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AUTOMERIZATIONS IN BENZENOID HYDROCARBONS. NEW MECHANISTIC INSIGHTS FROM THE THERMAL REARRANGEMENT OF BENZ[a]ANTHRACENE-5-^{13}C.[1]

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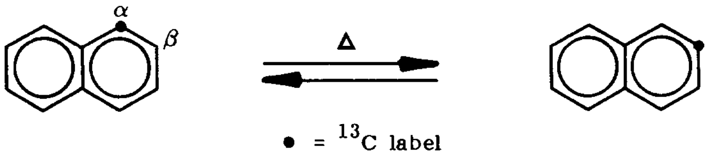
ABSTRACT: Scrambling of the carbon atoms in benz[a]anthracene between positions 5 and 6 has been shown to occur at high temperatures; a mechanism involving thermal generation of a carbene is proposed.

Prior to our 1977 report on the scrambling of α and β carbon atoms in naphthalene at high temperatures (eq 1),[2] thermal automerizations (degenerate skeletal rearrangements[3]) of aromatic compounds were unknown. Subsequent ^{13}C-labeling studies have uncovered thermal automerizations in azulene[4,5] and in pyrene[6] as well; however, the mechanisms by which these rearrangements occur all remain totally obscure.[7] Two plausible mechanisms for the naphthalene automerization have been tested and disproven.[6,7] In this paper, we report the results of a ^{13}C-labeling study on the thermal chemistry of benz[a]anthracene which sheds new light on the mechanism of automerizations in benzenoid hydrocarbons.



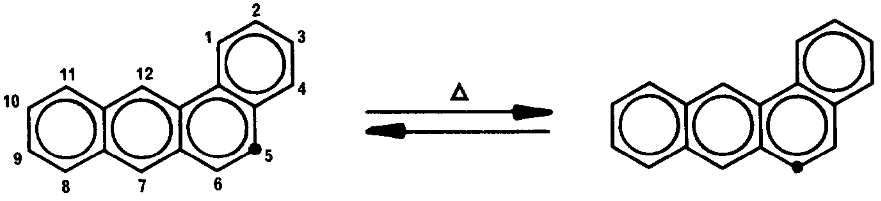
(1)

Benz[a]anthracene-5-^{13}C (1) was synthesized according to the procedure of Cox and Levy[8] using 90% ^{13}C-enriched KCN. A single strong peak at δ 127.94 for C(5) dominates the proton-decoupled 25 MHz ^{13}C NMR spectrum of benz[a]anthracene-5-^{13}C in acetone-d_6. From the proton-coupled ^{13}C NMR spectrum, the one-bond and two-bond C,H coupling constants $^1J_{C(5),H(5)} = 161$ Hz and $^2J_{C(5),H(6)} = 5.5$ Hz were easily determined. No additional long-range C,H coupling could be detected. The importance of these spectral data will become clear below.

Thermal automerization was effected by slowly subliming benz[a]anthracene-5-^{13}C (45 mg over a 24 h period) at atmospheric pressure into a stream of dry nitrogen which carried the sample through a hot quartz tube (contact time = 2 sec) and into a cold trap.[9] The temperature of the hot tube was maintained at 1035 °C. Under these conditions, benz[a]anthracene does not suffer any gross skeletal rearrangements, e.g., to chrysene or to other isomers, but can be recovered as benz[a]anthracene.

The proton-decoupled 25 MHz ^{13}C NMR spectrum of recovered benzanthracene in acetone-d_6 shows the expected peak at δ 127.94 for unchanged starting material, but a new peak is also seen at δ 128.14. No other new peaks appear. Clearly, the sample now contains a second benz[a]anthracene labeled at a position other than C(5). The ratio of the two NMR peak areas is 60:40, with the peak for starting material being the larger.

In the proton-coupled ^{13}C NMR spectrum, the new peak at δ 128.14 is split into a doublet of doublets with precisely the same coupling constants as those reported above for the peak at δ 127.94 (J = 161 and 5.5 Hz). No additional long-range coupling could be detected. From these data we conclude that the product of thermal automerization is benz[a]anthracene-6-^{13}C (2). Had the label migrated to any of the angular positions, the new peak would not have been split by a large one-bond coupling ($^1J_{C,H}$ = 161 Hz) in the proton-coupled NMR spectrum. Were the new label to reside in either of the terminal rings, the new peak would have been split by more than just two hydrogen nuclei in the proton-coupled spectrum. A ^{13}C label at C(6), C(7) or C(12) could give rise to a doublet of doublets, but the observed coupling constant of 5.5 Hz is far too large[10] to be a four-bond para $^4J_{C,H}$. On the other hand, one would expect the value for $^2J_{C(6),H(5)}$ to be very similar to that for $^2J_{C(5),H(6)}$. Both turn out to be 5.5 Hz. The chemical shift of C(6) should likewise be very similar to that of C(5), as is observed ($\Delta\delta$ = 0.20 ppm).[11] Thus, we have found a scrambling of carbon atoms between positions 5 and 6 in benz[a]anthracene at high temperatures (eq 2).

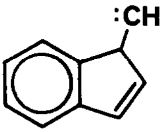


(2)

1 **2**

In our earlier study, we found that naphthalene-α-^{13}C gives 26% of naphthalene-β-^{13}C in 2 sec at 1035 °C.[2] Under the same conditions, benz[a]anthracene-5-^{13}C gives 40% of benz[a]anthracene-6-^{13}C. Thus, although neither system had time to reach equilibrium (50% of rearranged material), it is clear that benzanthracene automerizes more rapidly than does naphthalene at 1035 °C.

A mechanism consistent with this observation which has not previously been considered involves reversible formation of carbene 3 from naphthalene and of the corresponding carbene 4 from benz[a]anthracene.



