Thermal Rearrangements of Aromatic Compounds[1]

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Thermal rearrangements abound in organic chemistry. Most commonly, they can be found among the reactions of polyolefins, especially those in strained ring systems and have been studied both in the gas phase and in solution. Aliphatic compounds of the general formula $(CH)_n$ provide perhaps the most bewildering networks of thermal interconversions yet known, but the mapping of $(CH)_n$ energy surfaces still remains far from complete.[2]

Much of the fascination with thermal rearrangements stems from their simple beauty. The molecules involved often contain multiple rings arranged in an aesthetically pleasing three-dimensional geometry. The reactions are unimolecular, requiring no reagents other than heat. No heteroatoms or exotic functional groups are generally necessary; in fact, purely hydrocarbon systems have received the greatest amount of attention.

These features combine to make thermal rearrangements an attractive area of study not only for experimentalists but also for theoreticians. Large-molecule calculations have always proven more reliable for hydrocarbons than for compounds composed of more varied atoms, and unimolecular processes present fewer unknowns than do those of higher molecularity. On a different theoretical level, the Woodward–Hoffmann rules of orbital symmetry conservation[3] have also figured prominently in the development of this field, since a great many thermal rearrangements pass through pericyclic transition states. Controversies over which isomerizations take place via concerted mechanisms and which follow stepwise pathways have arisen repeatedly and will doubtless continue for many years to come.

Against this background, thermal rearrangements of aromatic compounds have emerged as a relatively new field of study. So entrenched has the historical distinction between aliphatic and aromatic compounds become that most chemists would regard members of the latter class as immune to thermal rearrangements.[4] Indeed, the extra thermodynamic stability associated with compounds that qualify as aromatic in the classical sense[4] should offer some protection to such molecules, but in quantitative terms this protection cannot exceed the magnitude of the delocalization energy lost during the course of isomerization. At sufficiently high temperatures, the large activation energy barriers which characterize thermal rearrangements of aromatic compounds can often be overcome. Photochemical rear-

rangements are also possible, of course, but fall outside the scope of the present subject.[2]

In this Account, attention will be given only to compounds which qualify as aromatic in the classical sense[4] and will focus primarily on hydrocarbons. The extensive chemistry of annulenes and their relatives will not be treated here. Attention will be further restricted to thermal rearrangements which directly involve atoms of the aromatic ring system, not just its substituents.

Within this framework, two major types of reactions can be identified. One entails a complete and permanent skeletal reorganization, as illustrated by the thermal isomerization of azulene to naphthalene (eq 1).
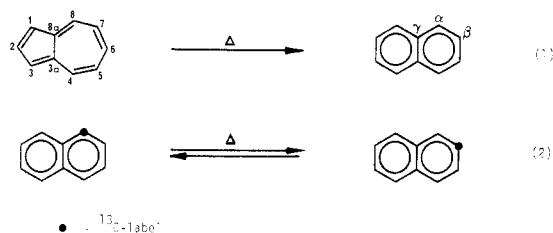
The other leads to no net change in the aromatic ring system but scrambles the atoms; such "automerization"[5] can be detected only by the presence of substituents or, preferably, by isotopic labels, as illustrated by the thermal automerization of naphthalene (eq 2).

Current research in this field follows two main lines. One is the search for new examples of thermal rearrangements of aromatic compounds. The other line aims at the design and execution of experiments intended to provide mechanistic insight. Do any of these reactions proceed via pericyclic transition states? If so, are the rules of orbital symmetry conservation obeyed? At the high temperatures required, do any totally new types of reactions emerge? Until fairly recently, mechanistic speculation has soared almost entirely unfettered by experimental facts.

This Account covers many different thermal rearrangements of aromatic compounds which span the

Professor Scott was born in Ann Arbor, MI, on June 11, 1944. He began working on $(CH)_n$ compounds as an undergraduate student with M. Jones, Jr., at Princeton University and continued research in the same area as a graduate student with R. B. Woodward at Harvard University (Ph.D., 1970). He then joined the faculty at UCLA and maintained an active interest in $(CH)_n$ compounds while initiating new research programs in other areas. In 1975 he moved to the University of Nevada, Reno, where he is now Professor of Chemistry. Dr. Scott's current research focuses on problems of cyclic conjugation in organic chemistry, particularly the synthesis and study of bridged annulenes, nonbenzenoid quinones, homoconjugated cyclic polyacetylenes, bridged homoaromatic ions, and fused bicyclic π systems, as well as the subject of this Account.

(1) This paper is part 5 in a series on "Thermal Rearrangements of Aromatic Compounds". For previous papers in the series, see: (a) Part 4: Scott, L. T.; Kirms, M. A. *J. Am. Chem. Soc.* 1981, *103*, 5875–9. (b) Part 3: Scott, L. T.; Highsmith, J. R. *Tetrahedron Lett.* 1980, 4703–6. (c) Part 2: Scott, L. T.; Kirms, M. A.; Minton, M. A. *Croatica Chem. Acta* 1980, *53*, 643–7. (d) Part 1: Scott, L. T.; Agopian, G. K. *J. Am. Chem. Soc.* 1977, *99*, 4506–7.

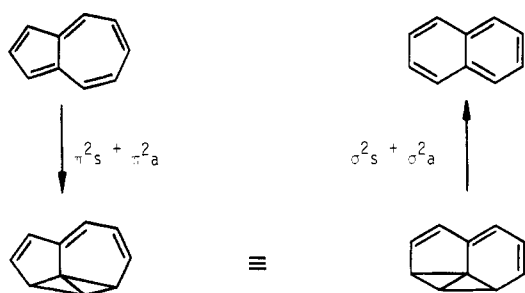(2) Scott, L. T.; Jones, M., Jr. *Chem. Rev.* 1972, *72*, 181–202.

