model system lacking an internal general acid.[7] Condensation reactions of HETpp would proceed with inversion and internal general base catalysis to avoid J, in analogy to reactions of acetyl coenzyme A.[25]

We are further examining the enzymatic and nonenzymatic reactions we have discussed to elucidate in detail the processes involved in catalysis by TPP of reactions involving pyruvate.

Acknowledgment. We thank Professor P. A. Frey, of The Ohio State University, for helping us obtain PDH and for interesting discussions.

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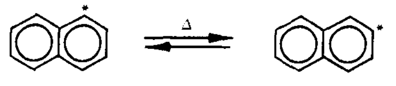
Automerization of Naphthalene

Sir:

We wish to report a ^{13}C-labeling experiment which reveals the scrambling of α and β carbon atoms in naphthalene at high temperatures[1] (eq 1).



(1)

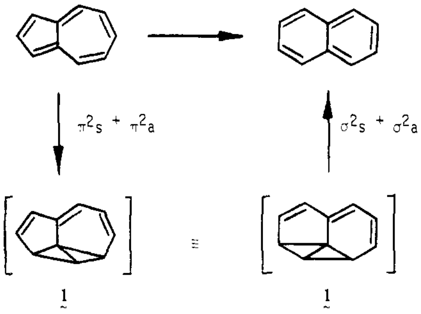
The possibility of this rearrangement[2] first occurred to us during our studies on the thermal isomerization of azulene to naphthalene, a venerable mechanistic puzzle in the chemistry of nonbenzenoid aromatic hydrocarbons.[4] One plausible mechanism for the latter transformation involves initial conversion of azulene to tetracyclic triene **1** followed by ring opening of the bicyclobutane intermediate to naphthalene (eq 2). The symmetry allowed nature of both steps[5] lends special appeal to this pathway.[6]

Reversibility of this process would provide a pathway for scrambling the α and β carbon atoms of naphthalene (eq 3). Note as a further consequence of the transformations proposed in eq 2 and 3 that the two angular carbon atoms (γ) are predicted to retain their original identity and never migrate to the α or β positions of naphthalene.

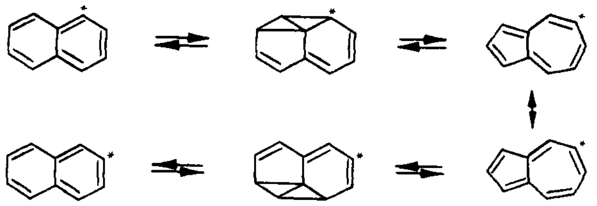
Table I. Distribution of the ^{13}C Label[a] (±4%) in the Pyrolysate of Naphthalene-*1*-^{13}C As a Function of Contact Time

Contact time, sec[b]	α, %	β, %	γ, %
0.0[c]	100%	0	0
1.0	78	18	4
2.0	71	26	3
5.0	58	40	2
8.0	55	43	2
11.0	52	46	2

[a] These values[11] have been corrected for the natural abundance of ^{13}C. [b] The "contact time" was calculated from the known rate at which naphthalene passed through the apparatus[10] and the volume of the hot zone. [c] This entry refers to the material before pyrolysis.[9]



(2)



(3)

From the reported activation parameters for the azulene → naphthalene isomerization[7] and the known difference in free energy between these two species,[8] one can estimate for the reverse reaction a $\Delta G^{\ddagger}$ of 86 kcal/mol at 1035 °C, a temperature at which isomerization should proceed to an observable extent in a flow system. Azulene should not accumulate to any significant extent during the equilibration, of course, since the thermodynamic stability of naphthalene greatly exceeds that of the nonbenzenoid isomer.[8]

To test the above predictions, we slowly sublimed naphthalene-α-^{13}C[9] through a quartz pyrolysis apparatus[10] heated to 1035 ± 5 °C. Collection of the pyrolysate in a liquid nitrogen trap and analysis[11] of the recovered naphthalene for distribution of the ^{13}C label gave the results summarized in Table I.[13]

These data clearly reveal scrambling of the α and β carbon atoms in naphthalene at high temperatures.[14] Furthermore, within experimental error (±4%), the angular carbon atoms (γ) retain their original identity and remain unlabeled even after several half-lives of the α-β scrambling. Both of these experimental observations stand in complete harmony with the mechanistic scheme outlined in eq 3.

