24% yield): mp 60–61 °C; IR (melt) 1530 and 1350 cm^{-1} (NO_2); ^1H NMR δ 5.04 (t, 2 H, J = 7.2 Hz) and 2.42 (t, 2 H, J = 7.2 Hz); ^{13}C NMR δ 59.14 (2 CH) and 19.02 (CH_2); MS m/e 132 (M^+).

Anal. Calcd for $C_3H_4N_2O_4$: C, 27.28; H, 3.05. Found: C, 27.57; H, 3.13.

Starting 1,3-dinitropropane (41 mg, 5% recovery) was obtained as a less mobile fraction during preparative TLC.

This reaction was carried out in the presence of 5 mol % di-*tert*-butyl nitroxide with no change in results. It was carried out under sunlamp irradiation and in the dark also with no change in results. Attempts to carry out cyclization in water or methanol led to no formation of **1a**.

Preparation of 2,4-Dibromo-2,4-dinitropentane (4). Cleaned Na (149 mg, 6.49 mmol) was added to distilled 1-butanol (5 mL), and the mixture was refluxed for 20 min under Ar to attain complete reaction. The resulting stirred solution was cooled (0–5 °C) and 2,4-dinitropentane (55:45 mixture of diastereomers, 277 mg, 1.71 mmol) was added dropwise over 1 min. After 5 min, the resulting thick suspension was added portionwise over 5 min to a cold (0–5 °C) stirred solution of Br_2 (1.02 g, 6.4 mmol) in CH_2Cl_2 (5 mL), water (2 mL) being used to complete the transfer. After 5 min, water (10 mL) and excess sodium bisulfite were added. The mixture was extracted with CH_2Cl_2 (three 10-mL portions), and the combined extracts were washed (10 mL water), dried (anhydrous Na_2SO_4), and concentrated at reduced pressure. Kugelrohr distillation of the resulting oil gave **4** (434.1 mg, 79% yield) which was >95% pure (GC, NMR). A purer product (>99%; 249 mg, 50:50 mixture of diastereomers) was obtained by preparative TLC (70:30 CCl_4–CH_2Cl_2 elution) by taking the lower three-fourths of the main band: NMR δ 4.07 (s, 2 H, R^*,R^*) superimposed on 4.04 (d, 1 H, J = 16.7 Hz, R,S), 3.91 (d, 1 H, J = 16.7, R,S), 2.28 (s, 6 H, R,S), and 2.17 (s, 6 H, R^*,R^*). The remaining one-fourth of the main band partially overlapped a minor band; the material isolated (71 mg) consisted of the R^*,R^* diastereomer of **4** and a small amount of butoxylated material.

Dibromodinitro compound **4** could also be prepared by using sodium methoxide in methanol, but a small amount of methoxylated side product, which could not be separated by TLC or simple distillation, contaminated the product.

Reaction of Dibromodinitro Compound 4 with the Lithium Salt of 2-Nitropropane. Without Added *m*-DNB. A solution containing **4** (81 mg, 0.25 mmol) in DMSO (5 mL) was stirred under Ar at 18–20 °C while a second solution containing the lithium salt of 2-nitropropane (45 mg, 0.48 mmol) in DMSO (5 mL) was added dropwise over 3 min. The resulting pink solution was stirred for 0.5 min and was added to water (100 mL). This mixture was then acidified with dilute HCl and extracted with CH_2Cl_2 (three 10-mL portions). The combined extracts were washed, dried, and concentrated at reduced pressure to give a semisolid: NMR and GC analysis indicated 2,3-dimethyl-2,3-dinitrobutane (**5**) (70%), dinitrocyclopropane **1b** (25%), and a trace of 2-bromo-2-nitropropane (**6**) (5%). Small amounts of unidentified materials were apparent from the NMR. Preparative TLC gave **5** (35 mg, 88% yield) and **1b** (6 mg, 15% yield) as a more mobile fraction. A small amount of less mobile material (unidentified mixture, 2 mg) was also obtained.