(3) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.

(4) For a readable discussion of aromaticity, see: Lewis, D.; Peters, D. "Facts and Theories of Aromaticity"; Macmillan: London, 1975.
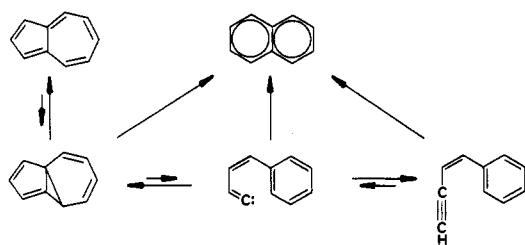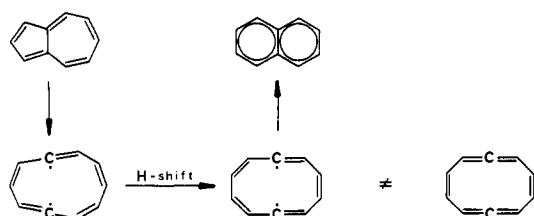
(5) The term "automerization" was introduced by Balaban to describe those isomerizations which are degenerate in the absence of a label: Balaban, A. T.; Farcasiu, D. *J. Am. Chem. Soc.* 1967, *89*, 1958–60. Unfortunately, the reaction to which this useful descriptor was first applied was later shown not to occur: Staab, H. A.; Haenel, M. *Angew. Chem., Int. Ed. Engl.* 1968, *7*, 548. Balaban, A. T.; Farcasiu, D.; Koptyug, V. A.; Isaev, I. S.; Gorfinkel, M. I.; Rezvukhin, A. I. *Tetrahedron Lett.* 1968, 4757. Staab, H. A.; Haenel, M. *Chem. Ber.* 1970, *103*, 1095.

Thermal Rearrangements

Scheme I

$$\pi^2{}_s + \pi^2{}_a$$

$$\sigma^2{}_s + \sigma^2{}_a$$

≡

Scheme II

Scheme III

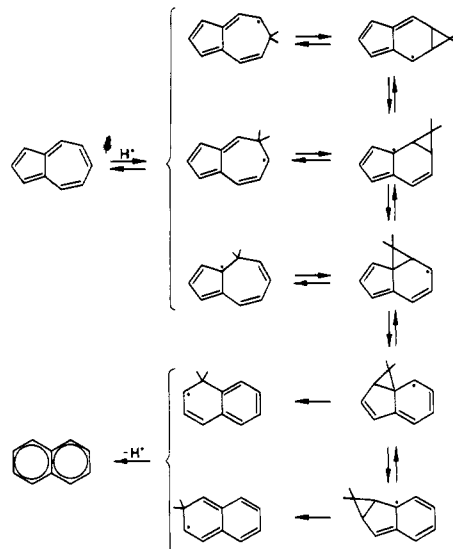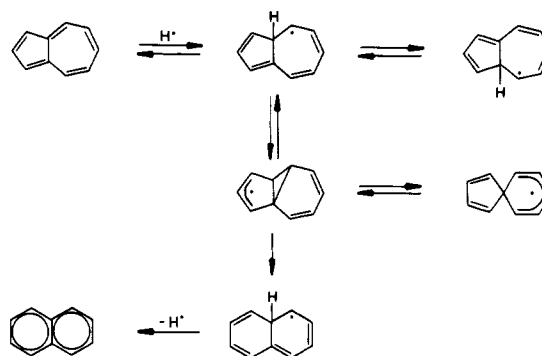H-shift

≠

Scheme IV

Scheme V

breadth of the field. Pertinent experimental facts are drawn together, both from the author's laboratory and from elsewhere, to provide a basis for critical evaluation of various mechanistic proposals.

Azulene

Thermal rearrangements of substituted azulenes were first noticed by natural products chemists early in this century during structural studies on sesquiterpenes.[6] Isomerization of the unsubstituted azulene molecule to naphthalene (eq 1) was subsequently reported by Heilbronner et al. in 1947.[7] Since azulene meets all the standards for aromaticity in the classical sense,[4] including the criterion of a large delocalization energy, despite the absence of benzene rings, this transformation represents the oldest, unequivocal, thermal rearrangement of an aromatic compound. It has also received more attention than any other over the years.

On the basis of kinetic studies conducted in the 1950s, Heilbronner concluded[8] that the rearrangement of azulene to naphthalene is "...essentially homogeneous and monomolecular" in the gas phase over the temperature range 370–430 °C. He further reports[8] a relatively large free enthalpy of activation ($\Delta H^{\ddagger}$ = 48.8 ± 0.8 kcal/mol) and a slightly negative entropy of activation ($\Delta S^{\ddagger}$ = −5.3 ± 3.6 eu) but cautions that "...both values require fur-

ther confirmation". Indeed, recent work (vide infra) indicates that the situation may be more complicated than once thought, and additional kinetic studies would be most welcome.