Isomerization of naphthalene-*1*-^{13}C to naphthalene-*2*-^{13}C under these conditions follows the rate law for a unimolecular reversible reaction with $K_{\text{eq}} = 1$ (Figure 1).[15] From the plot in Figure 1 (slope = $2k$), one can thus calculate for the automerization of naphthalene at 1035 °C an experimental $\Delta G^{\ddagger}$ of 86 kcal/mol,[16] a value in striking agreement with that estimated for the thermal isomerization of naphthalene to azulene.

It is tempting to conclude that naphthalene does indeed isomerize reversibly to azulene by the mechanism proposed in

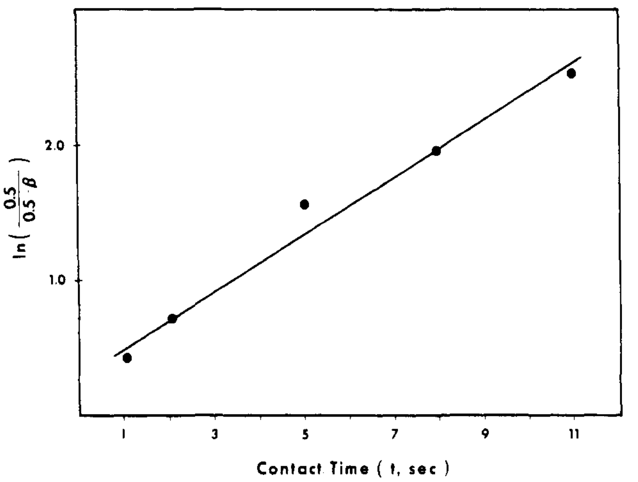
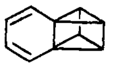
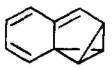


Figure 1. Plot of the data in Table I according to the rate law for a unimolecular reversible reaction with $K_{eq} = 1 (k = (1/2t)\ln (0.5/0.5 - \beta))$.[15]

eq 3; however, the experimental data do not yet justify such a conclusion. Intermediates other than azulene, e.g., **2** or **3**, could equally well account for the observed scrambling of α and β carbon atoms (but not γ) in naphthalene. The highly strained prismane (**2**) can presumably be excluded on energetic grounds, for it must certainly lie more than 86 kcal/mol above naphthalene,[17] but the benzvalene (**3**) appears no more strained than the isomeric bicyclobutane **1**. At present, we see no reason to favor intermediate **1** in preference to **3** except that conservation of orbital symmetry[5] forbids concerted valence isomerization of naphthalene to the latter in the ground state.[18] Suitable double-labeling experiments could distinguish between these two possibilities.


2


3

Even if naphthalene does automerize via azulene, as suggested by the agreement between $\Delta G^{\ddagger}_{\text{predicted}}$ and $\Delta G^{\ddagger}_{\text{exptl}}$, the mechanism for interconversion of those two aromatic hydrocarbons still remains open to speculation. We are currently studying the thermal isomerization of azulene-^{13}C to test the mechanistic hypothesis in eq 2.

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References and Notes

(1) Full details of this work can be found in the Ph.D. thesis (part II) of G. K. Agopian, UCLA, 1975; a preliminary account was presented at the 31st Northwest Regional Meeting of the American Chemical Society, Reno, Nev., June 14, 1976.

