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Azulene Thermal Rearrangements. ^{13}C-Labeling Studies of Automerization and Isomerization to Naphthalene[1]

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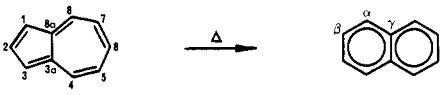
Abstract: The thermal rearrangement of azulene to naphthalene involves a rare conversion of one aromatic ring system into another. To help establish which atoms of azulene become which atoms of naphthalene, azulene-*1*-^{13}C and azulene-*3a*-^{13}C have been synthesized and isomerized to naphthalene in a base-washed, quartz flow system at high temperatures. NMR analysis of the naphthalene obtained from these two labeled azulenes revealed a distribution of ^{13}C label among the α, β, and γ (angular) positions of 55:39:6 and 32:15:53, respectively. Recovered azulene was analyzed in one case and found to have suffered automerization to a minor extent. The results of these fundamental experiments are discussed with respect to other experimental work and to the various published mechanistic proposals.

The distinction between aliphatic and aromatic compounds can be traced to the early days of organic chemistry and has persisted as a useful concept even into modern times.[2] Clear differences in the chemistry associated with members of the two families make this classification system a natural one. The recognition of azulene (**1**) and its derivatives as truly aromatic compounds, therefore, marked a major milestone in the first half of this century, for nonbenzenoid aromatic hydrocarbons had not previously been known.[3]

Isomerization of azulene to naphthalene (**2**) at high temperatures (eq 1)[4] constitutes the first documented thermal rearrangement of an aromatic hydrocarbon. Exothermic by nearly 40 kcal/mol,[5] it proceeds cleanly in the gas phase and obeys first-order kinetics with respect to azulene.[6] Despite years of speculation about the mechanism of this remarkable transformation, however, it is still not even known which atoms of azulene become which atoms of naphthalene. Interconversions of 1- and 2-substituted azulenes under similar conditions have also been reported (eq 2).[7]



1 2 (1)

(2)

Although countless examples of thermal rearrangements among ordinary polyolefins can be found,[8] the number of such processes involving aromatic hydrocarbons remains quite small. The transformations depicted in eq 1 and 2 thus take on special historical importance.

We became interested in the mechanisms of these long-known reactions and have conducted a series of ^{13}C-labeling studies. Other research groups have also contributed to this area.[9–11] Herein we describe the synthesis and thermal rearrangements of azulene-*1*-^{13}C and azulene-*3a*-^{13}C. Our results are discussed with respect to the several published mechanistic proposals.

Methods

Syntheses. At the outset of this project, none of the existing azulene syntheses were considered suitable for preparation of the desired ^{13}C-labeled azulenes. A new azulene synthesis was therefore devised (Figure 1).[12] This route is short and versatile and especially well suited for the controlled introduction of ^{13}C labels. For the synthesis of azulene-*1*-^{13}C, hydrocinnamic acid-*1*-^{13}C was prepared by the reaction of excess 2-phenylethylmagnesium bromide with $^{13}CO_2$. For the synthesis of azulene-*3a*-^{13}C, diazomethane-^{13}C was employed using our modified procedure[13] which requires only 1 equiv of diazomethane. Details of this intramolecular carbene addition route to azulenes are described elsewhere.[12]

Thermal Rearrangements. The original experiments of Heilbronner et al. on azulene rearrangement[4,6] were all conducted in static systems at about 400 °C. To reduce the probability of bimolecular interactions and chain reactions, however, we have carried out all of our experiments in a flow system. The much shorter heating times naturally require higher temperatures to effect complete conversion of the azulene, and experiments were typically run in the 700–900 °C range with contact times (t_c) of 0.3–3.1 min.

The flow system was constructed from a simple, base-washed quartz tube heated by an electric furnace (see Experimental Section). Thermal rearrangements were all performed by slowly subliming the azulene at atmospheric pressure (ca. 5–10 mg/h) into a stream of dry nitrogen which carried the sample through the hot zone and into a liquid nitrogen trap. By this method, contact times could be easily adjusted and the gas-phase concentration of azulene in the hot zone always kept extremely low.

