oil (91%). This product was taken immediately on without analysis to avoid decomposition.

1,2-^{13}C-Enriched Benzene. The entire crude 1,2-^{13}C-enriched 1,2-diacetoxycyclohexane (5.9 g) was dissolved in 1.0 mL of distilled *n*-octane and introduced into a vertical dropping pyrolysis apparatus consisting of a pressure-equalizing dropping funnel, a 15-cm Pyrex tube, and a round-bottom recieving trap with a sidearm gas exit port. The pyrolysis oven was preheated to 450 °C, and the hot zone was packed from the bottom up with a Pyrex wool plug, 2.0 g of 10% palladium on carbon, a Pyrex wool plug, and 20 cm of Pyrex beads. The oven was heated via a variac controlled heating tape wrapped around the outside of the Pyrex tube and insulated with tar coated Pyrex wool. The flow rate was adjusted by passing dry nitrogen carrier gas through the system at a rate of 30 mL/min, and the addition rate was adjusted to 2 drops/min. The products were trapped by collection in a liquid nitrogen cooled (−196 °C) 250-mL round-bottom flask. Upon completion of addition the system was flushed with 2 mL of distilled *n*-octane. This crude product was purified by preparative gas chromatography. The desired product, 1,2-^{13}C-enriched benzene, gave a retention time of 12.5 min on a 20 ft × $^3/_8$ in., 30% SE-30 on 45/60 Chromasorb W at 150 °C with a flow rate of 33 mL/min.

Pyrolysis of 1,2-^{13}C-Enriched Benzene. The purified (prep. GC) 1,2-^{13}C-enriched benzene was pyrolyzed in a horizontal quartz lined Lindberg furnace packed with quartz chips. The products were collected in a liquid nitrogen cooled (−196 °C) trap. The contact time was controlled via dry nitrogen carrier gas flow and routinely adjusted to a 2-s contact time. The sample was introduced into the oven in the solid state at −196 °C and allowed to warm slowly (over 0.5 h) to the liquification point. The sample was usually pyrolyzed in 10-mg batches; however, a 100-mg batch was used for the final detailed analysis. Samples were nitrated prior to analysis.

Nitration of 1,2-^{13}C-Enriched Benzene. This technique was typically performed on pyrolyzed material, and therefore accurate yields were not possible to determine. This specific procedure is based on nonpyrolyzed material. A 15-mg batch of 1,2-^{13}C-enriched benzene was frozen to −196 °C in a 50-mL Erlenmeyer flask. To this flask was added 10 mL of a −78 °C solution of 1:1 $FSO_3H:HNO_3$. The mixture was allowed to warm to room temperature and stand for 2 h. To this solution was added 10 mL of distilled H_2O, and the mixture was extracted with $DCCl_3$ (5 × 3 mL). The organic layers were combined and dried with anhydrous K_2CO_3 and filtered through a small plug of silica gel. The solution was concentrated to 1 mL and an internal standard added. Yield was judged by ^{1}H NMR to be 30.5 mg (96.5%). ^{13}C NMR ($DCCl_3$) 133.8, 133.4, 133.0, 131.0, 130.7, 130.3, 129.2, 128.8, 128.5, 119.5, 119.0, 118.7. GC–MS (nitration product of unpyrolyzed di-^{13}C-enriched benzene) 70 eV *m/e* (rel abundance) 171 (4.32), 170 (77.07), 169 (20.37), 168 (4.18), 154 (3.55), 124 (30.40), 123 (8.32), 94 (38.00), 93 (10.87), 79 (5.13), 78 (78.93), 77 (100), 76 (47.87), 75 (12.83), 66 (15.22), 65 (26.10), 64 (16.57), 63 (5.82), 54 (3.45), 53 (8.11), 52 (39.33), 51 (53.27), 50 (17.67), 46 (4.61), 41 (3.66), 40 (9.42). The high mass peaks were compared over five GC–MS runs. GC–MS 70 eV (mean (X), standard deviation (S)) *m/e* (rel abundance) 171 (X = 4.13, S = 0.08), 170 (X = 72.77, S = 0.37), 169 (X = 19.32, S = 0.23), 168 (X = 3.74, S = 0.04). GC–MS (nitration product of pyrolyzed di-^{13}C-enriched benzene 70 eV *m/e* (rel abundance) 171 (4.52), 170 (72.04), 169 (19.74), 168 (4.91), 154 (3.64), 124 (29.48), 123 (8.32), 94 (37.87), 90 (11.25), 92 (3.27), 84 (3.27), 79 (5.49), 78 (78.70), 77 (100), 76 (48.93), 75 (13.69), 66 (15.77), 65 (26.60), 64 (17.13), 63 (6.13), 52 (39.76), 51 (55.67), 50 (18.71), 46 (4.15), 41 (3.55), 40 (10.09). The high mass peaks were compared over five GC–MS runs. GC–MS 70 eV *m/e* (rel abundance) 171 (X = 4.51, S = 0.05), 170 (X = 71.17, S = 0.07), 169 (X = 19.51, S = 0.09), 168 (X = 4.82, S = 0.10).