Schemes I–V outline several mechanisms which have been proposed to account for the thermal rearrangement of azulene to naphthalene. One of these (Scheme I)[1d] involves a pair of successive, symmetry-allowed pericyclic reactions. Two other unimolecular pathways (Schemes II and III) pass through carbene[9] and diradical intermediatess,[1a] respectively. The remaining proposals (Schemes IV and V)[10] call for addition of a hydrogen atom (or ion) of unspecified origin to initiate the reaction; rearrangement would then take place on the $C_{10}H_9$ energy surface before final expulsion of the extra hydrogen. Complete equilibration among intermediates before opening to a bicyclo[4.4.0] system is assumed in Schemes IV and V.[10]

Experimental research on this rearrangement has concentrated mainly on establishing which atoms of azulene become which atoms of naphthalene. Extensive work with methyl substituents[8,10,11] has been followed by very recent ^{13}C-labeling studies on the unsubstituted

(6) (a) Heilbronner, E. In "Nonbenzenoid Aromatic Compounds"; Ginsburg, D., Ed.; Interscience: New York, 1959. (b) Gordon, M. *Chem. Rev.* **1952**, *50*, 127–200.

(7) Heilbronner, E.; Plattner, P. A.; Wieland, K. *Experientia* **1947**, *3*, 70. Heilbronner, E.; Wieland, K. *Helv. Chim. Acta* **1947**, *30*, 947–56.

(8) Heilbronner, E., in ref 6a, pp 263–268, discusses unpublished work from his laboratory: Kallen, H. J. Ph.D. Dissertation, Eidgenössische Technische Hochschule, Zürich, 1958.

(9) Becker, J.; Wentrup, C.; Katz, E.; Zeller, K.-P. *J. Am. Chem. Soc.* **1980**, *102*, 5110–12.

(10) (a) Alder, R. W.; Whittaker, G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 714–23. (b) Alder, R. W.; Wilshire, C. *Ibid.* **1975**, 1464–8. (c) Alder, R. W.; Whiteside, R. W.; Whittaker, G.; Wilshire, C. *J. Am. Chem. Soc.* **1979**, *101*, 629–32.

(11) Prislopski, M. C. M.S. Thesis, Wesleyan University, Middletown, CN, 1973.

Table I
Compounds Used in Labeling Experiments to Study the
Azulene → Naphthalene Rearrangement (Eq 1)

singly labeled azulenes	ref	multiply labeled azulenes	ref
1-^{13}C	1a	1-^{13}C,2-CH$_3$	10c
3a-^{13}C	1a, c	2-^{13}C,2-^{13}CH$_3$	10b
4-^{13}C	9	1,2-dimethyl	10b
2-D	10b	1,3-dimethyl	10a
4-D	9	4,5-dimethyl	10a
1-CH$_3$	10a	4,6-dimethyl	10a
2-CH$_3$	8, 10a	4,7-dimethyl	10a
4-CH$_3$	10a	4,8-dimethyl	11, 10a
5-CH$_3$	10a	5,6-dimethyl	10a
6-CH$_3$	10a	5,7-dimethyl	10a
1-CN	10b	4,5-dicarbomethoxy	10a
2-CN	10b	4,5-(-CO-O-CO-)	10a
		4,5-(-CO-NMe-CO-)	10a
		1,2-benzo	10a
		5,6-benzo	10a
		4,6,8-trimethyl	11
		4,7-^{13}C$_2$	12a

parent hydrocarbon.[1a,c,9,12a] Table I lists all the azulenes examined to date in this regard. Where comparisons can be made between the results from different laboratories, the agreement is generally satisfactory, despite wide variations in experimental conditions. Changes in temperature, surface composition, and surface area have little effect on the product distributions.[1,9,10] Neither the starting materials nor the products suffer significant scrambling of the label,[1,10] except in one case.[9]

Although a detailed tabulation of data from all the experiments listed in Table I cannot be given here, one important conclusion stands out clearly: *No single mechanism yet proposed (Schemes I–V) can adequately account for all the experimental facts.* Each mechanism predicts a particular labeling pattern in the naphthalene obtained from each azulene in Table I; however, none of the mechanisms considered thus far correctly predicts the outcome of all the labeling experiments. When azulene isomerizes to naphthalene under the conditions used in these experiments, therefore, it must do so either via some other pathway which has yet to emerge or by a combination of two or more mechanisms.

Supplementary experiments strongly support the latter explanation. Independent generation of the carbene intermediate in Scheme II, for example, gives both azulene and naphthalene as well as phenylbutenyne (cis and trans).[9] Interconversion of azulene and phenylbutenyne, in competition with naphthalene formation from each has also been demonstrated.[9] These results implicate the mechanism in Scheme II as one pathway by which azulene rearranges to naphthalene. Since some, but not all (vide supra), of the azulene rearranges by this mechanism, the remainder must re-

arrange by one or more additional pathways. Thus, the multiple-mechanism picture, with the pathway outlined in Scheme II as one component, appears inescapable.

The fact that different mechanisms compete effectively in high-temperature reactions should actually occasion no surprise. At room temperature, a difference in $\Delta G^{\ddagger}$ of just 2.0 kcal/mol between two competing mechanisms will suffice to channel 97% of the reaction along the lower energy pathway.[12b] At 800 °C, however, the same partitioning between two mechanisms requires a difference in $\Delta G^{\ddagger}$ of more than 7.0 kcal/mol.[12b] For a single pathway to dominate at high temperatures, therefore, it must be energetically favored by a substantial margin.