Product Analyses. Proton-decoupled ^{13}C NMR spectra of all azulene and naphthalene samples, both ^{13}C-enriched and natural abundance, were recorded in CDCl$_3$ on a JEOL FX 100 NMR spectrometer, all under identical instrument conditions (1.0-mm

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[1] "Thermal Rearrangements of Aromatic Compounds". Part 4. This work was first presented at the IUPAC Symposium on Aromaticity, Dubrovnik, Yugoslavia, Sept 1979: Scott, L. T.; Kirms, M. A.; Minton, M. A. *Croat. Chem. Acta* **1980**, 643. Part 3: Scott, L. T.; Highsmith, J. R. *Tetrahedron Lett.* **1980**, 4703.

[2] Lewis, D.; Peters, D. "Facts and Theories of Aromaticity"; Macmillan: London, 1975, and references cited therein.

[3] For an extensive discussion of early azulene chemistry see: Heilbronner, E. In "Nonbenzenoid Aromatic Compounds"; Ginsburg, D., Ed.; Interscience: New York, 1959; Chapt 5 and 6.

[4] Heilbronner, E.; Plattner, P. A.; Wieland, K. *Experientia* **1947**, *3*, 70. Heilbronner, E.; Wieland, K. *Helv. Chim. Acta* **1947**, *30*, 947–56.

[5] Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

[6] Kallen, H. J. Ph.D. Dissertation, Eidgenössische Technische Hochschule, Zürich, 1958; cited in ref 3, pp 263–8.

[7] Herz, W. *J. Am. Chem. Soc.* **1958**, *80*, 1243–6. Plattner, P. A.; Fürst, A.; Gordon, M.; Zimmermann, K. *Helv. Chim. Acta* **1950**, *33*, 1910–18. Otani, Y.; Okamoto, H.; Ogura, I. *Yakugaku Zasshi* **1968**, *88*, 807–10. *Chem. Abstr.* **1969**, *70*, 47614p. Kurokawa, S.; Safo, T.; Noguchi, T.; Yano, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1559-62. See also ref 10 and ref 3, pp 263–8.

[8] See, for example, Scott, L. T.; Jones, M. Jr. *Chem. Rev.* **1972**, *72*, 181–202.

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[11] Becker, J.; Wentrup, C.; Katz, E.; Zeller, K.-P. *J. Am. Chem. Soc.* **1980**, *102*, 5110–12.

[12] Scott, L. T. *J. Chem. Soc., Chem. Commun.* **1973**, 882–3. Scott, L. T.; Minton, M. A.; Kirms, M. A. *J. Am. Chem. Soc.* **1980**, *102*, 6311–14.

[13] Scott, L. T.; Minton, M. A. *J. Org. Chem.* **1977**, *42*, 3757.

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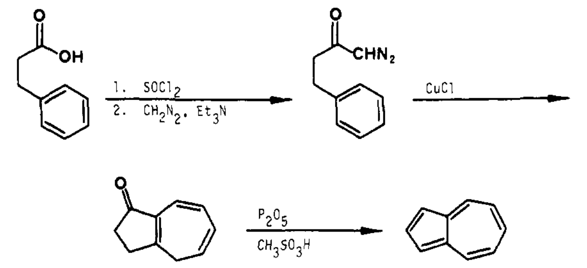


Figure 1. The intramolecular carbene addition route to azulenes.[12]

probe; pulse width = 5 μs; pulse delay = 10 s). Reproducibility of the integration data to within ±1% was confirmed by repeated analysis of the same sample on different days. It should be emphasized that our analysis does *not* require equal numbers of ^{13}C nuclei in different environments to give signals of equal intensities; in fact, they do not. The analysis requires only that the *dependence* of signal intensity on ^{13}C abundance at a given position remain constant from one sample to the next. A detailed discussion of the ^{13}C NMR analysis and an experimental determination of the errors involved (±3%) can be found in the Appendix.

Results

At 785 °C (t_c = 2.2 min), azulene-*1*-^{13}C gives naphthalene and recovered azulene in a ratio of 64:36. Examination of the recovered azulene revealed about 5% automerization with the ^{13}C label distributed 95:2:2:1 in the 1(3), 2, 3a(8a), and 4(8) positions, respectively. The distribution of ^{13}C label in the naphthalene was found to be 55:39:6 in the α, β, and γ positions, respectively.

To investigate the effect of temperature variations, thermal rearrangements of azulene-*1*-^{13}C were also carried out at 725 °C (t_c = 2.2 min) and 900 °C (t_c = 0.3 min).[14] The distribution of ^{13}C label in the naphthalene thus produced was found to be the same as that reported above (within ±3%) in both cases.