(2) The term "automerization" was introduced by Balaban[3a] to describe those isomerizations which are degenerate in the absence of a label. Ironically, the aluminum chloride catalyzed automerization of naphthalene reported in that paper[3a] was subsequently shown to be incorrect.[3b,c]

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(6) The mechanistic hypothesis shown in eq 2 was apparently conceived independently also by H. J. Reich, R. B. Woodward, and R. W. Alder (personal communication from each) and M. Prislopski.[4c]

(7) Reported as $\Delta H^{\ddagger} = 48.8 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger} = -5.3 \pm 3.6$ eu (375–425 °C): E. Heilbronner in "Nonbenzenoid Aromatic Compounds", D. Ginsburg, Ed., Interscience, New York, N.Y., 1959, p 264.

(8) The difference in free energy between azulene and naphthalene is almost completely independent of temperature: $\Delta\Delta G° = -30.66$ kcal/mol (298 K) and -30.57 kcal/mol (1000 K); $\Delta\Delta H° = -30.82$ kcal/mol (298 K) and -30.36 kcal/mol (1000 K); $\Delta\Delta S° = -0.53$eu (298 K) and $+0.01$ eu (1000 K): D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969.

(9) Naphthalene, 90% enriched with ^{13}C in one of the α positions, was synthesized by known methods.[3c]

(10) The pyrolysis apparatus consists of a quartz tube packed with quartz chips. A constant stream of nitrogen served to carry the naphthalene through the hot zone as it slowly sublimed at atmospheric pressure.

(11) The values listed in Table I were determined by a known method[12] involving mass spectral analysis of naphthoquinone (experimental error ±4%). The α:β isomer ratio was also checked in certain cases by ^{13}C NMR and ^{1}H NMR (of the ^{13}C satellites associated with the α and β proton resonance signals) and agreed well with those values listed in Table I.

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(13) The possibility that these results reflect a surface-catalyzed reaction rather than a strictly thermal, gas phase reaction cannot be rigorously excluded; however, omission of the quartz packing chips from the pyrolysis tube did not change the results significantly (i.e., 5.0-sec contact time → 61% α, 36% β, 3% γ). The entire pyrolysis apparatus was base washed prior to use.

(14) We have also observed the "automerization" of 1-methylnaphthalene, 2-methylnaphthalene, naphthalene-*1-d*, and naphthalene-*2-d* under similar conditions.

(15) K. J. Laidler, "Chemical Kinetics", 2nd ed, McGraw-Hill, New York, N.Y., 1965; *t* is taken as the contact time and β is the fraction of β isomer.

(16) The experimental value of 86 kcal/mol for $\Delta G^{\ddagger}$ should be considered an upper limit since the contact times in Table I may overestimate the interval during which the material is actually at 1035 °C.

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(18) See, however, M. J. S. Dewar and S. Kirshner, *J. Am. Chem. Soc.*, **97**, 2931, 2932 (1975); N. J. Turro, C. A. Renner, T. J. Katz, K. B. Wiberg, and H. A. Connon, *Tetrahedron Lett.*, 4133 (1976). Our experimental data do not exclude the intriguing possibility that this automerization involves internal conversion of "hot" naphthalene from the vibrationally excited ground state to the first singlet electronic excited state (S_1, $E = 90.8$ kcal/mol above S_0);[19] reversible isomerization to the benzvalene **3** would be symmetry allowed in the excited state;[5] cf. L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *J. Am. Chem. Soc.*, **87**, 675 (1965).

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Dibenzo[*gh,op*]nonalenide Dianion. A Novel Aromatic System Derived from Nonalene

Sir:

Fused conjugated systems containing $4n$ π electrons, similarly to the monocyclic cyclooctatetraene,[1] may acquire aromatic character either by oxidation to the corresponding dication, or by formation of the dianion. These ions behave like peripheral aromatic systems containing $(4n + 2)$ π electrons.[2] Only the heptalenide dianion[3] and the pentalenide dianion[4] are known in this series.[5] Benzannelated derivatives, e.g., the dibenzo[*cd,gh*]pentalenide dianion, have been prepared and exhibit aromatic character.[6] We wish to report the synthesis and properties of the dibenzo[*gh,op*]nonalenide dianion (**1**), the first derivative of the hitherto unknown nonalenide dianion