In the Presence of 78 mol % *m*-DNB. A solution containing **4** (81 mg, 0.25 mmol) and *m*-DNB (33 mg, 0.2 mmol) in DMSO (5 mL) was treated with the lithium salt of 2-nitropropane as in the preceding experiment. Bright red coloration was noted as each drop of the nitronate solution was added. The crude product was a pale yellow semisolid: NMR and GC analysis indicated *m*-DNB (50%), dinitrocyclopropane **1b** (20%), **6** (25%), and **5** (5%). Several other materials in trace amounts were apparent from the NMR. Preparative TLC gave *m*-DNB containing **5** (95:5, respectively) (33 mg), **1b** (12 mg, 29% yield), and a little of the volatile **6** (11 mg, 25% yield).

X-ray Analysis of 1a. A crystal of **1a** was mounted in a capillary to minimize sublimation, and crystallographic data were collected at 299 K. A set of 1771 $\pm h,\pm k,l$ reflections were measured with a sphere limited by 2θ = 120° using graphite-monochromated Cu Kα radiation (λ = 1.54184 Å). Three standard reflections ($\bar{2}52$, $\bar{2}13$, $\bar{2}\bar{1}3$) measured every 2000 s of exposure showed an intensity decrease of 2.2%. A total of 718 unique reflections with $I > 3\sigma(I)$ were used during structure determination. These data were corrected for Lorentz and polarization effects but not for absorption.[27] The structure was solved by direct methods using the MULTAN 11/82 package, which revealed all nine heavy atoms. Hydrogen atoms were located from a subsequent difference Fourier synthesis. Full-matrix least-squares refinement on F for 98 variables converged to R = 0.069 and R_w = 0.082.

Acknowledgment. Partial support of this work by ARDEC, Contract No. DAAA21-86-C-0101 (Geo-Centers, Inc. Subcontract GC-86-1686-005) is gratefully acknowledged.

Supplementary Material Available: Tables of crystallographic refined positional parameters, refined displacement (β) parameters, and bond distances and angles (3 pages). Ordering information is given on any current masthead page.

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[27] The Enraf-Nonius Structure Determination Package, Delft, Holland (1986) was used for data collection, data reduction, structure solution, and structure refinement.

Automerization of Benzene[1]

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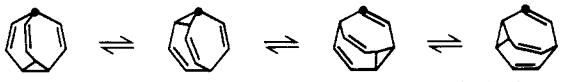
Abstract: It has been demonstrated that the atoms of benzene interchange positions *intra*molecularly (but not *inter*molecularly) at high temperatures in a quartz flow system. Thermolysis of benzene-*o*-$^{13}C_2$ at 1110 °C with a 2.0-s contact time gave ortho, meta, and para benzene-$^{13}C_2$ in a ratio of 72:24:4. The data point to a "1,2-switch" of atoms as the primary reaction pathway. Several mechanistic possibilities that could explain this automerization of benzene are considered. Of these, the reversible formation of benzvalene (eq 4) appears to be the most reasonable at this time.

Automerizations, the degenerate skeletal rearrangements of polyatomic molecules, have long held great fascination for organic chemists.[2] The degenerate Cope rearrangements of bullvalene that let every carbon atom in the molecule eventually occupy every possible site in the skeleton, for example, seem almost to mock the very concept that molecules have structure (eq 1).[3]


(1)

Other examples of thermal automerizations in hydrocarbons, heterocycles, and organometallic compounds abound.[4] For many

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[1] Thermal Rearrangements of Aromatic Compounds: Part 10. For Part 9, see ref 12c. A preliminary account of this work was presented at the 190th National Meeting of the American Chemical Society, Chicago, Illinois, September 11, 1985, abstract ORGN 150.

[2] 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.* **1968**, *89*, 1958.

[3] (a) Doering, W. von E.; Roth, W. R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 115. (b) Schröder, G. *Chem. Ber.* **1964**, *97*, 3140. (c) Merényi, R.; Oth, J. F. M.; Schröder, G. *Chem. Ber.* **1964**, *97*, 3150.

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years, however, aromatic compounds were thought to be immune to such skeletal rearrangements. Then in 1977, the thermal scrambling of ^{13}C-labeled naphthalene was reported (eq 2).[5] Since

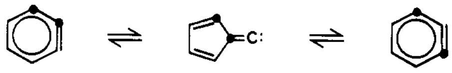
(2)

that time, thermal automerizations of azulene,[6] pyrene,[7] and benz[*a*]anthracene[8] have also been discovered. Not surprisingly, these degenerate rearrangements require temperatures considerably above those needed to effect isomerizations among compounds that lack the special thermodynamic stabilization[9] imparted by aromaticity; however, they do occur.