The flow system was then packed with quartz chips, and an additional experiment was run (also 900 °C, t_c = 0.3 min) to check the effect of increased surface area. To compensate for the 60% reduction in effective volume of the hot zone, an adjustment was made in the carrier gas flow rate. The distribution of ^{13}C label in the naphthalene thus obtained was found to be the same (within ±2%) as in the companion run in the unpacked tube under otherwise identical conditions.

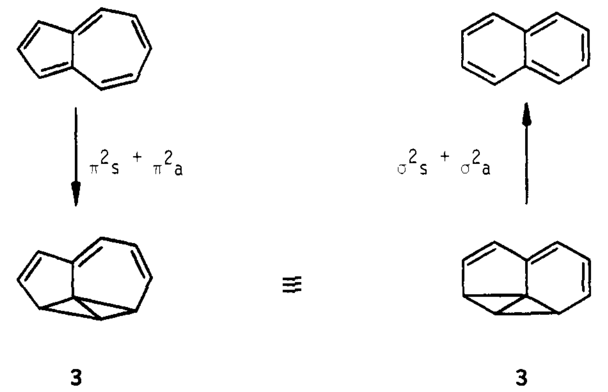
At 835 °C (t_c = 1.7 min), azulene-*3a*-^{13}C gives essentially complete conversion to naphthalene. The distribution of ^{13}C label was found to be 32:15:53 in the α, β, and γ positions, respectively.

Discussion

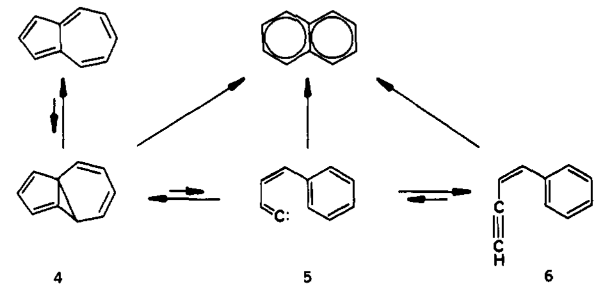
Isomerization to Naphthalene. We find that the ^{13}C distribution in the naphthalene obtained by thermal rearrangement of labeled azulene does not vary appreciably as a function of temperature or as a function of surface area in the hot zone. Wentrup et al. report a similar insensitivity of their results to temperature variations in the vacuum pyrolysis of azulene-*4*-^{13}C (1000–1180 °C).[11] Comparably small variations in the product composition as a function of temperature and surface area have also been reported by Alder and Whittaker for the thermal rearrangements of several methyl-substituted azulenes in sealed ampoules (440 °C, 2 h).[10a] The conditions under which these rearrangements are performed, therefore, do not seem critical. One must be careful in interpreting such experiments, however, not to dismiss entirely the possible contribution of catalysis by the wall to these high-temperature reactions; wall-catalyzed processes could play such a major (or minor) role that an increase in the number of catalytic sites would cause no more than small changes in the ^{13}C distribution.

Closely related to our work on azulene-*1*-^{13}C, a study by Alder et al. on the thermal rearrangement of 2-methylazulene-*1*-^{13}C has previously been reported.[10c] Both 1- and 2-methylnaphthalene were obtained (31:69) and examined by ^{13}C NMR spectroscopy. Although the distribution of ^{13}C label in these products was not reported in quantitative terms, the authors' comments allow one to estimate a ^{13}C distribution of α:β:γ = 48:37:15 for the two methylnaphthalenes taken together. The differences between these numbers and ours (α:β:γ = 55:39:6) from thermal rearrangement of unsubstituted azulene-*1*-^{13}C could reflect the influence of the methyl group or may simply represent the error associated with our attempted quantification of Alder's NMR data. Considering that the experiments were performed on different compounds in two separate laboratories under widely disparate conditions, the results actually agree reasonably well.

Scheme I. Bicyclobutane Mechanism



Scheme II. Norcaradiene–Vinylidene Mechanism



Before discussing the mechanistic implications of our ^{13}C NMR data, the relative importance of automerization should be clarified. From azulene-*1*-^{13}C at 785 °C we recover azulene and find that 5% of the label has scrambled to other positions. Since azulene constitutes only 36% of the $C_{10}H_8$ mixture, however, less than 2% of the starting material actually suffers automerization, while 64% isomerizes to naphthalene. Thus, the potential complication of automerization can be safely ignored when interpreting our naphthalene ^{13}C-distribution data. For reasons which are not yet understood, Wentrup et al. observe more nearly comparable rates of automerization and isomerization to naphthalene in their experiments.[11]

