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AUTOMERIZATION OF PYRENE
A TEST FOR THE MECHANISM OF NAPHTHALENE AUTOMERIZATION[1]

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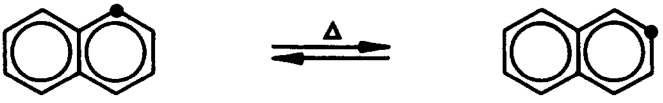
ABSTRACT. A ^{13}C-labeling experiment has revealed the scrambling of carbon atoms in pyrene at high temperature (eq 3); comparison between the rate of this process and the rate of naphthalene automerization (eq 1) provides evidence against one plausible mechanism for the latter reaction.

Thermal rearrangements of aromatic compounds have recently emerged as an intriguing new area of chemical study[2]. We reported the first unequivocal thermal rearrangement of a benzenoid aromatic ring system just five years ago (eq 1)[3]. At 1035 °C in a quartz flow system, naphthalene-1-^{13}C (1) isomerizes reversibly to naphthalene-2-^{13}C (2) with a half-life of *ca*. 2 sec. Long contact times lead to nearly complete equilibration of 1 and 2, but no ^{13}C label could ever be detected at the angular position[3]. Isomerizations such as this one, which are degenerate in the absence of a label, have been termed "automerizations"[4].



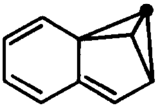
(1)

1 ● = ^{13}C label 2

To account for the automerization in eq 1, we originally suggested two plausible mechanistic pathways[3]. The first involves reversible rearrangement of naphthalene to azulene (eq 2) by a pathway which would scramble only the α and β carbon atoms of naphthalene. Detailed ^{13}C-labeling studies on the well-established thermal rearrangement of azulene to naphthalene, however, have subsequently disproven this mechanism[2,5].

(2)

Our alternative proposal[3], that naphthalene might automerize *via* the unknown hydrocarbon 3, has not been tested until now. Although obviously strained, 3 represents a *permissible* intermediate on energetic grounds[6].



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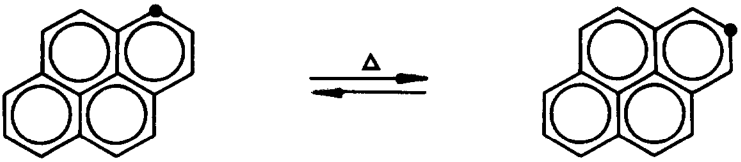
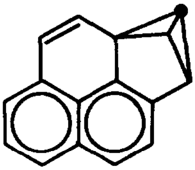
If this mechanism is correct, then pyrene should also automerize at high temperatures (eq 3). In fact, the loss of resonance energy associated with formation of intermediate 6 from pyrene (*ca.* 48 kcal/mol)[7] would not be as great as that associated with formation of 3 from naphthalene (*ca.* 61 kcal/mol)[7]. Since strain and other factors appear comparable, pyrene ought to automerize *faster* than naphthalene under the same conditions if these reactions occur *via* intermediates 3 and 6. We have examined the thermal behavior of 4 as a test for this mechanism of naphthalene automerization.



(3)

4 **5**



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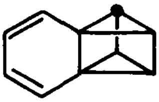
Pyrene-1-^{13}C (4), 90% enriched with the isotopic label[8], was passed through a hot quartz tube in the vapor phase at 1 atm (N_2 carrier gas), and the recovered material was purified by sublimation. ^{13}C NMR analysis of a sample heated to 1100 °C (contact time ≅ 2 sec) clearly reveals that pyrene-2-^{13}C (5) was formed from 4; no other labeled pyrenes could be detected. Thus pyrene does indeed automerize at high temperatures as depicted in eq 3.

The extent of pyrene automerization under these conditions, however, is quite low (only 2-3% of 5). Naphthalene-^{13}C scrambles to a much greater extent at substantially lower temperatures with the same contact time[3]. Thus, pyrene actually automerizes slower than naphthalene, not faster, and we must conclude that:

The automerization of naphthalene (eq 1)
does not occur via intermediate 3.

What is the mechanism for naphthalene automerization (eq 1)? To date, we have succeeded only in disproving both of our original hypotheses. Energetic considerations exclude mechanisms based on intermediates such as 7, 8 and 9[9]. No other alternatives have been proposed, nor are we inclined to speculate further at this time.



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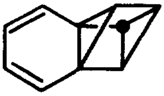

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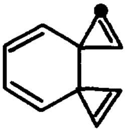

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The scrambling of carbon atoms in pyrene reported here represents the second example of thermal automerization in a benzenoid aromatic hydrocarbon. The mechanisms by which naphthalene and pyrene automerize remain unknown.

ACKNOWLEDGMENTS

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