What other mechanisms compete with the pathway shown in Scheme II? Contary to the original conclusions of Heilbronner and Kallen,[8] recent evidence points to the operation of a mechanistic component which is not "homogeneous and monomolecular". It has been reported for example, that (1) radical initiators promote the rearrangement of azulene to naphthalene,[10a] (2) an induction period can be observed in the experiments conducted in sealed ampules,[10c] and (3) the naphthalene obtained from thermal isomerization of azulene-4-d consists of d_0, d_1, and d_2 material in a ratio of ca. 12:76:12.[9] The radical pathways in Schemes IV and V nicely accommodate all of these observations, although their involvement cannot be considered proven. As Alder has pointed out,[10c] the pathways in Schemes IV and V, taken together, successfully account for essentially all the products and labeling patterns observed in the experiments based on substituted azulenes (see Table I) without predicting other products which are not observed. Unfortunately, the ^{13}C-labeling results do not agree so well in a quantitative sense.[1a,c,9,12a] Nevertheless, these radical pathways represent likely contributors to the overall reaction.[12a]

Are the pathways in Schemes I and III followed at all? Do still other pathways contribute? At this stage, it is difficult to exclude *any* mechanism as an additional partial contributor.[12a] It can be shown, in fact, that no linear combination of the three mechanisms in Schemes II, IV, and V will quantitatively account for the ^{13}C-labeling results. Either one (or more) of these mechanisms must therefore be modified or an additional pathway must also be accessible. Such complexity is most ungratifying.

If the nonhomogeneous component of this reaction could be suppressed, the multimechanism picture might simplify to just one or two unimolecular pathways. With this goal in mind, we have recently sought and found a method to induce the rearrangement of azulene to naphthalene in the gas phase with a CO_2 laser beam.[13,14] Under such conditions, the walls of the cylindrical cell remain relatively cool so that surface catalysis should be minimized. Studies with ^{13}C-labeled azulenes have just begun.[14]

Superimposed on this already complicated picture and in competition with the rearrangement of azulene to naphthalene, azulene-to-azulene isomerizations (autotomerizations) have also been observed. Reports in the

(12) (a) After writing this Account, I learned of a beautiful double-labeling experiment on the thermal rearrangement of azulene-4,7-^{13}C$_2$. The ^{13}C-label distribution in the naphthalene-^{13}C$_2$ obtained from this experiment *unambiguously excludes* both the bicyclobutane pathway (Scheme I) and the methylene walk pathway (Scheme IV) as significant contributors to the composite mechanism. The experimenters cite this new result as support for the pathway in Scheme II; however, those illustrated in Schemes III and V are equally compatible. I thank these investigators for a preprint of the article which has now appeared: Zeller, K.-P.; Wentrup, C. *Z. Naturforsch. B* 1981, *36B*, 852–7. (b) Calculations based on rate ∝ (kT/h) exp$(-\Delta G^{\ddagger}/RT)$ from absolute rate theory: Eyring, H. *Chem. Rev.* 1935, *17*, 65.

(13) For a nice example of the possible differences between laser excitation and classical flow system pyrolysis, see: Berman, M. R.; Comita, P. B.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* 1980, *102*, 5692–4.
(14) Earl, B. L.; Scott, L. T. *Spectrochim. Acta, Part A* 1980, *36A*, 649–51, and subsequent unpublished work.

old sesquiterpene literature on rearrangements such as that illustrated in eq 3 were followed by a careful study

(3)
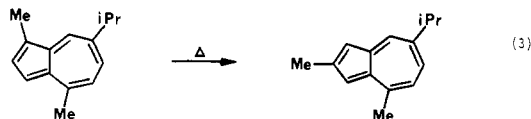
on the interconversion of 1- and 2-phenylazulene, approaching the equilibrium from both sides.[6] More recent investigations with methyl-substituted azulenes have furthermore shown that small amounts of isomeric methylazulenes invariably accompany the α- and β-methylnaphthalenes formed at high temperatures (440 °C, ca. 0.05 atm, 2 h).[10] Since the isomeric methylazulenes always constitute less than 2% of the product mixture, however, the activation energy for this process must be significantly greater than that for isomerization to the naphthalene ring system.

From such experiments, it is not clear whether the azulene-to-azulene rearrangements involve true skeletal reorganizations or simply substituent migrations. Two recent ^{13}C-labeling studies,[1a,9] however, demonstrate that the ring atoms of azulene actually can change positions at high temperatures. Thus, a second, completely distinct, thermal rearrangement of this $C_{10}H_8$ aromatic hydrocarbon has been established. More specifically, automerization to an extent of 2–3% was noted during the isomerization of azulene-*1*-^{13}C to naphthalene-[13]C (785 °C, 1 atm of N_2 carrier gas in a flow system, contact time = 2.2 min).[1a] Scrambling of the label was also detected in the recovered azulene from flash vacuum pyrolysis of azulene-*4*-[13]C (1000 °C, 10^{-3} torr).[9] The partitioning between automerization and rearrangement to naphthalene-^{13}C in this latter reaction (ca. 50:50)[9] contrasts sharply with that observed in all other cases (ca. 2:98)[1a,10] and presumably depends on the unique conditions employed.

In all the azulene automerizations reported to date, migration of the label (either ^{13}C or a substituent) to an adjacent position of the aromatic nucleus predominates over relocation to more distant sites. Migration of ^{13}C labels between the 1(3) position in the five-membered ring and the 4(8) position in the seven-membered ring of azulene, however, has actually been observed in both directions as a measurable process.[1a,9]

None of the mechanisms in Schemes I–V, as presented, can account for the automerization results. Scheme IV could explain the scrambling of atoms within the seven-membered ring, and Scheme V provides a pathway (via 9) for scrambling atoms within the five-membered ring, but none can account for migration of a label from one ring to the other. Thus the mechanism of azulene automerization also remains unknown. Hopefully, the laser experiments on ^{13}C-labeled azulenes will provide new insights into both types of azulene thermal rearrangements.[14]

Naphthalene

Can naphthalene rearrange thermally back to azulene (eq 4)? In principal, all reactions are reversible.

