

Final Technical Report

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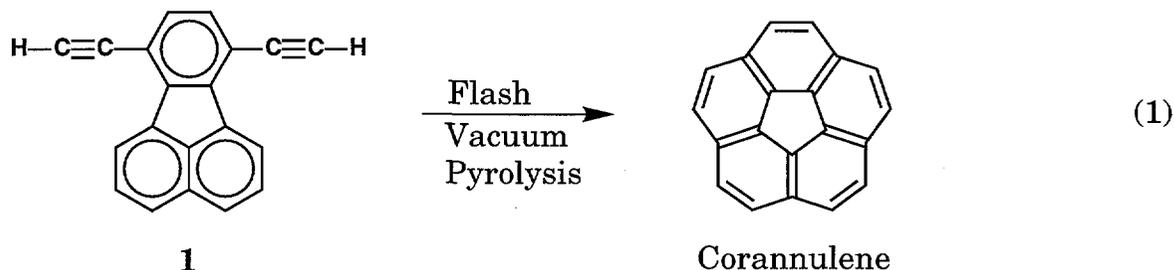
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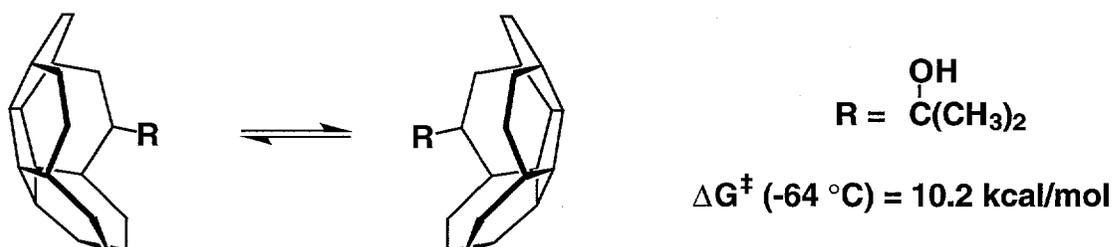
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If any single contribution from this project had to be identified as the one most enthusiastically received by the chemical community, it would almost certainly be our convenient new synthesis of corannulene, the prototypical bowl-shaped polycyclic aromatic hydrocarbon (eq 1).^{1a} Bis-acetylene **1** can be easily prepared on a large scale in five steps from commercially available starting materials.



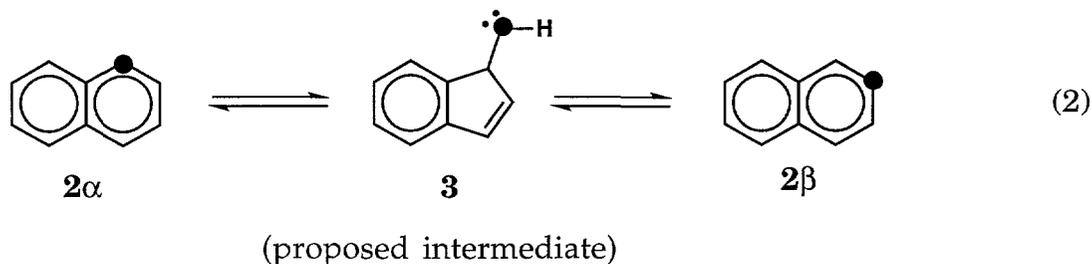
To our knowledge, this isomerization is the first well-defined demonstration of a chemical reaction that captures a planar polycyclic aromatic hydrocarbon (PAH) in a temporary nonplanar geometry to build a convex surface. Cyclophanes and other bent benzenoid hydrocarbons are also known, of course, but their π surfaces approximate more the shape of a saddle, rather than a bowl or a dome (superphane being an exception). It is not difficult to envisage applications of this principle to the elaboration of other curved molecular surfaces based on trigonal-carbon lattices, e.g., spheroidal C_{60} and additional subunits thereof.