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work. High-field ^{13}C NMR spectra (125 MHz) were obtained at the NSF-supported Southern California Regional NMR facility, California Institute of Technology.

Registry No. 1, 109432-68-0; **2**, 109432-69-1; **3**, 109432-70-4; **4**, 109432-71-5; K^{13}CN, 25909-68-6; [1,6-^{13}C]adiponitrile, 109432-72-6; 1,4-dichlorobutane, 110-56-5; [1,6-^{13}C]diethyl adipate, 80607-20-1; [1,2-^{13}C]-1,2-trimethylsilyloxycyclohexane, 109432-73-7; (*cis*)-[1,2-^{13}C]-1,2-cyclohexanediol, 109432-74-8; (*trans*)-[1,2-^{13}C]-1,2-cyclohexanediol, 109432-75-9; (*cis*)-[1,2-^{13}C]-1,2-diacetoxycyclohexane, 109432-76-0; (*trans*)-[1,2-^{13}C]-1,2-diacetoxycyclohexane, 109432-77-1; [1,2-^{13}C]benzene, 109432-78-2; benzene, 71-43-2.

Benzene Ring Contractions at High Temperatures. Evidence from the Thermal Interconversions of Aceanthrylene, Acephenanthrylene, and Fluoranthene[1]

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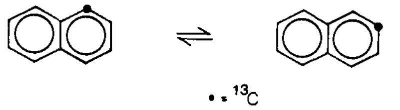
Contribution from the Department of Chemistry and Center for Advanced Study, College of Arts and Science, University of Nevada, Reno, Nevada 89557-0020. Received January 5, 1987

Abstract: The predicted interconversions of the title compounds (**11**, **13**, and **15**) at high temperatures have been verified (Table I) and represent the first examples of thermal rearrangements of aromatic hydrocarbons in which one benzenoid skeleton is transformed into another benzenoid skeleton. Equilibrium concentrations of **11**:**13**:**15** were found to be 17:9:74 at 1100 °C. Acephenanthrylene (**13**) is the primary product of thermal rearrangement when starting from either aceanthrylene (**11**) or fluoranthene (**15**). It is also shown that acephenanthrylene rearranges more rapidly to fluoranthene than to aceanthrylene. These data are summarized in the qualitative energy profile in Figure 1. The mechanism by which these rearrangements occur appears to involve a carbon 1,2-shift (benzene ring contraction) and a hydrogen 1,2-shift, both across the same carbon–carbon bond but in opposite directions. The precise timing of these two shifts relative to each other remains uncertain. The range of possibilities is conveniently illustrated in the More O'Ferrall–Jencks diagram in Figure 2. The demonstration that aceanthrylene, acephenanthrylene, and fluoranthene can be interconverted thermally constitutes the first solid evidence for benzene ring contractions at high temperatures.

Since our preliminary report on the thermal automerization of naphthalene[2] (eq 1), similar carbon atom scramblings have been uncovered by ^{13}C-labeling studies in a number of other



(1)

aromatic hydrocarbons, e.g., pyrene,[3] azulene,[4] benz[*a*]-

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(1) Thermal Rearrangements of Aromatic Compounds: Part 11. For Part 10, see ref 6; for Part 9, see: Scott, L. T. *J. Org. Chem.* **1984**, *49*, 3021. A preliminary account of this work was presented at the 190th National Meeting of the American Chemical Society, Chicago, IL, September 11, 1985; paper ORGN 151.