(4)
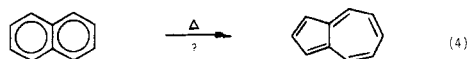
Attempts to detect such a transformation by passage of naphthalene through a quartz tube at 1080 °C

(contact time $\simeq$ 2 s) gave back naphthalene unadulterated by azulene (<1 ppm).[15] Higher temperatures and longer contact times greatly reduced the recovery of monomeric material. Since the isomerization in eq 4 would be endothermic by nearly 40 kcal/mol[16a] and must overcome a $\Delta G^{\ddagger}$ of approximately 90 kcal/mol,[16b] the experimental results can hardly be considered surprising. In fact, the future discovery of any thermal isomerization which leads to a permanent skeletal change in this very stable $C_{10}H_8$ hydrocarbon appears quite unlikely.

Automerization of naphthalene (eq 2), on the other hand, has been revealed by ^{13}C labeling.[1d] This reaction constitutes the first documented thermal rearrangement of a *benzenoid* aromatic hydrocarbon in which the ring atoms are known to move. The high-temperature equilibration of α- and β-methylnaphthalene, which superficially resembles the transformation in eq 2, has been shown to occur by migration of the substituents only, while the ring atoms remain in place.[17] Interconversions of other substituted naphthalenes presumably follow a similar course and likewise do not represent true ring automerizations.

As expected from the difference in delocalization energies of naphthalene and azulene,[18] automerization of the benzenoid isomer has a $\Delta G^{\ddagger}$ some 30 kcal/mol higher than that for azulene thermal rearrangements and requires far more brutal conditions (half-life $\simeq$ 2 s at 1035 °C).[1d] No automerization of naphthalene occurs, therefore, under the less severe conditions employed during the azulene-to-naphthalene rearrangement studies described in the previous section.

At 1035 °C in a flow system, naphthalene-*1*-^{13}C isomerizes reversibly to naphthalene-*2*-[13]C (eq 2), but no ^{13}C label leaks into the angular position (γ) even under conditions which yield an α:β ratio of nearly 50:50 (contact time $\simeq$ 10 s).[1d] To explain these results, we originally proposed that naphthalene might rearrange first to azulene (eq 4) and then back again (eq 1) according to the mechanism in Scheme I.[1d] Subsequent ^{13}C-labeling studies on the isomerization in eq 1, both in Reno[1a,c] and elsewhere,[9,12a] however, have proven that azulene does not rearrange to naphthalene via the pathway in Scheme I to any major extent (vide supra). Furthermore, these recent studies show that reversible formation of azulene from naphthalene-*1*-^{13}C would necessarily produce both β- and γ-labeled naphthalene in significant amounts. Since no naphthalene-γ-^{13}C was observed experimentally, even after several half-lives of $\alpha \rightleftharpoons \beta$ scrambling, *the automerization of naphthalene cannot involve azulene as an intermediate.*

What is the mechanism, then, for naphthalene automerization? Several unimolecular pathways can be envisaged. Reversible formation of polycyclic inter-
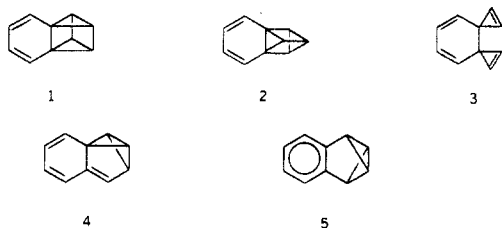
(15) Scott, L. T.; Utterback, D., unpublished results.

(16) (a) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. (b) The $\Delta G^{\ddagger}$ for eq 4 is estimated from $\Delta G^{\ddagger}$ for isomerization in the reverse direction[8] (eq 1) and ΔG for the overall reaction.[16a]

(17) Vorozhtsov, N. N., Jr.; Koptyug, V. A. *J. Gen. Chem. USSR* **1960**, *30*, 1014.

(18) Although a wide range of absolute values for the delocalization energies of both azulene and naphthalene have been reported, there is general agreement that the *difference* in delocalization energy between the two equals ca. 30 kcal/mol: (a) Badger, G. M., "Aromatic Character and Aromaticity"; Cambridge University Press: Cambridge, 1969; pp 45, 50. (b) Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969; p 177.

mediates such as **1, 2, 3,** or **4,** for example, would suc-

cessfully account for the scrambling of α and β (but not γ) carbon atoms in naphthalene. An upper limit on $\Delta G^{\ddagger}$ of ca. 86 kcal/mol (at 1035 °C) has been measured for naphthalene automerization,[1d] however, so the exorbitantly strained hydrocarbons **1–3** can be rigorously excluded on energetic grounds.[19a] For compound **4,** one can estimate a $\Delta H_f^{\circ} \cong 120.9$ kcal/mol, i.e., 84.8 kcal/mol above naphthalene,[19b] which makes it (barely) an energetically permissible intermediate. The isomeric naphthvalene, **5,** undoubtedly lies lower in energy than **4** but could lead to an interchange only of β-carbon atoms with each other.