As a side project, we prepared a derivative of corannulene bearing diastereotopic methyl groups on a substituent and measured the coalescence temperature for the methyl NMR signals. From these experiments, we determined the bowl-to-bowl inversion barrier for the corannulene ring system to be quite low, $\Delta G^\ddagger = 10.2 \pm 0.2$ kcal/mol.^{1b} This is almost identical to the barrier for inversion of cyclohexane from one chair conformation to the other and came as a shock to most organic chemists.

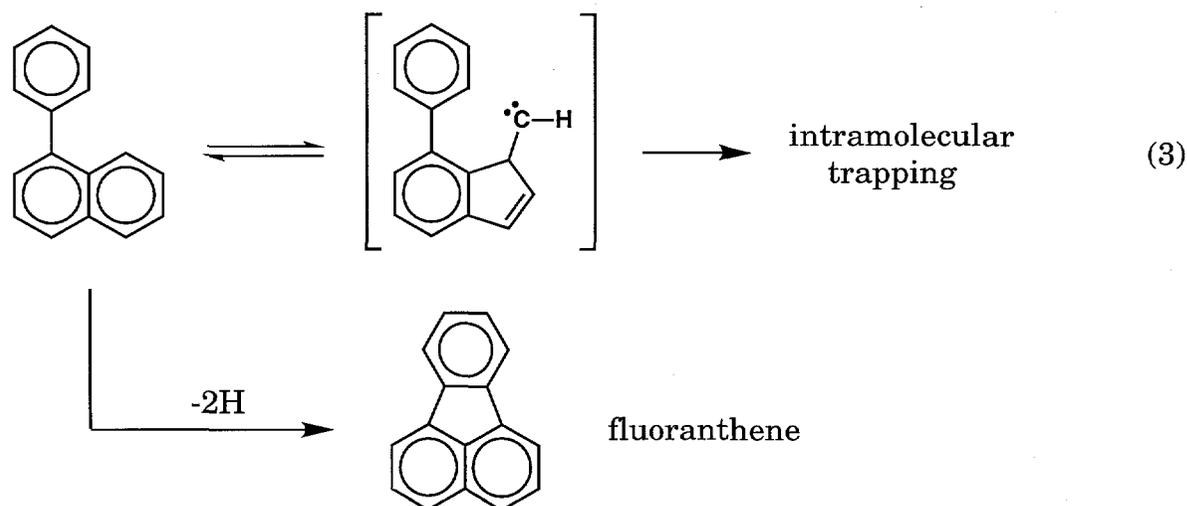


The transformation shown in eq 1 represents our first venture into the area of high temperature organic synthesis (bond construction, as opposed to bond cleavage). Our original interest in high temperature gas phase organic chemistry, however, was aroused by mechanistic problems. The thermal interconversion of α - ^{13}C -naphthalene (2α) and β - ^{13}C -naphthalene (2β) was first uncovered in our lab many years ago,² and we subsequently observed the 1,2-scrambling of carbon atoms at high temperatures in a variety of other polycyclic aromatic hydrocarbons,³⁻⁷ as well as in benzene- $^{13}\text{C}_2$.^{8,9} Considerable evidence suggests that the mechanism of these "automerization" reactions and related thermal rearrangements of benzenoid hydrocarbons involves

reversible contraction of a benzene nucleus to a five-membered ring intermediate.^{6,10,11} For quite a while, we favored a mechanism involving the reversible formation of indenyl carbene (3) to account for our results (eq 2).