0002-7863/87/1509-5461$01.50/0 © 1987 American Chemical Society

anthracene,[5] and even benzene.[6] In all of these thermal automerizations,[7] the labeled carbon atom appears to trade places with a neighboring carbon atom by a "1,2-switch" process that is not yet well understood;[8] migration of the label to more distant sites in the molecules is only rarely observed as a minor process[4,6] and may simply reflect secondary rearrangements of the primary automerization products. Migration of the label from a methine position to a ring junction position also seems to be strongly disfavored.[2-5]

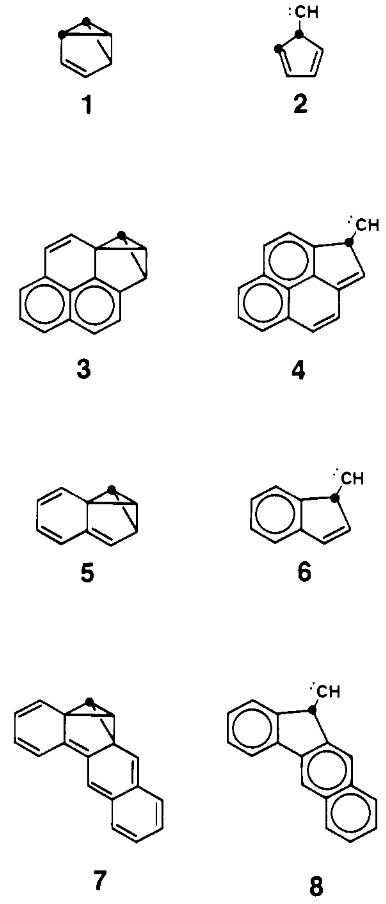
What is the mechanism by which neighboring ring atoms in aromatic hydrocarbons trade places at high temperatures? Does this 1,2-switch of atoms follow the same mechanistic pathway in all aromatic compounds? These questions provided the motivation for the investigations described herein.

Any mechanism proposed for these automerizations not only must account for the ^{13}C-labeling results but also must satisfy certain energetic criteria. Theoretical calculations provide one means of estimating the activation parameters for various alternative reaction pathways.[9] Unfortunately, no precise experimental kinetic data are yet available for any thermal rearrangement of a benzenoid aromatic hydrocarbon.[10] Nevertheless, it has been possible to obtain *relative* rates of reaction by studying different molecular systems in the same apparatus under comparable conditions.[3,5,6]

A reversible valence isomerization of benzene to benzvalene (**1**) appears to be the most likely explanation for the thermal automerization of benzene; an alternative pathway involving ring contraction to the cyclopentadienyl carbene **2**, though plausible, is considered less attractive on energetic grounds.[6] By the same reasoning, we favor the "valene" of pyrene (**3**) over carbene **4** as the intermediate responsible for automerization of pyrene.

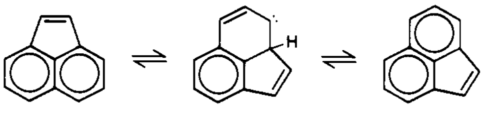
The situation is different, however, for naphthalene and benz[*a*]anthracene. In these molecules, formation of the valene isomers (**5** and **7**) would disrupt the aromatic character of every ring, whereas ring contraction to carbenes **6** and **8** would leave all aromatic rings intact except the ones in which the 1,2-switches occur. Of all these species, valene **7** should show the greatest loss of resonance energy relative to the starting hydrocarbon,[11] yet benz[*a*]anthracene has been found to automerize *faster* than benzene, naphthalene, or pyrene under comparable conditions.[5] This fact leads us to favor carbene **8** as the intermediate responsible for automerization of benz[*a*]anthracene.[5] Though less compelling, the same argument leads us to favor carbene **6** as the intermediate responsible for automerization of naphthalene. Only in the cases of benzene and pyrene, where the loss of aromaticity is the same for both of the proposed intermediates (**1** vs. **2** and **3** vs. **4**), do energetic considerations favor the valene mechanism.

Chart I



We emphasize at this point that the prejudices expressed above represent only a working hypothesis. They do account for all the known facts, but they are by no means the only conceivable viewpoint. Our contention that certain polycyclic benzenoid hydrocarbons suffer ring contraction at high temperatures (e.g., **6** and **8**) would be greatly strengthened, of course, if we could divert the carbene intermediate onto another pathway and actually isolate a product containing a five-membered ring. Unfortunately, the typical methods for trapping carbenes in solution or in the gas phase at lower temperatures cannot be used under the extreme conditions required for the automerization of aromatic compounds. The interception of a thermally contracted benzene ring is thus subject to some rather severe boundary conditions.

Consider, however, the acenaphthylene molecule (**9**). A ring contraction analogous to that proposed for naphthalene (cf. **6**) would produce carbene **10**. The extra two-carbon unit in this



9 **10** **9** (2)

system has two virtues. First, it should prevent consummation of the 1,2-switch process, since an etheno-bridge cannot span the distance from C(1) to C(7) on a naphthalene skeleton. More importantly, it presents an opportunity for trapping the proposed ring-contracted intermediate. A simple 1,2-hydrogen shift in carbene **10**, which should be very favorable, would aromatize the third ring and leave the original aromatic ring that suffered ring contraction as a five-membered ring in the product. Our goal would thus be attained.