Scheme VI outlines an alternative mechanism for naphthalene automerization which resembles the "methylene walk" pathway previously proposed for azulene isomerization (cf. Scheme IV). As in the azulene case,[8] however, changes in the surface area of the hot zone produce negligible changes in the rate of rearrangement.[1d] No other evidence for or against this pathway has been reported.

The mechanism by which the α- and β-carbon atoms of naphthalene exchange positions at high temperatures thus remains unknown. Double-labeling experiments might provide further insight.

Benzene

Thermal rearrangements which lead to permanent skeletal change of the archaromatic benzene ring have been reported only twice (eq 5[20a] and 6[20b]). In both
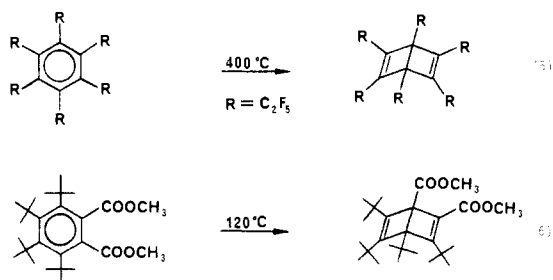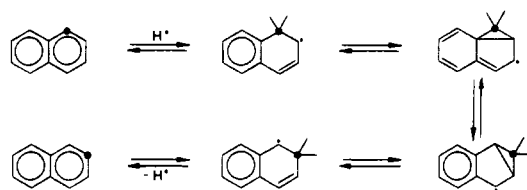

cases, relief of steric strain created by compression of contiguous bulky groups in the benzenoid isomer compensates for the loss of aromaticity. Analogous reactions of simpler benzene derivatives have never been observed.
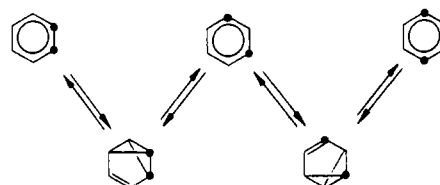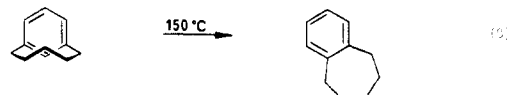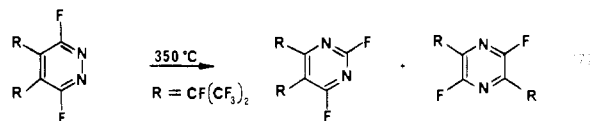
Scheme VI

Scheme VII

Table II
Isomeric Products Obtained from Thermal Rearrangement of Each $C_6H_4F_2$ (Partial Conversion)

starting material	products	
	major isomer	minor isomer
o-$C_6H_4F_2$	meta	para
m-$C_6H_4F_2$	para	ortho
p-$C_6H_4F_2$	meta	ortho

Thermal automerization of the benzene ring system has also been reported as an important process only for rather special derivatives (eq 7[21] and 8[22]). Benzvalene

intermediates were postulated to explain both of these reorganizations (Scheme VII). Although the mechanism is not known with certainty, there is no question that the ring atoms actually move in the perfluorodialkylpyridazine rearrangement (eq 7); control experiments rule out the possibility of scrambling via fragmentation–recombination or Diels–Alder dimers.[21a] In the isomerization of [5]metacyclophane (eq 8),[22a] it is less clear whether the ring atoms move or the pentamethylene arm simply migrates. Isotopic labeling studies with a more complex analogue have demonstrated that even weak acids can catalyze the rearrangement of a [5]metacyclophane to its less-strained ortho isomer without redistribution of the ring atoms.[22b]

The search for benzene automerization in less bizarre systems has recently uncovered the high-temperature

(19) (a) For a discussion of the strain energy in prismane and bicyclopropenyl, see: Grayston, M. W.; Lemal, D. M. *J. Am. Chem. Soc.* **1976,** *98,* 1278–80 and references cited therein. (b) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; Chapter 2.

(20) (a) Clifton, E. D.; Flowers, W. T.; Haszeldine, R. N. *Chem. Commun.* **1969,** 216. (b) Maier, G.; Schneider, K.-A. *Angew. Chem., Int. Ed. Engl.* **1980,** *19,* 1022–3. The analogous reaction of 1,2,3,4-tetra-*tert*-butyl-5-phenylbenzene has also been observed: Krebs, A.; Franken, E., reported at the Fourth International Symposium on Novel Aromatic Compounds, Jerusalem, Sept 1981.

(21) (a) Chambers, R. D.; Sargent, C. R.; Clark, M. *J. Chem. Soc., Chem. Commun.* **1979,** 445 and previous papers in this series. Note added in proof: The most recent report by these authors concludes that radical intermediates are probably involved: Chambers, R. D.; Musgrave, W. K. R.; Sargent, C. R. *J. Chem. Soc., Perkin Trans. 1* **1981,** 1071–7. (b) Mahler, W.; Fukunaga, T. *J. Chem. Soc., Chem. Commun.* **1977,** 307. (c) For prior work on unsubstituted pyrazine, see: Crow, W. D.; Wentrup, C. *Tetrahedron Lett.* **1968,** 3115–8.

(22) (a) van Stratten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1977,** 4667. (b) Grice, P.; Reese, C. B. *J. Chem. Soc., Chem. Commun.* **1980,** 424–5.

interconversion of *o*-, *m*-, and *p*-$C_6H_4F_2$.[1b] Table II summarizes the results. The more rapid accumulation of *m*-$C_6H_4F_2$ when starting from either the ortho or para isomer nicely agrees with predictions based on the mechanism in Scheme VII. Analogous scrambling of the xylenes has also been rationalized in this way.[23] Alternatively, a "methylene walk" mechanism (cf. Schemes IV and VI) could be formulated to fit the data. Both pathways involve migration of the ring atoms. Mechanisms requiring 1,2 shifts of fluorine cannot be rigorously excluded but find little precedent in organofluorine chemistry. The use of ^{13}C labels instead of substituents, of course, would eliminate such ambiguities, and experiments with benzene-$^{13}C_2$ are currently under way.