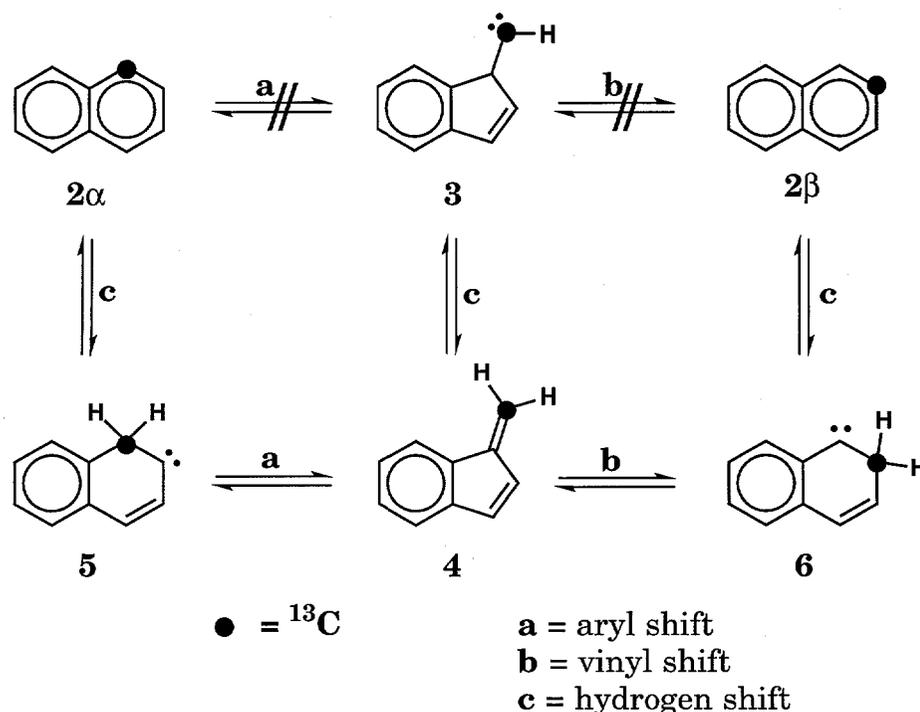


Attempts to intercept the proposed carbene 3 by introduction of a pendent phenyl group on the adjacent ring, however, were thwarted by intervention of a lower energy cyclization reaction leading to fluoranthene (eq 3).¹²

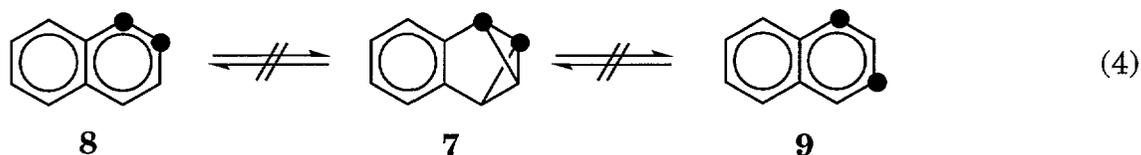


Although we were initially disappointed by the above result, a subsequent experiment on the thermal aromatization of isotopically labeled benzofulvene, enriched to 99% ¹³C in the methylene group (4) provided evidence that deposited indenyl carbene (3) as a candidate for the five-membered ring intermediate in favor of benzofulvene, formed either concertedly or *via* the six-membered ring carbenes 5 and 6 (Scheme 1).¹³ The arguments leading to this conclusion, which are too lengthy to recount here in detail, stem from our observation that flash vacuum pyrolysis of labeled benzofulvene 4 yields a surprisingly disparate mixture of the two labeled naphthalenes ($2\alpha:2\beta = 21:79$); such an uneven product ratio at 900 °C/10⁻³ mm is extremely difficult to reconcile with any mechanism that involves two competing low-barrier reactions at the point of reaction divergence ($3 \rightarrow 2\alpha$ vs 2β). This new insight, together with other considerations, enabled us to show that the pathways between naphthalene and benzofulvene (4) lie lower on the C₁₀H₈ energy surface than those leading from naphthalene to indenyl carbene (3).

