group of 2-methylazulene remains attached to the same carbon during 1-methylnaphthalene formation. (b) In a double irradiation experiment the ^{1}H methyl peak at δ 2.65 was observed while scanning the ^{13}C aromatic region with an irradiating field. Two and only two INDOR effects were observed corresponding to the C-9 and C-2 peaks ($J_{^{13}C-C-C-H}$ coupling). The absence of an INDOR effect corresponding to the −133.6-ppm peak is more compatible with C-10 than C-1 labeling (four-bond vs. two-bond coupling). The same type of INDOR experiment was performed on the 2-MN (the experiment was done on the crude product mixture). Here INDOR effects were observed for C-1 and C-3 labeling (see below for assignments) but not for C-4 (four-bond coupling again). We conclude that the 1-methylnaphthalene product is labeled at both C-9 and C-10 and to approximately equal extents.

The proton-decoupled ^{13}C spectrum of the 2-MN showed

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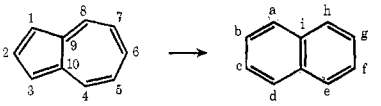
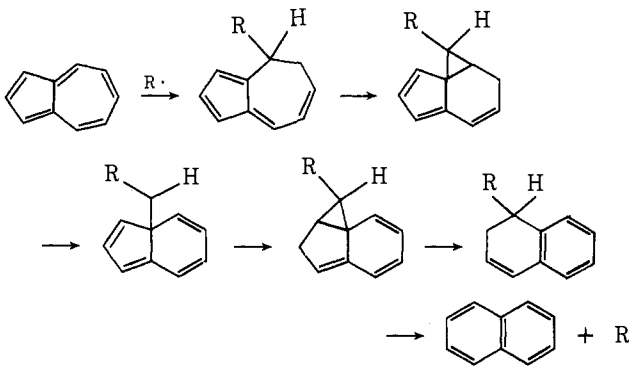
Table I



a. Methylene Walk Pathway Products										b. Spiran Pathway Products									
a	b	c	d	e	f	g	h	i	j	a	b	c	d	e	f	g	h	i	j
1	2	3	4	5	6	7	8	9	10	*1	2	3	10	4	5	6	7	8	9
1	2	4	3	5	6	7	8	9	10	*1	2	3	10	7	6	5	4	9	8
1	4	2	3	5	6	7	8	9	10	*1	2	3	10	5	6	7	8	9	4
4	1	2	3	5	6	7	8	9	10	*1	2	3	10	8	7	6	5	4	9
1	2	3	5	4	6	7	8	9	10	2	3	10	9	4	5	6	7	8	1
1	2	5	3	4	6	7	8	9	10	2	3	10	9	7	6	5	4	1	8
1	5	2	3	4	6	7	8	9	10	2	3	10	9	5	6	7	8	1	4
5	1	2	3	4	6	7	8	9	10	2	3	10	9	8	7	6	5	4	1
1	2	3	6	4	5	7	8	9	10	3	10	9	1	4	5	6	7	8	2
1	2	6	3	4	5	7	8	9	10	3	10	9	1	7	6	5	4	2	8
1	6	2	3	4	5	7	8	9	10	3	10	9	1	5	6	7	8	2	4
6	1	2	3	4	5	7	8	9	10	3	10	9	1	8	7	6	5	4	2
1	2	3	7	4	5	6	8	9	10	10	9	1	2	4	5	6	7	8	3
1	2	7	3	4	5	6	8	9	10	10	9	1	2	7	6	5	4	3	8
1	7	2	3	4	5	6	8	9	10	10	9	1	2	5	6	7	8	3	4
7	1	2	3	4	5	6	8	9	10	10	9	1	2	8	7	6	5	4	3
1	2	3	8	4	5	6	7	9	10	*9	1	2	3	4	5	6	7	8	10
1	2	8	3	4	5	6	7	9	10	*9	1	2	3	7	6	5	4	10	8
1	8	2	3	4	5	6	7	9	10	*9	1	2	3	5	6	7	8	10	4
8	1	2	3	4	5	6	7	9	10	*9	1	2	3	8	7	6	5	4	10