With regard to the thermal automerization of benzene, one final observation deserves comment. At 1000 °C, with a contact time of ca. 5 s in a flow system, $C_6H_4F_2$ suffers no detectable isomerization (less than 0.1%).[1b] The energy barrier (ΔG^*) for automerization must therefore exceed 90 kcal/mol![24] Experiment thus confirms our intuition that *benzene displays an extreme reluctance to participate in thermal rearrangements*.

Polybenzenoid Hydrocarbons

Unlike benzene and naphthalene, most of the larger benzenoid hydrocarbons belong to families comprised of two or more isomeric ring systems. Skeletal isomerization of one fully aromatic benzenoid hydrocarbon to another would represent a completely new class of thermal rearrangement. In many cases, such as in the potential conversion of anthracene to phenanthrene (eq 9), isomerization would actually be exothermic.[16a] The

$$\Delta H^* = -6 \text{ kcal/mol} \tag{9}$$
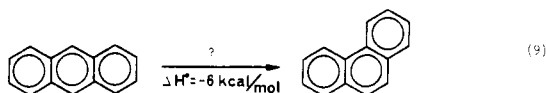
real question, then, reduces to whether or not energetically accessible pathways exist for such skeletal reorganizations.

Were the transformation in eq 9 to occur with uninterrupted preservation of one benzene ring, then the temporary loss of aromaticity in the other two rings would be less than that required for automerization of naphthalene, assuming simultaneous disruption of cyclic conjugation in two rings also during the latter reaction.[25] Conceivably, therefore, the isomerization in eq 9 could proceed more readily than the scrambling of atoms in naphthalene.

To investigate this possibility, we heated anthracene under conditions which cause extensive automerization in naphthalene (1035 °C, contact time ≅ 5 s). The recovered material, however, contained anthracene but no detectable phenanthrene.[26] Raising the temperature to 1100 °C still failed to produce any phenanthrene (<0.1%).[27] It can be concluded, therefore, that the

isomerization depicted in eq 9 must have a ΔG^* greater than that for naphthalene automerization and may require the simultaneous loss of aromaticity in all three rings at some point along the reaction pathway. Experiments with benz[*a*]anthracene at high temperatures are currently in progress.

Automerization in polybenzenoid hydrocarbons has been examined so far only in pyrene-1-^{13}C (6),[28] which

6   7   via 8?
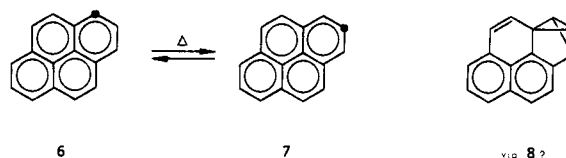
can be viewed as a derivative of naphthalene-1-^{13}C festooned with two extra benzene rings. By analogy with the known automerization of naphthalene (eq 2), 6 should interconvert thermally with pyrene-2-^{13}C (7). This anticipated automerization has, in fact, been confirmed experimentally.[27] As in the bicyclic case, no label scrambles into the angular position.

One important difference was noticed, however, between the automerization of pyrene and that of naphthalene. Whereas naphthalene-1-^{13}C rearranges to an extent of ca. 25% in a flow system at 1035 °C,[1d] pyrene-1-^{13}C scrambles only to an extent of about 3%, even at 1100 °C[27] (contact time ≅ 2 s in both cases). If these reactions were to occur via bicyclobutane intermediates 4 and 8, respectively, then pyrene would suffer the smaller loss of delocalization energy[25] and, consequently, should rearrange *faster* than naphthalene. Since we observe the opposite result experimentally,[27] mechanistic pathways involving bicyclobutane intermediates such as 4 and 8 appear unlikely for the automerization of benzenoid hydrocarbons.

With certain larger polybenzenoid hydrocarbons, another new class of thermal rearrangements has been observed. Optically active hexahelicene, for example, on heating either neat or in solution, rearranges reversibly to its enantiomer, i.e., it racemizes (eq 10).[29]

$$\xrightarrow[\Delta H^{\ddagger} = 36.8 \text{ kcal/mol}]{194 \text{ °C}} \tag{10}$$
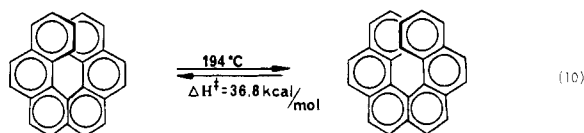
Higher benzologues in this family also racemize (including undecahelicene!), albeit somewhat more slowly.[29]

A mechanism based on purely conformational changes, with no rupture of any bonds, has been proposed to account for these remarkable interconversions of helicenes.[29] Such a stretch-and-bend process, of course, would impose severe distortion on the individual benzene rings and might be dismissed as untenable by anyone unfamiliar with the limits of aromaticity. Cyclic conjugation, however, has been found to persist in many

(23) Crow, W. D.; Wentrup, C. *Tetrahedron Lett.* 1968, 3111-4.