Scheme 1

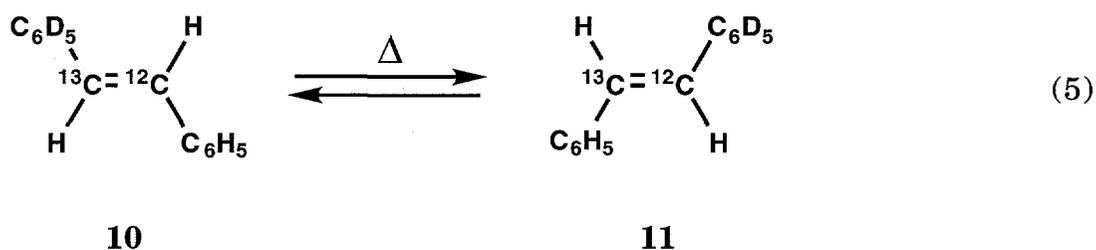


In addition to learning more about the mechanistic details of such unusual but fundamental reactions, we actively sought as a separate goal of this project to discover other new high temperature reactions that have no counterpart under ordinary laboratory conditions. Along these lines, thermochemical considerations suggested to us that naphthvalene (7) should be accessible from naphthalene at high temperatures. According to Dewar, however, this reaction should be symmetry forbidden and, therefore, unfavorable.¹⁴ We looked for this reaction by examining the pyrolysis of naphthalene-1,2- $^{13}\text{C}_2$ (8), a doubly labeled hydrocarbon that we were able to synthesize in nine steps. Our results¹⁵ support Dewar's prediction: hydrocarbon 8 does not rearrange to naphthalene-1,3- $^{13}\text{C}_2$ (9), the product expected from reversible formation of naphthvalene (eq 4), even under conditions that do scramble carbon atoms 1 and 2 of naphthalene (cf. Scheme 1). Co-pyrolysis of naphthalene-1- ^{13}C (2α) and naphthalene-1,2- $^{13}\text{C}_2$ (8) led to scrambling only of the mono-labeled naphthalene.

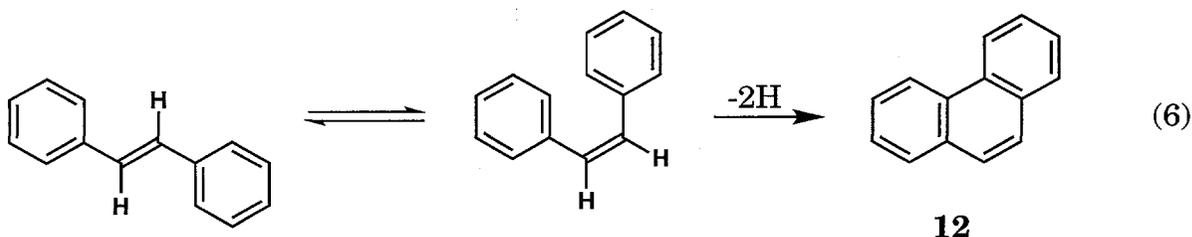


Another search for new reactions at high temperatures proved more rewarding. Having demonstrated the generality of thermal 1,2-carbon atom exchange reactions in polycyclic aromatic hydrocarbons, we decided to see if such a reaction could occur at a carbon-carbon double bond that was not incorporated into a benzene ring. Prior reports that low levels of ^{13}C -label scrambling could be detected in the pyrolysis of 8- ^{13}C -styrene