There are, however, also two problems with this hypothetical reaction of acenaphthylene. One is that it would be degenerate (eq 2, starting material and product identical), so it could not be detected without the introduction of some desymmetrizing element.

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[2] Scott, L. T.; Agopian, G. K. *J. Am. Chem. Soc.* **1977**, *99*, 4506.

[3] Scott, L. T.; Kirms, M. A.; Berg, A.; Hansen, P. E. *Tetrahedron Lett.* **1982**, *23*, 1859.

[4] (a) Scott, L. T.; Kirms, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 5875. (b) Becker, J.; Wentrup, C.; Katz, E.; Zeller, K.-P. *J. Am. Chem. Soc.* **1980**, *102*, 5110–5112.

[5] Scott, L. T.; Tsang, T.-H.; Levy, L. A. *Tetrahedron Lett.* **1984**, *25*, 1661.

[6] Scott, L. T.; Roelofs, N. H. *J. Am. Chem. Soc.*, preceding paper in this issue.

[7] The term "automerization" was introduced by Balaban to describe those isomerizations that are degenerate in the absence of a label: Balaban, A. T.; Farcasiu, D. *J. Am. Chem. Soc.* **1967**, *89*, 1958.

[8] Scott, L. T. *Acc. Chem. Res.* **1982**, *15*, 52.

[9] Extensive calculations on the $C_{10}H_8$ energy surface have been reported: (a) Dewar, M. J. S.; Merz, K. M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 5142–5145. (b) Dewar, M. J. S.; Merz, K. M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 5146–5153.

[10] A rough measure of the activation barrier for automerization of naphthalene is reported in ref 2. A detailed kinetic analysis of the isomerization of azulene (a *non*-benzenoid aromatic hydrocarbon) to naphthalene was carried out long ago: Kallen, H. J. Ph.D. Dissertation, Eidgenössische Technische Hochschule, Zürich, 1958, cited by: Heilbronner, E. In *Non-benzenoid Aromatic Compounds*; Ginsburg, D., Ed.; Interscience: New York, 1959; pp 263–268.

[11] Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961; p 241.

Table I. Thermal Interconversions of Aceanthrylene (**11**), Acephenanthrylene (**13**), and Fluoranthene (**15**) (Contact Time = 2 s)

starting material	temp (°C)	**11** (%)	**13** (%)	**15** (%)
11	950	96	4	trace
	1000	91	2	7
	1100	39	14	47
13	880	0	96	4
	910	trace	92	8
	940	trace	88	12
	1050	6	34	60
	1096	24	15	61
15	920	0	1	99
	1000	0	3	97
	1115	9	19	72

Fortunately, this desymmetrization can be achieved quite easily, in principle, either by appending a substituent or by incorporating a ^{13}C label. A potentially more serious problem is that the etheno-bridge might simply break off at temperatures below those required for contraction of the benzene ring. Nevertheless, we deemed the possible rewards of studying this reaction to be worth the gamble.

Herein we report results from our experiments with substituted acenaphthylenes that reveal this invisible reaction and lend credence to our hypothesis of benzene ring contractions at high temperatures. We chose to employ an annealed benzene ring as the desymmetrizing "substituent", since few other molecular subunits were expected to be capable of surviving the thermolysis conditions. Extrapolation of eq 2 to the tetracyclic homologues aceanthrylene (**11**), acephenanthrylene (**13**), and fluoranthene (**15**) leads to the prediction that these three benzannelated acenaphthylenes should interconvert at high temperatures (eq 3), and this is precisely what we have found.

Results

At the outset of this project, aceanthrylene (**11**) was unknown, and acephenanthrylene (**13**) had been reported only in a brief communication;[12] fortunately, fluoranthene (**15**) was commercially available. Syntheses of **11** and **13** were therefore worked out, and these have been reported elsewhere.[13,14]

The thermal rearrangements were effected by slowly subliming each of the starting hydrocarbons, in separate experiments, into a stream of dry nitrogen gas that carried the samples through a conventional quartz pyrolysis oven and into a cold trap. The contact time of the material in the hot zone was controlled by varying the nitrogen flow rate. To minimize the possibility of bimolecular reactions, the concentration of material in the hot zone was kept low by maintaining a slow rate of sublimation (ca. 1 mg/h).