We first became attracted to this field by the possibility that azulene might rearrange to naphthalene via a sequence of concerted pericyclic reactions. Electrocyclic closure of azulene to bicyclobutane **3** followed by reopening to naphthalene constitutes an appealing, symmetry-allowed[15] pathway (Scheme I). We initially suggested this mechanism as a reversible process to account for the interconversion of α- and β-naphthalene-^{13}C at 1035 °C.[16]

Very recently, Wentrup et al. have proposed a second unimolecular mechanism,[11] i.e., electrocyclic closure of azulene to norcaradiene **4**, subsequent fragmentation to vinylidene **5**, and then a hydrogen shift to give phenylbutenyne **6**; the three interconverting intermediates so generated could each proceed directly to naphthalene (Scheme II). Some convincing experimental support for this "norcaradiene–vinylidene" mechanism has been cited.[11]

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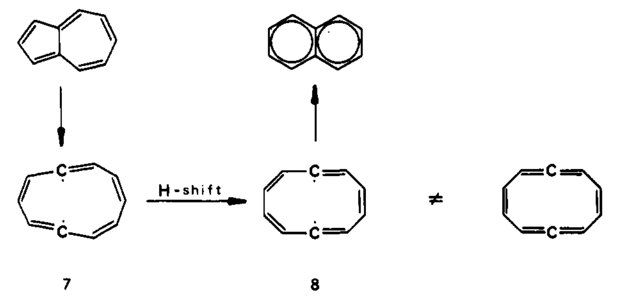
[14] The control experiments were performed using 18% ^{13}C azulene.

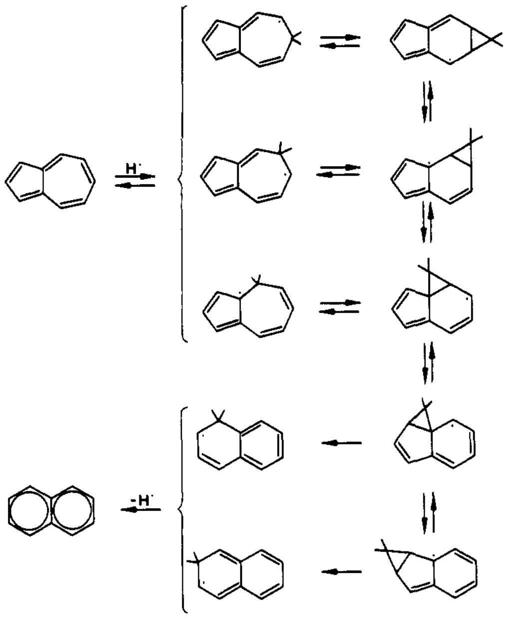
[15] Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970; pp 76–8.

[16] Scott, L. T.; Agopian, G. K. *J. Am. Chem. Soc.* 1977, *99*, 4506–7.

Scheme III. Diradical Mechanism



Scheme IV. Methylene Walk Mechanism



One obvious mechanism (also unimolecular) which has received little attention heretofore also deserves mention. Homolysis of the weakest bond in azulene followed by shift of a hydrogen atom and reclosure could produce naphthalene without ever disrupting the conjugated ten-electron π system (Scheme III).[6,17] A concerted, dyotropic variant of this diradical mechanism can also be envisaged.[18]

Finally, Alder et al. have proposed a pair of competing (but related) pathways.[10] Both begin with the addition of a hydrogen atom of unspecified origin to the azulene molecule; rearrangement then takes place on the $C_{10}H_9$ energy surface before final expulsion of the extra hydrogen atom. Schemes IV and V, although somewhat abbreviated for clarity, contain all the essential elements of the original proposal. Complete equilibration among intermediates before the opening to a bicyclo[4.4.0] system is assumed. Analogous pathways involving cationic intermediates generated by proton transfer from the wall also seem plausible.[9] In support of these mechanisms, recent evidence from various sources indicates that unimolecular pathways alone cannot account for all of the naphthalene derived from rearrangement of azulene.[10,11] Additional arguments have also been forwarded in favor of the "methylene walk" and "spiran" mechanisms.[10]

Tables I and II summarize the distributions of ^{13}C label predicted by each of these mechanisms for the isomerization of azulene-*1*-^{13}*C* and azulene-*3a*-^{13}*C*, respectively, together with our experimental results. *It is immediately clear from these data that no single pathway yet proposed, by itself, can adequately account for our results.*