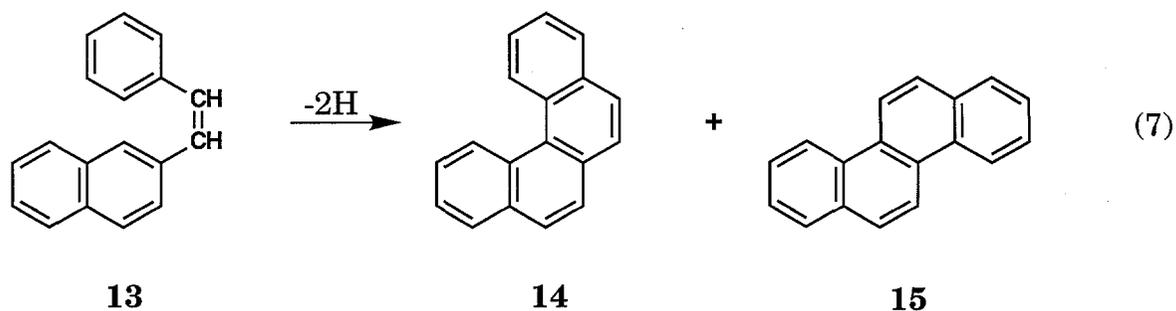
suggested that such a reaction might be feasible.¹⁶ The molecule we chose for study was the doubly labeled stilbene **10**, which could be prepared in a multi-step synthesis from ¹³C-barium carbonate and benzene-d₆. Careful vacuum pyrolysis of **10** in a flow system over a range of temperatures from 800 - 1100 °C revealed that the scrambling depicted in equation 5 does indeed occur at high temperatures and that it leads to almost complete equilibration of **10** with **11** above 1000 °C.¹⁵ This clearcut example of a double 1,2-shift ("dyotropic rearrangement") of substituents across a nonaromatic carbon-carbon double bond firmly establishes that the automerization reaction of PAHs extends to olefinic compounds as well. Whether the two substituent migrations occur concertedly or stepwise *via* carbene intermediates cannot be determined from the data currently available.



While working out experimental conditions for the above stilbene study (eq 5), we observed the appearance of several products other than stilbene in the pyrolysate.¹⁵ The most abundant of these, especially at the highest temperatures, was phenanthrene (**12**). We presume that phenanthrene is formed by thermal isomerization of the stilbene from *trans* to *cis* (rotation not possible at room temperature), followed by cyclization and loss of two hydrogens (eq 6). Photolysis of stilbene under oxidizing conditions is well-known to generate phenanthrene, but we are unaware of any precedent for this transformation under thermal conditions in the absence of dehydrogenation reagents. It would be energetically permissible for the vibrationally excited molecules in our experiments to undergo intersystem crossing to electronically excited states, but we have no evidence for such a reaction pathway.