In preliminary experiments, aceanthrylene was passed through the hot tube at 1100 °C with a contact time of 2 s. Analysis of the crude product mixture by 500-MHz ^{1}H NMR showed well-resolved peaks that were clearly assignable to each of the three title compounds. Integration of the peak areas indicated the ratio of **11**:**13**:**15** to be 40:14:46 in the product mixture. Capillary gas chromatographic analysis, corrected for the different flame ionization detector response factors, and GC/MS analysis confirmed this result. Under the same conditions, anthracene without the etheno-bridge gives no trace (<0.1%) of phenanthrene.[15]

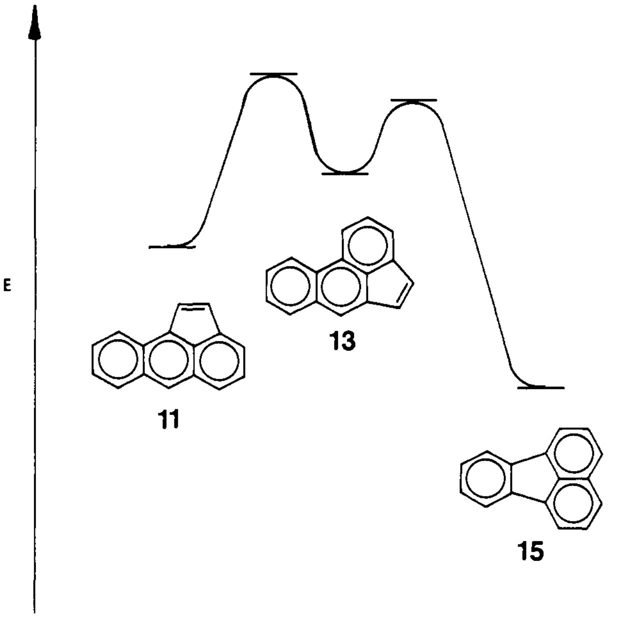

Figure 1. Qualitative energy profile for the high-temperature interconversion of aceanthrylene (**11**), acephenanthrylene (**13**), and fluoranthene (**15**).

Systematic investigation of the interconversion of aceanthrylene, acephenanthrylene, and fluoranthene starting from each of the three isomers gave the results listed in Table I. Although it is doubtful that complete equilibration was ever achieved in any of these runs, it is clear from the high-conversion runs that fluoranthene represents the thermodynamic sink on this portion of the $C_{16}H_{10}$ energy surface at high temperatures.

To determine the relative stabilities of the title compounds under rearrangement conditions, we made an educated guess as to the equilibrium concentrations of the three hydrocarbons, based on the results in Table I. A mixture of this composition, prepared from authentic materials, was then passed through the hot tube at 1100 °C (contact time = 2 s), and the changes in the isomer ratio were determined by GC. From the results of this experiment, a new guess was made as to the equilibrium concentrations, and the experiment was repeated starting with authentic materials mixed in the new proportions. Successive iterations of this procedure utimately led to an isomer mixture (**11**:**13**:**15** = 17:9:74) that did not change under rearrangement conditions (1100 °C, 2 s).

Discussion

Our results confirm the prediction that the title compounds should interconvert at high temperatures. Furthermore, from the low-conversion runs (Table I), it is clear that acephenanthrylene (**13**) is the *primary product* of thermal rearrangement when starting from either aceanthrylene (**11**) or fluoranthene (**15**); production of fluoranthene from aceanthrylene and vice versa appears to result from secondary rearrangement of acephenanthrylene, as predicted by eq 3.

Also in agreement with the mechanism outlined in eq 3 is the observation that acephenanthrylene rearranges more rapidly to fluoranthene than to aceanthrylene (Table I). Contraction of the central ring of a phenanthrene nucleus, leaving two separate benzene rings intact (e.g., **14**), should be more favorable energetically[11] than contraction of a terminal ring, leaving a naphthalene nucleus intact (e.g., **12**).

These conclusions, when taken together with the equilibrium composition data (**11**:**13**:**15** = 17:9:74 at 1100 °C), allow us to draw a qualitative energy profile for this reaction network (Figure 1). Thus, acephenanthrylene is the least stable isomer and lies along the pathway connecting the other two; fluoranthene is the most stable isomer, and the transition state separating acephenanthrylene from fluoranthene is lower than that separating acephenanthrylene from aceanthrylene.

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(12) Krishnan, S.; Hites, R. A. *Anal. Chem.* **1981**, *53*, 342.