Scheme V. Spiran Mechanism

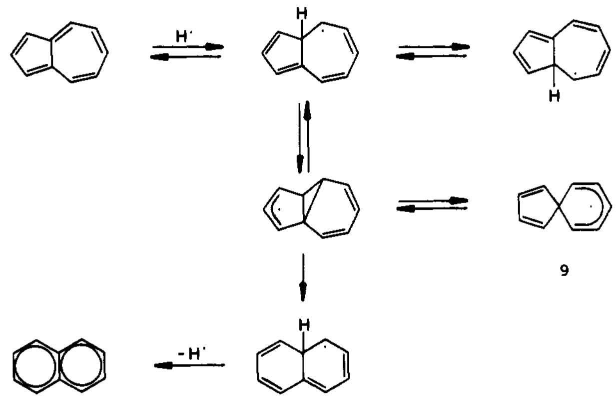


Table I. Predicted and Observed Distributions of the ^{13}C Label in Naphthalene Obtained from Thermal Rearrangement of Azulene-*1*-^{13}*C*

	α	β	γ
bicyclobutane mechanism	50	50	0
norcaradiene-vinylidene mechanism	50	50	0
diradical mechanism	50	50	0
methylene walk mechanism	75	25	0
spiran mechanism	40	40	20
experimental results	55	39	6

Table II. Predicted and Observed Distributions of the ^{13}C Label in Naphthalene Obtained from Thermal Rearrangement of Azulene-*3a*-^{13}*C*

	α	β	γ
bicyclobutane mechanism	0	0	100
norcaradiene-vinylidene mechanism	50	0	50
diradical mechanism	50	0	50
methylene walk mechanism	0	0	100
spiran mechanism	40	40	20
experimental results	32	15	53

Exclusive rearrangement of azulene-*3a*-^{13}*C* via either the bicyclobutane mechanism or the methylene walk mechanism would leave 100% of the label at the ring junction (γ position) in naphthalene; however, we find nearly half of the label distributed between the α and β positions. The pathways outlined in Schemes II and III, which cannot be distinguished from one another by any single-labeling experiments such as these, come closer to predicting the observed ^{13}C distributions in both cases but still fail to account for the minor products (6–15%). In fact, only the spiran mechanism predicts *any* γ-naphthalene-^{13}*C* from azulene-*1*-^{13}*C* and β-naphthalene-^{13}*C* from azulene-*3a*-^{13}*C*.

Alder et al. have proposed the simultaneous operation of both the methylene walk and the spiran mechanisms, with neither being the sole pathway.[10c] Any linear combination of these two mechanisms, however, would predict equal amounts of α- and β-naphthalene-^{13}*C* from azulene-*3a*-^{13}*C* (Table II), whereas the experimental ratio is 32:15. Indeed, it can be seen from Table II that no linear combination of *any* two mechanisms can correctly predict the experimental results. Fortuitously, a 1:1:1 combination of the methylene walk, the spiran, and the norcaradiene–vinylidene mechanisms almost exactly reproduces the ^{13}C distribution for both of our experiments, i.e., azulene-*1*-^{13}*C* → α:β:γ = 55:38:7 and azulene-*3a*-^{13}*C* → α:β:γ = 30:13:57 (cf. Tables I and II, respectively). This particular combination of mechanisms, however, predicts a ^{13}C distribution in the naphthalene obtained from azulene-*4*-^{13}C which disagrees markedly with the experimental results of Wentrup et al.[11]

Some of the mechanisms in Schemes I–V can be modified in ways which alter the predicted ^{13}C distributions. In the spiran mechanism, for example, variations in the degree of equilibration via intermediate **9** can change the predicted α:β:γ ratio all the way from 40:40:20 to 50:0:50. By juggling a sufficiently large

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(17) A mechanism similar to this has been suggested for the *photochemical* conversion of azulene to naphthalene: Kaupp, G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 150–68; section 4.1. We thank Professor Wentrup for bringing this reference to our attention.

(18) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 129–30.

number of such variables it would be possible to fit these mechanisms to virtually any experimental data, although we have not attempted to do so.

As experimentral results accumulate on the isomerization of azulene to naphthalene, it becomes increasingly clear that more than a single pathway must be involved. At high temperatures, the partitioning of a reaction among several competing pathways is less sensitive to differences in activation energies than at ordinary temperatures, of course, so multiple mechanisms should not be unexpected. Individually, all of the mechanisms in Schemes I–V fail to accommodate the experimental results; however, none of them can be totally excluded as partial contributors to the overall reaction.