(24) The transition state for aromatization of benzvalene lies 93.4 kcal/mol above benzene (experimental value): Turro, N. J.; Renner, C. A.; Katz, T. J.; Wiberg, K. B.; Connor, H. A. *Tetrahedron Lett.* 1976, 4133-6.

(25) The temporary loss in delocalization energy can be calculated as the difference in delocalization energy between the starting material and that fragment thereof in which cyclic conjugation survives continuously; see ref 18a and 18b for tables of values.

(26) Scott, L. T.; Agopian, G. K. unpublished results.

(27) Scott, L. T.; Kirms, M. A., unpublished results.

(28) A sample of pyrene-1-^{13}C was kindly provided by A. Berg, University of Aarhus, Denmark.

(29) (a) Martin, R. H.; Marchant, M. J. *Tetrahedron Lett.* 1973, 3707. (b) Martin, R. H.; Marchant, M. J. *Tetrahedron* 1974, *30*, 347-9. (c) Lindner, H. J. *Ibid.* 1975, *31*, 281-4. (d) Bockent, J. H.; Laarhoven, W. H. *Ibid.* 1978, *34*, 2565. Martin, R. H.; Libert, V. *J. Chem. Res. (M)* 1980, 1940-50. [12]Helicene decomposes without racemization on heating: Martin, R. H. personal communication.

Hückel π systems which deviate drastically from planarity,[30] so this proposal deserves to be taken seriously. Nevertheless, it is intriguing to consider whether or not the racemization of helicenes might be related mechanistically to the automerization of naphthalene and other benzenoid hydrocarbons. Experimental data in this whole area remain scarce.

Overview and Outlook

Many types of thermal rearrangements of aromatic compounds have been observed. Some lead to a permanent change in the molecular skeleton, e.g., the isomerization of azulene to naphthalene and the electrocyclization of heavily substituted benzene rings to the corresponding Dewar benzenes. Others leave the carbon framework unaltered but interchange the atoms among various positions. Such "degenerate rearrangements" or "automerizations" have been revealed by ^{13}C labeling in azulene, naphthalene, and pyrene and have been proposed also to account for thermal interconversions of several benzene derivatives. Stereochemical thermal rearrangements are exemplified by the racemization of optically active helicenes at high temperatures. The only major class still without representation is the uncatalyzed thermal isomerization of one fully aromatic benzenoid hydrocarbon to another (e.g., anthracene → phenanthrene), even though such transformations should be thermodynamically favorable.

As one would expect for reactions which disrupt aromaticity, many of these thermal rearrangements are impeded by extraordinarily large energy barriers and occur only at very high temperatures, e.g., 1000–1100 °C (contact time = several seconds). Despite all the effort devoted to mechanistic study of these unusual reactions, however, not a single one can be considered fully understood at the present time. The isomerization of azulene to naphthalene appears to occur via one or more unimolecular pathways in competition with various radical processes, and similar mechanistic complexities may exist in other cases as well.

Several lines of further work ought to advance our understanding of these reactions.

(1) Infrared lasers provide an alternate means of effecting rearrangement. With this form of vibrational excitation, any complications due to wall effects should be minimized. Azulene rearranges cleanly to naphthalene when irradiated with a CO_2 laser, and ^{13}C-labeling experiments have been initiated.[14]

(2) Multiple-labeling studies will help to trace more precisely the course of movement of various atoms.

(3) It should be possible to reduce the aromaticity of the rings suffering rearrangement, and thereby lessen the temperature required for isomerization, by strategic incorporation of additional fused benzene rings.[25] For example, automerization in the terminal ring of anthracene might be easier than automerization in naphthalene, despite the failure of anthracene to suffer skeletal rearrangement to phenanthrene. Benz[f]-azulene rearranges to phenanthrene *much* more rapidly than azulene rearranges to naphthalene.[10a] Under milder conditions the mechanistic morass might simplify.

(4) The shortage of good kinetic studies must be rectified.

The past decade has seen thermal rearrangements of aromatic compounds grow from an isolated curiosity in azulene chemistry to a well-established area of organized research. Much remains to be learned, and the years ahead should bring new examples of such reactions as well as greater insight into the mechanisms they follow.

(30) (a) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *102*, 5216–20 and references cited therein. (b) Misumi, S.; Otsubo, T. *Acc. Chem. Res.* **1978**, *11*, 251–6 and references cited therein.

The λ⁵-Phosphorins

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The phenomenon of aromaticity has intrigued chemists ever since the days of Kekulé.[1] Among the many questions that have arisen is to what extent heterocyclic analogues of benzene, compounds containing one or more heteroatoms in place of the carbon atoms of benzene, are aromatic. For many such substances, structures with alternating single and double bonds around the ring can be written according to common concepts of valence. But do they actually have aromatic properties?

Karl Dimroth was born in Bad Tölz, Bavaria, in 1910. After university studies in München and Würzburg, he took his Ph.D. at Göttingen under A. Windaus and also did his Habilitationsarbeit at Göttingen. In 1944 he became Dozent in Marburg and in 1949 Professor Extraordinarius in Tübingen. In 1949 he returned to Marburg, first as Professor of Physiological Chemistry and since 1952 as Director of the Chemical Institute. He became Professor Emeritus in 1979.

(1) (a) G. M. Badger, "Aromatic Character and Aromaticity", Cambridge University Press, New York, 1969; (b) P. J. Garratt, "Aromaticity", McGraw-Hill, London 1971; (c) G. Binch, *Naturwissenschaften*, 60, 369 (1973); (d) G. Maier, *Chem. Unserer Zeit*, 9, 131 (1975).