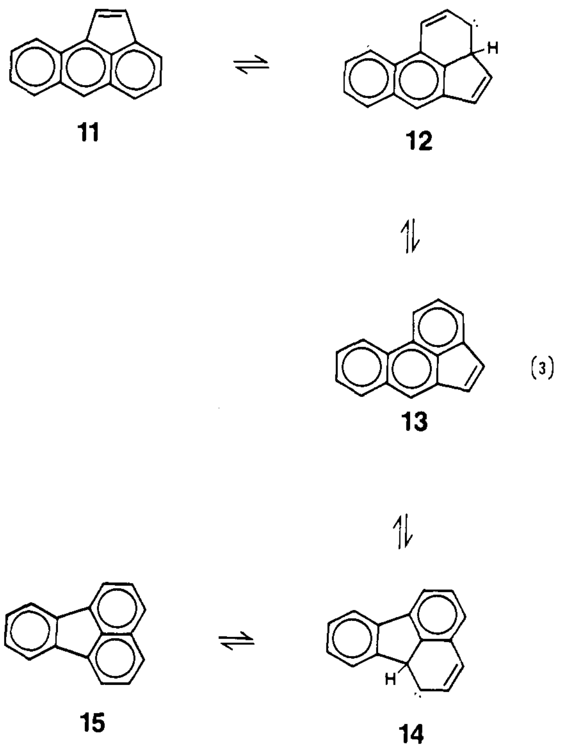
(13) Aceanthrylene (**11**): Cohen, Y.; Roelofs, N. H.; Reinhardt, G.; Scott, L. T.; Rabinovitz, M. *J. Org. Chem.*, in press. During the course of this project, several other syntheses of aceanthrylene were reported: (a) Plummer, B. F.; Al-Saigh, Z. Y.; Arfan, M. *J. Org. Chem.* **1984**, *49*, 2069–2071. (b) Becker, H.-D.; Hansen, L.; Andersson, K. *J. Org. Chem.* **1985**, 277–279. (c) Sangaiah, R.; Gold, A. *Org. Prep. Proced. Int.* **1985**, *17*, 53–56.

(14) Acephenanthrylene (**13**): Scott, L. T.; Reinhardt, G.; Roelofs, N. H. *J. Org. Chem.* **1985**, *50*, 5886. For an alternative synthesis, see: Neumann, G.; Müllen, K. *Chimia* **1985**, *39*, 275–276.

(15) Scott, L. T.; Kirms, M., unpublished observation. **Note Added in Proof**: recent reinvestigation of this reaction shows a few percent of phenanthrene formed from anthracene at 1100 °C (2 s).

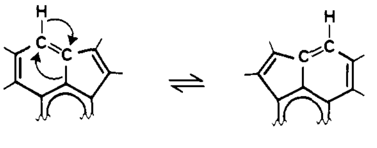
We were somewhat surprised to find that acephenanthrylene (**13**) is slightly *less* stable than aceanthrylene (**11**) under the rearrangement conditions. In the absence of the etheno-bridge, the angularly fused tricyclic hydrocarbon phenanthrene is more stable than the linearly fused isomer, anthracene.[16] Simple Hückel molecular orbital calculations predict the isomers with the phenanthrene nucleus to be the more stable in both cases, yet our results unambiguously point to a reversal of this order in the etheno-bridged compounds (at 1100 °C). We have no explanation for this curious observation.

Of greater importance to the question of mechanism is the fact that anthracene fails to yield any trace of phenanthrene under conditions where the etheno-bridged compounds undergo extensive interconversion.[15] Close examination of the ring contraction mechanism proposed in eq 3 reveals that there exists no analogous pathway for the interconversion of anthracene and phenanthrene. Thus, the etheno-bridge definitely plays more than a spectator role in the tetracyclic series.



(3)

All the results of our experiments with these compounds stand in complete harmony with the ring contraction mechanism outlined in eq 3. One can construct, however, some variations on this mechanism that are equally compatible with the results. For example, the ring contraction (a carbon 1,2-shift) need not precede the hydrogen 1,2-shift; the two shifts could take place simultaneously to give the isomeric hydrocarbon in a single concerted step (eq 4). Such isomerizations, in which groups at opposite ends of the same bond swap places simultaneously, have been termed "dyotropic rearrangements".[17]



(4)

A second variation would be for the carbon and hydrogen 1,2-shifts still to occur as two discrete steps but in the reverse order (eq 5).