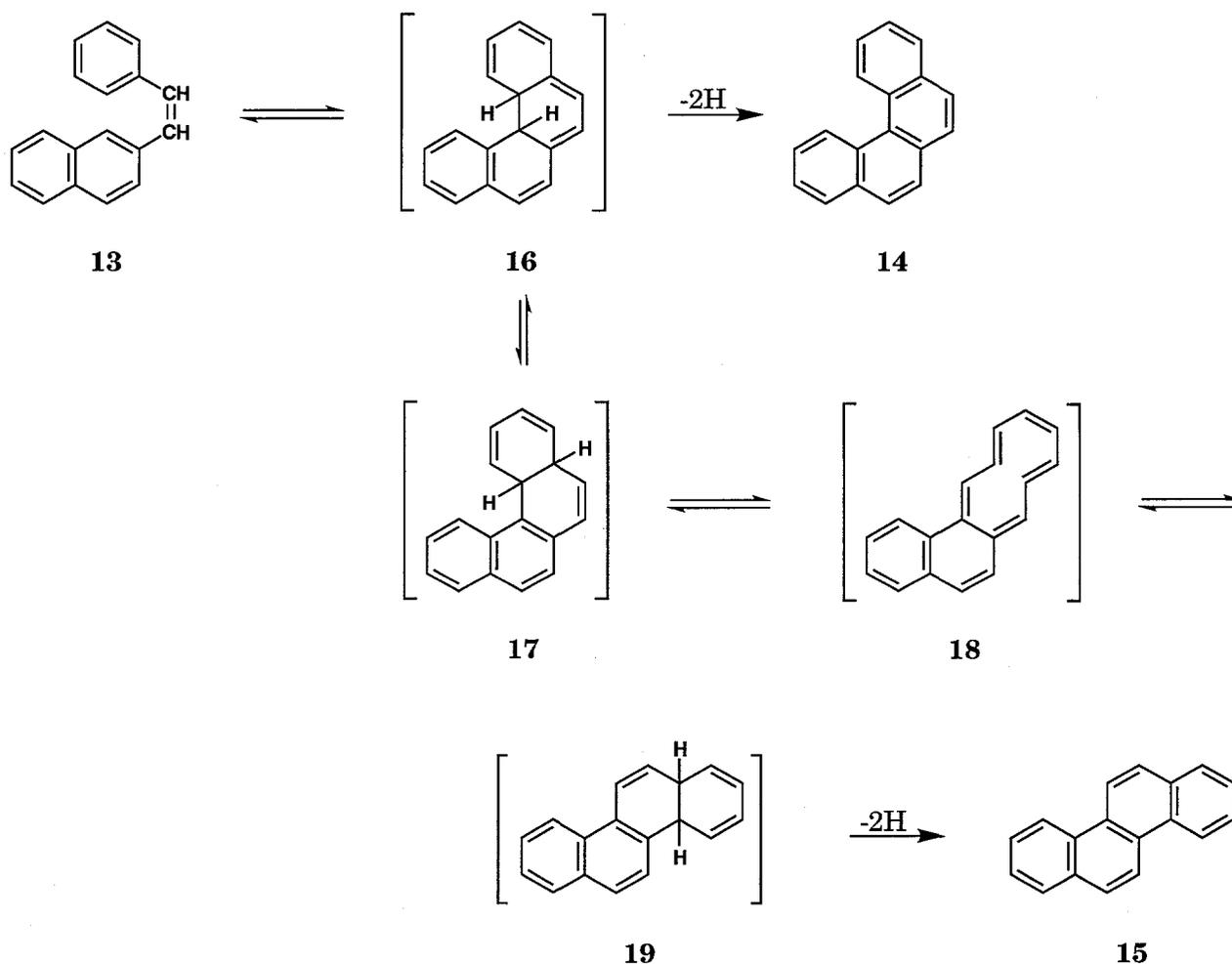


The unexpected discovery of this thermal cyclization reaction (eq 6) inspired us to explore the possibility of applying it to a high temperature synthesis of hexahelicene. As a prelude to that project, we examined the pyrolysis of 2-(β -styryl)naphthalene (**13**) and found that it does indeed cyclize to benzo[*c*]phenanthrene ("tetrahelicene," **14**) in *ca.* 15% yield, but the major product turned out to be chrysene (**15**), which came as a complete surprise (eq 7).¹⁵



In retrospect, the formation of chrysene from **13** can be easily rationalized. A 1,5-hydrogen shift in the first-formed intermediate (**16**) could readily give a 9,10-dihydronaphthalene (**17**) that is capable of rearranging to an isomeric 9,10-dihydronaphthalene (**19**) by way of the [10]annulene intermediate **18** (Scheme 2, stereochemical implications unintended). Such isomerizations of 9,10-dihydronaphthalenes *via* [10]annulene intermediates are well known from the early work of Vogel *et al.*¹⁷ Our surprise resulted from a failure to anticipate that sigmatropic shifts might compete with hydrogen loss in these thermal cyclizations.

Scheme 2



To summarize, we not only gained new insight into the mechanism and generality of PAH thermal automerization reactions during the course of this project, we also uncovered several new high temperature reactions and added a third dimension to our program by applying high temperature chemistry to problems in organic synthesis. Our synthesis of corannulene has attracted much recent attention; however, we believe that the uncatalyzed "cyclodehydrogenation reactions" which form 5-membered rings (e.g., eq 3) and 6-membered rings (e.g., eq 6) at high temperatures may prove to be of greater general importance in the long term.

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