Automerization. From the previous reports on thermal interconversions of 1- and 2-substituted azulenes (eq 2),[7] it is not clear whether such rearrangements involve true skeletal reorganizations or simply substituent migrations. Our results unambiguously show that azulene-*1*-^{13}C can isomerize to azulene-*2*-^{13}C in the gas phase at 785 °C, albeit to a minor extent with respect to naphthalene formation (ca. 1:90). Furthermore, we have discovered additional products of automerization which were not (or could not be) detected by the use of substituents as labels. Thus a ^{13}C label originating at the 1 position in azulene can migrate not only to the 2 position but also to the 3a(8a) position and even to the 4(8) position in the other ring. Scrambling of the label to distant sites in the molecule occurs less readily than migration to an adjacent position. Completely analogous results have been reported recently by Wentrup et al.[11]

As presented, the mechanisms in Schemes I–V cannot account for our automerization results. The spiran mechanism does provide a pathway (via **9**) for the scrambling of carbon atoms within the five-membered ring but fails to rationalize the observed migration of label from position 1 to position 4 (and the reverse process). Thus, the mechanism of automerization remains unknown.

Conclusions

The experiments presented here are very simple and yield fundamental new information about the high-temperature rearrangements of azulene. Several mechanistic pathways have been proposed for the isomerization of azulene to naphthalene (Schemes I–V), but none can adequately account for our results (Tables I and II). From all the data presently available, it seems most probable that azulene rearranges to naphthalene by more than one pathway. Other recent investigators have reached the same conclusion[10,11] and have offered experimental support for at least partial involvement of the mechanisms in Schemes II, IV, and V. None of the proposed pathways, however, can be completely discarded.

Under the conditions employed here, scrambling of the carbon atoms within azulene (automerization) does occur as a minor process. The mechanism of automerization is not known.

A complete understanding of azulene thermal rearrangements has not yet been achieved. Further labeling studies should provide a broader data base to guide future mechanistic thought, and good kinetic studies in a flow system of variable surface area are needed to probe the question of wall catalysis.

Experimental Section

3-Phenylpropanoic Acid-*1*-^{13}C.[19] A 250-mL three-neck flask was fitted with an addition funnel, a reflux condenser, and a CO_2 inlet tube designed to extend below the surface of the reaction mixture. The CO_2 inlet tube was connected through a stopcock to the CO_2 generator (see below). The top of the condenser and the CO_2 generator were also both connected, through stopcocks, to a manifold attached to a water aspirator and a nitrogen source. The entire system was flame-dried under nitrogen before use. A magnetic stirring bar and 1.90 g (79.2 mmol) of oven-dried magnesium turnings were placed in the reaction vessel, and the addition funnel was charged through a serum cap with 10.0 mL (73.2 mmol) of 2-phenylethyl bromide (98%, Aldrich) and 200 mL of freshly distilled ether. The alkyl bromide solution was added dropwise to the magnesium turnings with constant stirring over a period of 30 min, during which the reaction mixture refluxed spontaneously. Heat was applied to maintain reflux for an additional 1.5 h. The brown solution of Grignard reagent was then cooled to liquid nitrogen temperature, and the entire system, including the CO_2 generator, was evacuated.

The CO_2 generator consisted of a 100-mL three-neck flask equipped with an addition funnel and a magnetic stirrer. One gas line was connected to the CO_2 inlet in the Grignard reaction flask and another gas line was connected to the manifold as previously described. After the Grignard reagent was prepared, it was frozen solid with liquid nitrogen, and the entire system was evacuated. The stopcock between the manifold and the aspirator was then closed, and the solution of Grignard reagent was allowed to warm up to −20 °C in a dry ice/H_2O/$CaCl_2$ bath. All remaining stopcocks on the manifold were then closed so that the CO_2 would pass into the solution of Grignard reagent through the inlet tube. Generation of $^{13}CO_2$ was begun by the careful, dropwise addition of 80 mL of concentrated sulfuric acid onto 10.177 g (51.3 mmol) of dry $Ba^{13}CO_3$ (90%, Stohler) and continued at such a rate that CO_2 evolution did not become too vigorous. The reaction mixture was stirred 1 h more at −20 °C after completion of the CO_2 generation.