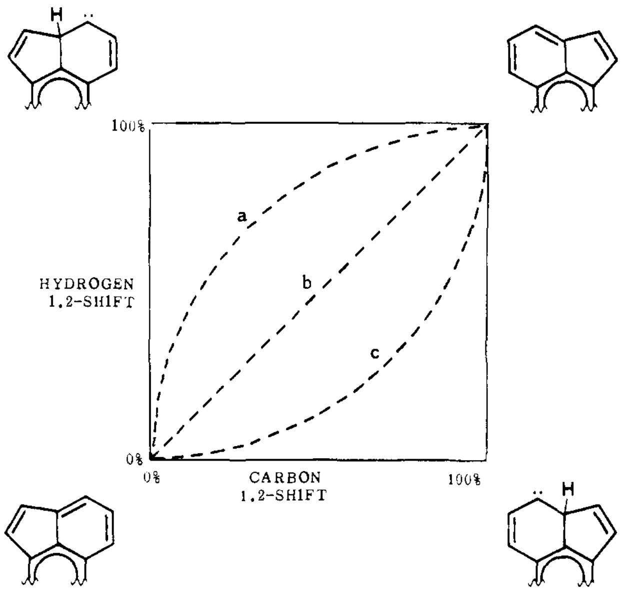
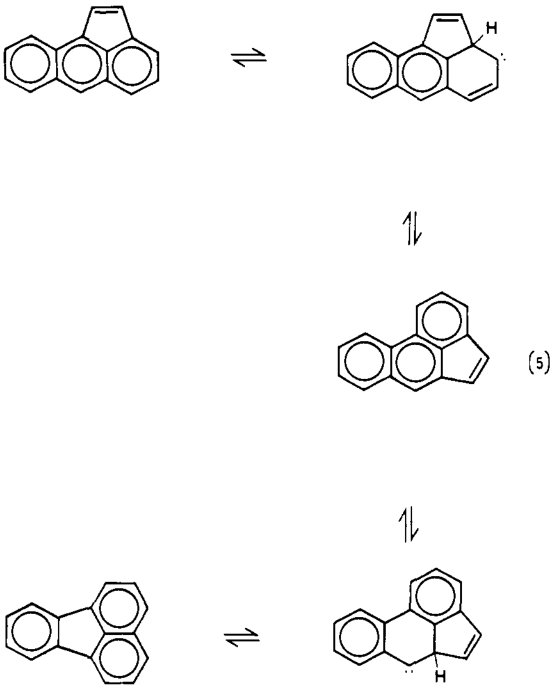


Figure 2. More O'Ferrall–Jencks diagram for the thermal rearrangement of etheno-bridged benzenoid aromatic hydrocarbons; see text for discussion.



(5)

In fact, one can imagine an infinite set of "concerted but non-synchronous"[18] dyotropic rearrangement mechanisms that fall between the two stepwise mechanisms depicted in eq 3 and 5. This family of possibilities is best pictured in a More O'Ferrall–Jencks diagram (Figure 2). The two stepwise pathways follow the vertical and horizontal axes of the diagram (counterclockwise for eq 3; clockwise for eq 5), and the synchronous dyotropic rearrangement, in which both 1,2-shifts progress at the same rate, lies along the diagonal (path b). All concerted but non-synchronous mechanisms in which the carbon 1,2-shift lags behind the hydrogen 1,2-shift lie above the diagonal, e.g., path a, whereas all concerted but non-synchronous mechanisms in which the hydrogen 1,2-shift lags behind the carbon 1,2-shift lie below the diagonal, e.g., path c. At present, we have no way of distinguishing among these

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[16] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

[17] (a) Reetz, M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 129–130. (b) Reetz, M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 130–131. (c) Brook, A. G.; Bassindale, A. R. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, Chapter 9.

[18] A distinction between the terms "concerted" and "synchronous" has been proposed: Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209–219.

various mechanistic possibilities, which differ only in the timing of the two 1,2-shifts, and there is no guarantee that we have not overlooked still other possible mechanisms. These uncertainties, however, do not mollify our basic conclusions.

Conclusions

The demonstration that aceanthrylene, acephenanthrylene, and fluoranthene can be interconverted thermally constitutes the first strong evidence for the occurrence of benzene ring contractions at high temperatures. These interconversions furthermore represent the first examples of thermal rearrangements of aromatic hydrocarbons in which one benzenoid skeleton is transformed into another benzenoid skeleton. The mechanism by which these rearrangements occur appears to involve a carbon 1,2-shift and a hydrogen 1,2-shift, both across the same carbon–carbon bond but in opposite directions. The precise timing of these two shifts relative to each other remains uncertain.

Experimental Section

All gas chromatograms (GC) were recorded on a Vaian 1400 GC fitted with a 25 m broad bore (0.75 mm, SPB-5) capillary column. GC–MS analyses were performed on a Finnigan 4023 GC–MS operated by Roger Scholl. Aceanthrylene (**11**)[13] and acephenanthrylene (**13**)[14] were prepared by the literature methods of Scott, Roelofs et al. Fluoranthene (**15**) was purchased from Aldrich Chemical Co.