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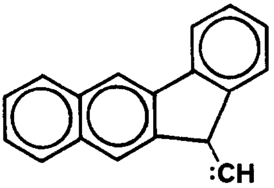
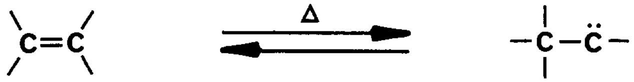


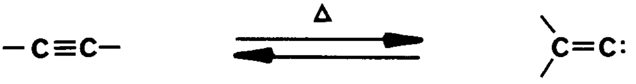
4

Since carbene **3** still contains a benzene ring, the loss in aromaticity associated with its formation from naphthalene can be estimated as the difference in aromaticity between naphthalene and benzene, i.e., 61 - 36 = 25 kcal/mol.[12] This loss of aromaticity will necessarily contribute to the overall activation energy for formation of **3** from naphthalene. An analogous computation reveals that formation of carbene **4** from benzanthracene requires a loss in aromaticity of only 15 kcal/mol.[12] Thus, other factors being comparable, the activation energy for automerization by this mechanism should be lower for benzanthracene than for naphthalene, and benzanthracene should automerize faster, just as we have observed.

Eq 3 depicts the essential features of the proposed mechanism. Rearrangement of a carbene to an olefin by a 1,2-shift, which corresponds to the re-aromatization step from carbenes **3** and **4**, has ample precedent; however, to our knowledge the reverse process has not been demonstrated heretofore in hydrocarbon systems.[13] The fact that unsaturated carbenes can be generated reversibly from acetylenes at high temperatures[14] (eq 4) does suggest that the equilibration in eq 3 should be possible in a system devoid of alternative reaction channels.



$$\mathrm{>C{=}C<} \;\overset{\Delta}{\rightleftharpoons}\; -\overset{|}{\underset{|}{\mathrm{C}}}-\ddot{\mathrm{C}}- \tag{3}$$



$$-\mathrm{C{\equiv}C}- \;\overset{\Delta}{\rightleftharpoons}\; \mathrm{>C{=}C\!:} \tag{4}$$

It must be noted that a hydrogen shift in carbenes **3** and **4** can compete with ring expansion. The fulvenes thus formed, however, are less stable than their fully aromatic isomers and would never accumulate to any appreciable extent. In fact, benzfulvene is known to rearrange to naphthalene at high temperatures.[15] Carbene **3** may well be the intermediate in that process.

The mechanisms involving thermal generation of carbene intermediates proposed here accommodate all the known facts regarding thermal automerizations in benzenoid hydrocarbons and may have relevance also for the thermal rearrangement of azulene to naphthalene. Experiments designed to test this mechanism have been initiated.

ACKNOWLEDGMENTS

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REFERENCES AND NOTES

1. This paper is Part 9 in a series on "Thermal Rearrangements of Aromatic Compounds." For Part 8, see L. T. Scott, J. Org. Chem., submitted. For Part 7, see L. T. Scott and B. L. Earl, J. Chem. Soc., Chem. Commun., 1373 (1983). For Part 6, see ref 6.

2. L. T. Scott and G. K. Agopian, J. Am. Chem. Soc., **99**, 4506 (1977).

3. The term "automerization," used to describe rearrangements which would be degenerate in the absence of a label, was first introduced by A. T. Balaban and D. Farcasiu, J. Am. Chem. Soc., **89**, 1958 (1967).

4. J. Becker, C. Wentrup, E. Katz, and K.-P. Zeller, J. Am. Chem. Soc., **102**, 5110 (1980). K.-P. Zeller and C. Wentrup, Z. Naturforsch. B., **36B**, 852 (1981). See also K.-P. Zeller, Angew. Chemie, Internat. Ed. Engl., **21**, 440 (1982).

5. L. T. Scott and M. A. Kirms, J. Am. Chem. Soc., **103**, 5875 (1981).

6. L. T. Scott, M. A. Kirms, A. Berg, and P. E. Hansen, Tetrahedron Lett., **23**, 1859 (1982).

7. L. T. Scott, Acc. Chem. Res., **15**, 52 (1982) and references cited therein.

8. R. H. Cox and L. A. Levy, Org. Magn. Reson., **21**, 173 (1983).

9. An apparatus and procedure similar to that described in ref. 5 was used.

10. P. E. Hansen, Progress in NMR Spectroscopy, **14**, 175 (1981).

11. In prior reports on the ^{13}C NMR spectrum of benz[a]anthracene, the chemical shifts of C(5) and C(6) were reported to be identical: R. S. Ozubko, G. W. Buchanan, and I. C. P. Smith, Can. J. Chem., **52**, 2493 (1974). See also ref. 8.

12. A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, 1961, p 241. Somewhat smaller absolute values are obtained for the aromaticities of naphthalene, benz[a]anthracene, carbene **3**, and carbene **4** using the compilation of M. J. S. Dewar and C. de Llano, J. Am. Chem. Soc., **91**, 789 (1969); however, the relative ordering of energies remains the same.

13. The thermal interconversion of 1,1- and 1,2-dideuterioethylene [J. E. Baldwin, private communication] may proceed by the mechanism illustrated in eq 3.

14. R. F. C. Brown, F. W. Eastwood, and G. P. Jackman, Aust. J. Chem., **31**, 579 (1978) and references cited therein. For a review, see: R. F. C. Brown, "Pyrolytic Methods in Organic Chemistry," Academic Press, New York, 1980, pp 124-127.

15. R. F. C. Brown, G. E. Gream, D. E. Peters, and R. K. Solly, Aust J. Chem., **21**, 2223 (1968) and C. Wentrup, private communication.

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