Scheme I

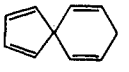


only three peaks, −128.1 (76%), −127.7 (47%), and −126.8 ppm (100%), readily assigned to C-3, C-4, and C-1, respectively (the INDOR experiment described above provides confirmation). No peaks could be found where C-9 or C-10 of 2-MN absorb. Owing to the expected low intensity of these peaks we can only say that there is not more than 15% of the amount of label at C-1 in either of these positions. From comparison with peak intensities in natural abundance spectra, it appears that there is as much label at C-1 as at C-3 and C-4 put together, as required by the symmetry of 2-methylazulene.

Discussion

The patterns of labeling in the 1-MN and 2-MN products from [1-^{13}C]-2-methylazulene are strikingly different. We will discuss the simpler 2-MN product first. Labeling at C-1, C-3, and C-4, but not at bridgehead carbons, is in excellent accord with the mechanism for the azulene to naphthalene rearrangement which we advanced in an earlier paper[1] (now called the methylene walk pathway), which fails, however, to predict the formation of 1-MN from 2-methylazulene at all. The methylene walk pathway proposes that rearrangement is initiated by addition of a radical[4] to the 4, 5, 6, 7, or 8 position of an azulene. The azulene radical adduct then rearranges by a sequence of homoallyl → cyclopropylcarbinyl → homoallyl rearrangements. A short sequence from azulene to naphthalene is shown in Scheme I; there are clearly many more elaborate pathways. We assume that all the rearrangement steps are reversible except the final ring opening to the [4.4.0]decane skeleton. This assumption is in agreement with the work of Sustmann and Lubbe[5] on the bicyclo[3.1.0]hexenyl radical and with the earlier work of Friedrich and Holmstead.[6] With this assumption the methylene walk pathway predicts the formation of the 20 naphthalenes shown in Table Ia. For [1-^{13}C]-2-methylazulene the label should appear at C-1, C-3, and C-4 with labeling at C-1 equal to the sum of labeling at C-3 and C-4 (assuming ^{13}C isotope effects to be negligible).

The formation of 1-MN from 2-methylazulene, and the labeling pattern we now report in that product, clearly demands the operation of a distinctly different pathway. Either hydrogen shifts or hydrogen abstractions followed by readditions (or vice versa) must occur. The labeling patterns in the 1- and 2-methylnaphthalene products suggested to us the possibility that the carbons of the five-membered ring of azulene had become rotated relative to their initial position in the 1-methylnaphthalene product. These considerations led us toward the spiro[4.5]decatetraenyl radical (I), and its possible transfor-

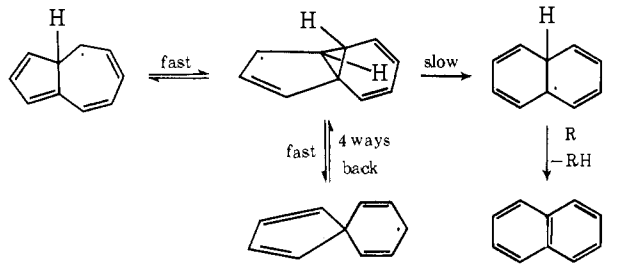


I

mations via homoallyl → cyclopropylcarbinyl rearrangements. We will now present one mechanism (which we call the spiran pathway) which employs this idea. Our results do not exclude many alternative mechanisms, but we have been unable to devise any which account so naturally for the labeling in the 1-MN (particularly at C-10), which fit in with the methylene walk pathway, and which make fewer ad hoc assumptions.