Pyrolysis of Aceanthrylene, Acephenanthrylene, and Fluoranthene. The title compounds were pyrolyzed in a horizontal quartz lined Lindberg tube furnace (purchased from Kontes Glass Inc.) packed with quartz chips. The contact time was controlled by varying the flow rate of nitrogen carrier gas and was typically held at 2 s. The sample was adsorbed on Pyrex wool and placed in an attached head. The head was warmed to 100 °C via an aluminum sleeve wrapped with heating tape. The sample was typically pyrolyzed in 10-mg batches, and the product was collected in a liquid-nitrogen trap. The sample was washed out of the trap with $CDCl_3$, and analysis was carried out via ^1H NMR (500 MHz), capillary GC, and GC–MS. The results are summarized in Table I. Mass balance typically ranged from 70% at 880 °C to 35% at 1200 °C.

Acknowledgment. We thank Gerd Reinhardt and Scott Fielder for early synthetic work and the National Science Foundation for financial support of this work. High-field ^1H NMR spectra (500 MHz) were obtained at the University of California, Davis Medical NMR Facility.

Registry No. 11, 202-03-9; **13**, 201-06-9; **15**, 206-44-0.

Steric Effects on Acidities of 9-Alkyl-, 9-(Alkylthio)-, and 9-Alkoxyfluorenes and on the Electron-Transfer Abilities of Their Conjugate Bases

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Abstract: Perturbations caused by steric effects in 9-alkylfluorenes (9-R-FlH) account, in part, for the effects of changing alkyl size on acidities and, in turn, for the failure of the acidity–oxidation potential (AOP) method to provide reasonable estimates for the radical-stabilizing effects of large alkyl substituents, such as *t*-Bu, *t*-$BuCH_2$, and $PhC(Me)_2CH_2$. Increases in alkyl size along the series Me, Et, *i*-Pr, and *t*-Bu for 9-RS-FlH and 9-RO-FlH fluorenes cause progressive increases in acidities due to increases in polarizability effects, but the radical-stabilizing effects of these substituents on the 9-fluorenyl radical, as estimated by the AOP method, remain essentially contant at 5.4 ± 0.3 kcal/mol for RS and 6.5 ± 0.5 kcal/mol for RO. Rate constants (log k_{obsd}) for single-electron transfer to an electron acceptor from 9-R-Fl-, 9-RO-Fl-, 9-RS-Fl^-, and 9-R_2N-Fl^- ions, where R is varied in size, plot linearly with their oxidation potentials, indicating that rates of electron transfer from these carbanions are much less subject to steric hindrance than are rates of S_N2 reactions of these anions with alkyl halides.

Investigations of the acidities and reactivities of fluorenes have provided a fertile field for studies of substituent effects for the past three decades.[1-8] Substituents at the 1, 2, 3, and 4 positions, although remote from the acidic hydrogen atoms in the 9-position, have large effects on acidity (the Hammett ρ is 7 for the "meta" 2-position) and substituents at the 9-position have very large effects.[8] The progressive decrease in acidity caused by 9-alkyl groups along the series Me, Et, *i*-Pr, and *t*-Bu, which has been observed in aqueous Me_2SO,[2] cyclohexylamine,[3] and Me_2SO,[5] has been attributed primarily to a polar effect based on a Taft correlation ($\rho^* = 4.5$) on the one hand,[3,7] and primarily to steric effects on the other.[5] The progressive decrease in S_N2 reactivities toward $PhCH_2Cl$ of 9-alkylfluorenide ions, 9-R-Fl^-, along the series Me, Et, *i*-Pr, and *t*-Bu, at the same basicities, has also been attributed to steric effects.[9] Recently, oxidation potentials, $E_{ox}(A^-)$, for 2-G-Fl^-, 3-G-Fl^-, and 9-G-Fl^- carbanions have been measured for a variety of substituents and combined with pK_{HA} values of their conjugate acids to give acidity-oxidation-potential (AOP) values, which provide estimates of substituent effects on the relative bond dissociation energies (BDEs) or stabilities of 9-fluorenyl radicals.[10] The $E_{ox}(A^-)$ values for 12 2-G-Fl^- and 2,7-G-Fl^- ions were found to correlate directly with the pK_{HA} values of their conjugate acids, indicating that these remote ("meta") substituents had little or no ability to stabilize (or destabilize) the radical. Small increases in $E_{ox}(A^-)$ values beyond

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