The reaction mixture was finally warmed to 0 °C and quenched with dilute HCl. The ether layer was separated and washed once with dilute HCl, and the combined aqueous layers were extracted with three 200-mL portions of ether. The combined ether extracts were then concentrated to a small volume and extracted with six equal portions of saturated $NaHCO_3$ solution to separate the phenylpropanoic acid from neutral byproducts. The combined aqueous extracts were acidified with concentrated HCl and extracted with six 250-mL portions of ether. The combined ether extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give 7.967 g (91.5% yield based on $Ba^{13}CO_3$) of 3-phenylpropanoic acid-*1*-^{13}C as a white, crystalline solid, mp 46.5–48.5 °C [lit.[20] mp 47.5–48.5 °C for unlabeled material].

Azulene-*1*-^{13}C. A 3.5 g sample of 3-phenylpropanoic acid-*1*-^{13}C (90% ^{13}C) was converted to the corresponding acid chloride with excess thionyl chloride and then to the diazo ketone with 1 equiv of diazomethane as previously described.[13] Cyclization and dehydration according to conditions detailed elsewhere[12] gave azulene-*1*-^{13}C which was sublimed prior to use (13% overall yield): ^{13}C NMR ($CDCl_3$) δ 140.1 (3a, 8a), 137.1 (6), 136.9 (2), 136.5 (4, 8) 122.6 (5, 7), 117.9 (1, 3).

1-Diazo-4-phenyl-2-butanone-*1*-^{13}C. A 1.021-g sample of (*N*-[^{13}C]-methyl-*N*-nitroso)-*p*-tolylsulfonamide (90% ^{13}C, Merck) was mixed with 3.989 g of unenriched material (1.1% ^{13}C) to give 5.010 g (23.4 mmol) of diazomethane precursor which was calculated to contain 19% ^{13}C in the *N*-methyl group. This precursor gave 17.5 mmol of diazomethane-^{13}C (19% ^{13}C) as an ethereal solution when treated with base in the usual way.[21] The diazomethane solution was cooled to −78 °C and treated with 1 equiv each of triethylamine and 3-phenylpropanoyl chloride according to our previously described procedure[13] to give 2.995 g (98.4% yield based on $^{13}CH_2N_2$) of 1-diazo-4-phenyl-2-butanone-*1*-^{13}C as a bright yellow oil.

Azulene-*3a*-^{13}C. A 2.995-g sample of 1-diazo-4-phenyl-2-butanone-*1*-^{13}C (19% ^{13}C) was cyclized and the resulting trienone dehydrated as described previously[12] to give azulene-*3a*-^{13}C which was sublimed prior to use (7% overall yield): ^{13}C NMR ($CDCl_3$) δ 140.1, 137.1, 136.9, 136.5, 122.6, 117.9.

Thermal Rearrangements. The flow system was assembled from a simple quartz tube (400 mm × 16 mm internal diameter) with ground joints. A glass coil trap was attached to one end of the tube and immersed in liquid nitrogen. A flask containing 18–45 mg of azulene was connected to the other end of the tube by means of a side-arm adapter (simple distillation head). A nitrogen inlet needle was inserted through a serum cap on the third opening of the adapter. Heating of the quartz tube was effected by a multiple unit electric furnace (Hevi Duty Electric Co., Milwaukee). The "hot zone" was taken to be the region within the furnace which was lined with heating coils (355-mm length or 71.5-mL volume). Temperatures were measured with a chromel/alumel thermocouple and varied as much as 30 °C from the center of the hot zone to the edge. Temperatures reported in the text correspond to the center of the hot zone and therefore slightly overstate the severity of the average conditions. Contact times were easily adjusted by varying the nitrogen flow rate, which was measured with a common GLC bubbler at the exit port of the trap. Flow rates were monitored before, during, and after each run. At room temperature with the nitrogen flow rates used (30–60 mL/min), azulene sublimes too slowly to be practical. Therefore, the sample flask and side-arm adapter were warmed to about 60 °C with a kugelrohr oven and a heating tape, respectively, to attain the desired rate of sublimation (ca. 5–10 mg/h). All glassware was washed successively

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(19) This procedure was patterned after that reported by Staab, H. A.; Haenel, M. *Chem. Ber.* **1970**, *103*, 1095.

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with $Na_2Cr_2O_7/H_2SO_4$, concentrated NH_4OH, soap, and distilled water prior to each run. At the end of each run, the trap was rinsed with EtOH or pentane, and the solvent was cautiously evaporated. Under conditions which gave complete conversion of azulene, the pale yellow residue was either sublimed or analyzed directly by ^{13}C NMR spectroscopy; no products other than naphthalene were detected by NMR. Under conditions which gave incomplete conversion, the azulene and naphthalene were separated and collected by preparative GLC (5 ft × $^1/_4$ in., 15% Carbowax 20M on Chromosorb W). The incomplete material balance (30–50%) is attributed principally to losses in trapping and product isolation.