The methylene walk pathway ascribes no role in the rearrangement to the 1- (3-), 2-, and 9- (10-) radical adducts of azulene. However, the evidence concerning radical attack on azulene[1] suggests that the 1- and 2-radical adducts are actually the most readily formed. There is no direct evidence for the 9-adduct and one might expect it to be the least stable. It is hard to see what unimolecular rearrangements could take place for the 1- and 2-adducts. Ring closure to the bicyclo[2.1.0]-

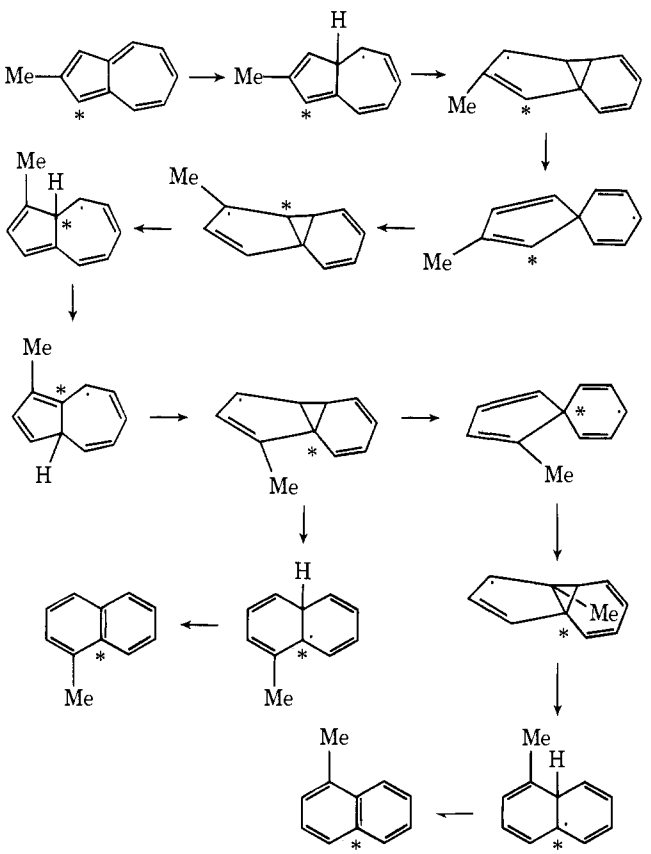
Scheme II



pentene skeleton seems unlikely.[7] These adducts can, however, be looked upon as cyclopentadienes and might undergo 1,5-hydrogen shifts. This could provide an additional route to the 9-adduct, to which we now ascribe a key role. This adduct, like the 4-, 5-, and 6-adducts, should cyclize readily (homoallyl → cyclopropylcarbinyl, alternatively, cycloheptatriene → norcaradiene rearrangement), initiating the sequence of steps shown in Scheme II. We propose that ring opening of the tricyclic radical is stereoelectronically controlled, in line with precedents.[5,6] Ring opening to the 9-adduct and to the spiran should be fast and reversible (good overlap of the breaking cyclopropane bond and the allylic radical π orbitals), while ring opening to the naphthalene skeleton should be slow (poor overlap) and is, we propose, irreversible. The spiran radical has four pathways for recyclization and this opens up some new possibilities. This scheme in itself is, however, not enough to explain the formation of 1-MN from 2-methylazulene. Formally it gives rise to the eight naphthalenes marked with an asterisk in Table Ib.

