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ON THE MECHANISM OF THE THERMAL NAPHTHALENE AUTOMERIZATION, A COMMENT

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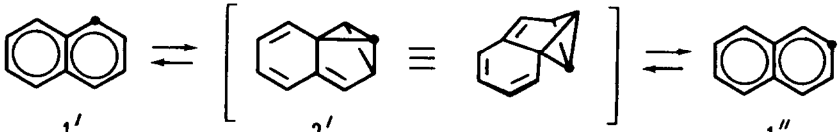
Abstract. The title reaction is suggested to proceed by a reversible valence isomerization *via* a laterally bridge benzvalene (2). No analogous behaviour is expected for pyrene.

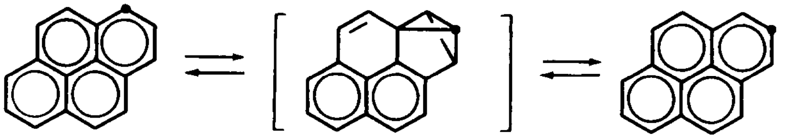
α-^{13}C-naphthalene (1') is known to rearrange thermally into β-^{13}C-naphthalene (1") following a rate law in accordance with an unimolecular reversible process. At 1035°C in a flow system the half-life of 1' is ca. 2 sec.[1] The mechanism of this fascinating automerization apparently is unknown.[2] Extensive ^{13}C-labelling studies have unambiguously shown that the reaction is mechanistically disconnected from the classic azulene→naphthalene isomerization.[3] Surprisingly, the simplest mechanism one can postulate, i.e. the energetically and orbital symmetry allowed valence isomerization *via* the benzvalene type intermediate (2'), has recently been rejected[4] (equation 1). It was expected that 1-^{13}C-pyrene (3') would undergo an analogous automerization (equation 2) and at a higher rate than naphthalene. This assumption was based on the evaluation of loss in resonance energy for the reaction steps 1'→2' (61 kcal/mole) *versus* 3'→4' (48 kcal/mole). Experimentally, however, automerization of pyrene was hardly detectable. Conversion of 2-3%, based on ^{13}C-NMR spectroscopic analysis was found. Under similar conditions α-^{13}C-naphthalene had automerized to a large extent.[4]

Equation
(1)
• = ^{13}C-label



1' 2' 1"

Equation
(2)
• = ^{13}C-label



3' 4' 3"

We wish to draw attention to an intriguing peculiarity of benzvalene type hydrocarbons which has emerged from studies of the thermal behaviour in solution and which may provide a key to solve this puzzle. Thermal aromatization, so far, has been observed only for those benzvalene derivatives in which the bicyclobutane moiety is bridged by an ordinary double bond. Pertinent examples are given in the table under group A. The structurally important part of the molecules is drawn in bold face. Dewar and Kirschner[5] have pointed out that the double bond in the parent benzvalene (5) plays a decisive role in making the aromatization reaction (5→6) a concerted process of low activation energy. This has found substantial experimental support.[6] Simple and multiple alkylation in any position of benzvalene does not affect the behaviour (e.g. 7→8).[7] Neither does additional lateral bridging alter the situation (9→10).[8]

A dramatic change, however, is brought about by replacing the double bond of benzvalene by a benzo-annellation, i.e. by going from the parent compound 5 to the benzo-benzvalene 11. As is seen from the examples compiled as group B in the table, the activation barrier for aromatization now rises so drastically that an entirely different reaction takes over. Exo-methylene derivatives (e.g. 12, 14, 16) are the outcome. A retrocyclopropanation followed by a hydride shift associated with a positive activation entropy may be invoked. To our knowledge these rearrangements are uncatalyzed.

Considering the hypothetical intermediates of equations 1 and 2 respectively, it is immediately seen that the naphthalene isomer 2 belongs to the group A type hydrocarbons. It is expected to collapse thermally to naphthalene.[10] The pyrene isomer 4, however, contains the areno-bridged bicyclobutane unit typical for the compounds of group B. Its re-aromatization, a necessary condition for equation 2 to be valid, is not expected to be the principal thermal reaction. Thus, the reported behaviour of 1-^{13}C-pyrene (3')[4] does not disprove the validity of equation 1. In contrast, it provides support for it ! Therefore we suggest that the valence isomerization depicted in equation 1 should be maintained as the best mechanistic description of the thermal naphthalene automerization.

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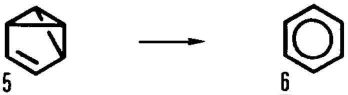
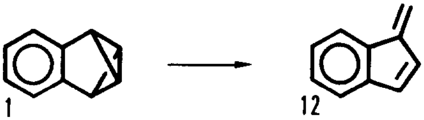
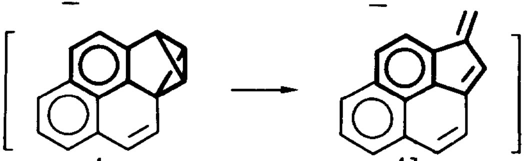
Table. Thermal rearrangements of benzvalene type hydrocarbons (main reaction in solution)

Group A	Remarks
 5 → 6	n-heptane, 30°C, $\tau_{\frac{1}{2}} \approx 3$ hrs[6]
 7 → 8	R = methyl in any position Et_2O, 30°C $\tau_{\frac{1}{2}} \approx$ several hrs[7]
 9 → 10	Et_2O or D_2CCl_2, <0°C[8]
 2 → 1	Expectation.[10] See also the outlook in ref. 8

Group B	Remarks
 11 → 12	CCl_4, 75°C $\tau_{\frac{1}{2}} \approx 1.3$ days[6a]
 13 → 14	benzene-d_6, 160°C $\tau_{\frac{1}{2}} \approx 15$ min[9]
 15 → 16	benzene-d_6, 70°C $\tau_{\frac{1}{2}} \approx 15$ min[9] (the reaction is repeated by the second bicyclobutane moiety)
 4 → 17	Expectation

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10. MINDO-3 predicts for hydrocarbon 2 a heat of formation $\Delta H_{f_{25}}$ = 135.4 kcal/mole. 2 is protected against aromatization by a barrier $\Delta H^{\ddagger}$ = 19.0 kcal/mole. This result is obtained by taking a lateral bicyclobutane bond (starting from the quaternary C-atom of 2) as reaction co-ordinate and following the procedure given in ref. 5. Compound 2 thus is predicted to be kinetically somewhat less stable than the parent 5 ($\Delta H^{\ddagger}$ = 21.5 kcal/mole[5]).

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