Appendix

The method for calculating the amount of ^{13}C label at various positions in azulene and naphthalene is illustrated here for the thermal rearrangement of azulene-*3a*-^{13}C. A set of four equations with four unknowns was developed using the following definitions: $R \equiv$ the amount of ^{13}C derived from natural abundance at a given position (later to be given a value of 1.108% per atom);[22] $A_x \equiv$ the total amount of ^{13}C from all sources (natural abundance + enrichment) at position x in azulene; $N_x \equiv$ the total amount of ^{13}C from all sources (natural abundance + enrichment) at position x in naphthalene; $I_x \equiv$ intensity of the ^{13}C NMR signal from the atom at position x in an unenriched sample (natural abundance); and $I_x' \equiv$ intensity of the ^{13}C NMR signal from the atom at position x in an enriched sample.

The first equation simply states that the total amount of ^{13}C in the original azulene must equal the total amount of ^{13}C in the derived naphthalene.

$$A_{1,3} + A_2 + A_{3a,8a} + A_{4,8} + A_{5,7} + A_6 = N_\alpha + N_\beta + N_\gamma \quad \text{(A1)}$$

Since it is known from the synthesis that all the enrichement resides at positions 3a and 8a in the original azulene, eq A1 can be simplified to

$$A_{3a,8a} + 8R = N_\alpha + N_\beta + N_\gamma \quad \text{(A2)}$$

The remaining three equations (eq 7-9) all depend on the premise that an increase in the amount of ^{13}C at a given position in a molecule will cause a corresponding increase in the intensity of the ^{13}C NMR signal associated with that position (relative to a standard), e.g.,

$$I'_\alpha/I_\alpha = N_\alpha/4R \quad \text{(A3)}$$

$$I'_\beta/I_\beta = N_\beta/4R \quad \text{(A4)}$$

$$I'_\gamma/I_\gamma = N_\gamma/2R \quad \text{(A5)}$$

The accuracy of the data obtained by the method developed here (see discussion of error below) attests to the validity of this premise. Equations A3 and A4 can be combined to give

$$\frac{I'_\alpha/I_\alpha}{I'_\beta/I_\beta} = \frac{N_\alpha/4R}{N_\beta/4R} \quad \text{(A6)}$$

Rearranging the left side of eq A6 gives a form for which NMR data are available.

$$\frac{I'_\alpha/I'_\beta}{I_\alpha/I_\beta} = \frac{N_\alpha}{N_\beta} \quad \text{(A7)}$$

Combining eq A3 and A5 and rearranging in like manner gives

$$\frac{I'_\gamma/I'_\alpha}{I_\gamma/I_\alpha} = \frac{2N_\gamma}{N_\alpha} \quad \text{(A8)}$$

In the ^{13}C NMR spectrum of azulene, the signals from atoms 2, 4, 6, and 8 fall too close together to permit reliable individual integration, so they were integrated collectively. The final equation can then be derived as above.

$$\frac{I'_{3a,8a}/I'_{2,4,6,8}}{I_{3a,8a}/I_{2,4,6,8}} = \frac{A_{3a,8a}}{2R} \quad \text{(A9)}$$

Thus we have four equations (A2, 7, 8, 9) with four unknowns (N_α, N_β, N_γ, $A_{3a,8}$), all expressed in terms of experimentally available peak intensity ratios from individual NMR spectra and the constant R. Note that the percent ^{13}C at the site of enrichment in the original azulene is treated as an unknown ($A_{3a,8a}$) so that all ^{13}C percentages rely on the same analytical method. By comparison of data from the spectra of enriched and natural abundance samples of azulene (eq A9), an NMR value of 18.6% ^{13}C is obtained for $A_{3a,8a}$. The actual value is 19.2% ^{13}C (see Experimental Section). Thus, the error associated with this NMR analysis falls in the range of ±3%.

The values of N_α, N_β, and N_γ obtained by the above treatment represent the *total* amount of ^{13}C at each position in naphthalene, and the contribution from natural abundance must be subtracted in order to obtain the distribution of just the ^{13}C label.

The naphthalene and recovered azulene from azulene-*1*-^{13}C were analyzed in an entirely analogous manner.

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