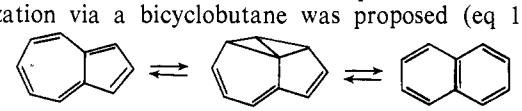
We now propose that 9- and 10-adducts are readily interconverted by a hydrogen shift. This is essentially an ad hoc assumption. 1,2-Hydrogen shifts in radicals are rare,[14] though few systems remotely similar to the present one have been studied. Once again, the shift is formally a cyclopentadiene 1,5 shift. Salem[8] has pointed out that the energy of the transition state for such a hydrogen shift may be principally controlled by the highest (singly) occupied molecular orbital. In the case in question this orbital will be mainly derived from the LUMO of azulene. This orbital, although overall antibonding, is locally strongly bonding between C-9 and C-10. The presence of the hydrogen atom in this region should stabilize this orbital and lead to a relatively low-lying transition state. Essentially, however, we make this assumption of the 9- → 10-hydrogen shift because it produces a satisfactory explanation of the formation of 1-MN and of its labeling pattern. One route from [1-^{13}C]-2-methylnaphthalene to [9-^{13}C]- and [10-^{13}C]-1-methylnaphthalene is shown in Scheme III. The full sets of possibilities generated by this extra assumption are those without an asterisk in Table Ib. This full set of possibilities is for azulene itself where each 1,2 shift will be of a hydrogen atom. With methyl- and dimethylazulenes we suggest, in line with experience of cyclopentadiene chemistry,[9] that 1,2-CH_3 shifts are too slow to compete with other steps. In 1,3-dimethylazulene rearrangement is blocked so that only Scheme II can operate, giving 1,3-dimethylnaphthalene (54.9% of products[1]), along with the methylene walk pathway giving 1,3- and 1,4-dimethylnaphthalenes (26.2%). Formation of 1,2- and 2,3-dimethylnaphthalenes is in fact barely detectable (1.2 and <0.3%). Formation of 1,4-dimethylnaphthalene from 1,2-dimethylazulene is also negligible (0.5% of products[2]); this product could only arise by the spiran pathway and then only if methyl shifts occur.

Scheme III



Our proposal for the overall mechanism of the azulene to naphthalene rearrangement at 440 °C for several hours in a sealed bulb is therefore as follows. The reaction is radical initiated (see below) and rearrangement occurs in radical adducts. The 4- (8-), 5- (7-), and 6-adducts rearrange via the methylene walk pathway. The 9- (10-) adduct rearranges via the spiran pathway. The 1- (3-) and 2-adducts may be unproductive or (more likely) they may provide an additional route to the 9-adduct via hydrogen shifts. The two pathways are in competition, and both are required to explain our results (numerous products from the dimethylazulenes studied earlier are readily explained by the methylene walk mechanism but not predicted by the spiran pathway). We believe that the competition between the two pathways is influenced by substituents. Thus the spiran pathway may be favored by 5-ring substitution; at least some of the 2-MN from 2-methylazulene must arise from the spiran pathway (it can only be labeled at C-1 and C-3), so in this case >25%, maybe 50%, of products arise through the spiran pathway. On the other hand, the indications are that a substantial proportion of products from the 7-ring methylated azulenes arises through the methylene walk pathway. It may be that formation of 4-, 5-, 6-, 7- and 8-radical adducts is more favorable in these compounds. This overall mechanism accounts for essentially all the products and labeling patterns which we have observed, without predicting others which are not observed. It achieves this while predicting the formation of only 40 possible permuted naphthalenes (Table I) out of a possible 10!/4 = 907 200 permutational possibilities.

We now discuss some variants and alternatives. Scott and Agopian[10] have recently suggested that the scrambling of ^{13}C between α and β (but not bridgehead positions) in naphthalene at 1035 °C occurs via azulene. A simple unimolecular isomerization via a bicyclobutane was proposed (eq 1). This



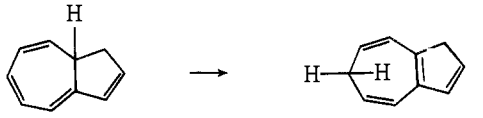
(1)

mechanism was our original incentive for investigating the azulene to naphthalene rearrangement. We quickly abandoned

it when we found that benz[*f*]azulene gives phenanthrene (>98%) with less than 1% anthracene.[1] It must surely be anticipated that bicyclobutane formation would occur so as to preserve the aromaticity of the benzo ring—this leads to anthracene. Scott correctly points out[11] that, with this exception, the largest single product from any azulene we have studied is that predicted by the bicyclobutane mechanism. However, this mechanism fails to account for our labeling results and overall gives a poor account of product composition. We also feel that the evidence for radical initiation under our conditions is strong (the flash thermolysis conditions employed by Scott should favor any unimolecular mechanism). In addition to the previous evidence for the involvement of radicals, we have observed an induction period for naphthalene formation from carefully purified azulene under our standard conditions. Azulene was purified by two acid extractions, recrystallization, and two sublimations, and thermolyzed in base-washed ampules after careful removal of oxygen (evacuation to 10^{-4} mmHg, venting to O_2-free N_2, and reevacuation before sealing). While 2 h at 440 °C gave >50% naphthalene formation, 15 min at 440 °C gave less than 2% rearrangement. Initial radical generation is probably a complex wall reaction, but we believe that the bulk of the rearrangement proceeds in the gas phase. Heilbronner and Kallen's work[12] and our own limited studies[1] showed that variation of the area and nature of the ampule surface had a moderate effect on the rate of rearrangement but almost no effect on product ratios. The observation of an induction period renders the activation parameters quoted by Heilbronner largely meaningless.

If the evidence for radical initiation of rearrangement is accepted, there are still many alternatives to our proposal of competitive operation of the methylene walk and spiran pathways. In most cases we have no clear-cut evidence which excludes these. Brief comments on two which have occurred to us seem necessary.

(1) The spiran and methylene walk pathways could be linked via a 9- to 6- or similar hydrogen shift (eq 2).



(2)

(from spiran pathway) (to methylene walk pathway)

One then expects [3-^{13}C]-1-methylnaphthalene and [9-^{13}C]- and [10-^{13}C]-2-methylnaphthalene from [1-^{13}C]-2-methylazulene. The former is found in small amount, and we have pointed out that small amounts of the latter two might go undetected. It should be noted the exclusive exit from Scheme II via a 9- to 6- *rather than* 9- to 10-hydrogen shift fails to predict the formation of [10-^{13}C]-1-methylnaphthalene.

(2) Dihydroazulenes may be formed during thermolysis and they open a Pandora's box of rearrangement possibilities themselves. We have to take their involvement as major rearrangement intermediates seriously. Large parts of the spiran and methylene walk pathways have analogies in potential sigmatropic and electrocyclic reactions of these hydrocarbons and the hydrogen shifts necessary for the spiran pathway then present no problems. Nevertheless, we are inclined to believe that they are not of central importance. Firstly, it is hard to explain how the migrating carbon in the dihydroazulene analogue of the methylene walk pathway can finish up in an α-naphthyl position, which is clearly required by our earlier results.[1] Secondly, the activation energies for the hydrocarbon rearrangement steps are certainly much higher than that for the homollyl-cyclopropylcarbinyl process (<14 kcal mol^{-1}).[5,13] A compromise mechanism in which the hydrogen shifts go via dihydroazulenes, and other steps proceed in radical adducts, requires competition between bimolecular and unimolecular processes in the rearrangement mechanism. This is incompatible with the observed[1] invariance of product composition to changes of temperature and pressure. Thirdly, our observation[1] that di-*tert*-butyl peroxide induces rearrangement in the gas phase but not in solution is most simply explained by unimolecular rearrangements of the radical adducts in the gas phase and bimolecular processes (e.g., hydrogen abstraction) in solution. Dihydroazulene formation clearly requires a second bimolecular step. In fact our results in general speak against extensive occurrence of hydrogen abstraction processes during thermolysis. If these occurred isomeric azulenes, e.g., 1-methylazulene from 2-methylazulene, would appear and build up to moderate concentrations during thermolysis, since the rates of rearrangement of isomeric azulenes are very similar.[1] However this is not observed. Hydrogen abstraction must occur, of course, for some of the longer lived naphthyl radicals which are the terminus of rearrangement.

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(3) P. R. Wells, D. P. Arnold, and D. Doddrell, *J. Chem. Soc., Perkin Trans. 2*, 1745 (1974), and references cited therein. Dr. Wells informs us that there is an error in the shift reported for C-5 in the first column of Table I (the entry should be 128.7); also that the assignments for C-4 and C-8 of 2-methylnaphthalene (fourth column of Table I) should be reversed.
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(8) L. Salem, personal communication.
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