The mechanisms by which aromatic hydrocarbons automerize remain a mystery. While some evidence has accumulated to *dis*prove the involvement of certain pathways, no unified mechanistic picture for these processes has yet emerged.[10] Part of the attraction this area of study offers, in fact, is the prospect that new or unusual reaction types might be uncovered at such extreme temperatures. Few organic compounds other than aromatic hydrocarbons can be recovered after more than the briefest exposure to temperatures in excess of 1000 °C. An understanding of the mechanistic principles that govern automerizations in simple aromatic molecules should provide, inter alia, a basis for understanding the high-temperature transformations of coal and other carbonaceous materials.

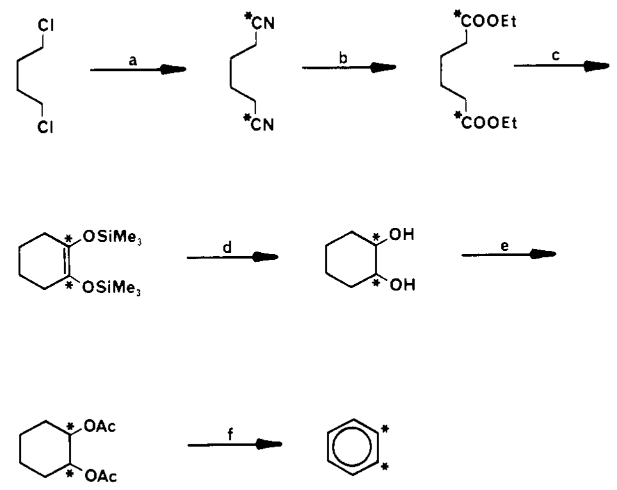
Dewar and Merz have recently published two full papers[11] describing their extensive calculations on the $C_{10}H_8$ energy surface, which include the evaluation of several possible mechanistic pathways for both the automerization of naphthalene and the isomerization of azulene to naphthalene.[12] This detailed theoretical analysis beautifully complements the experimental work being done on thermal rearrangements of aromatic compounds.

In light of the growing number of examples of automerizations in polycyclic aromatic compounds, it is inevitable that chemists should ultimately want to know whether the quintessential aromatic compound, i.e., benzene, also suffers automerization at high temperatures. Thermal interconversions of the xylenes[13] and of the difluorobenzenes[14] in the gas phase have been reported, but there is no assurance that these isomerizations involve true skeletal reorganizations, as opposed to substituent migrations. Thus, we resolved to examine the question of benzene automerization using di-^{13}C-labeled benzene. It is interesting to note that evidence for the automerization of benz*yne* in the gas phase (eq 3) has already been reported by Brown et al.[15]



(3)

Scheme I[a]



[a] (a) K*CN. (b) EtOH, H_2SO_4. (c) Na, ClSiMe$_3$. (d) NaBH$_4$, NaOH. (e) Ac_2O, pyridine. (f) Pd/C, 450 °C.

Since benzene-$^{13}C_2$ is not commercially available, it was necessary to prepare a sample by total synthesis. Of the three possible target molecules, the ortho isomer was considered more desirable than the meta and para because it could provide the most information about the relative importance of the "1,2-switch" vs. the 1,3-switch vs. the 1,4-switch of atoms, if one or more of these processes could occur. A 1,3-switch of atoms in benzene-*m*-$^{13}C_2$ would be undetectable, as would a 1,4-switch of atoms in benzene-*p*-$^{13}C_2$.

Thus, this project consisted of three parts: synthesis of the double-labeled benzene, thermolysis of the synthetic material, and analysis of the recovered benzene to determine the location of the labels.

Results

Synthesis. Starting from a relatively inexpensive source of ^{13}C, we developed the synthesis of benzene-*o*-$^{13}C_2$ outlined in Scheme I. The first three steps of this synthetic sequence are unexceptional; however, step d deserves two comments. First, with respect to mechanism, it seems most likely that the silylated enediol reacts initially with the sodium hydroxide to produce 2-hydroxycyclohexanone and that sodium borohydride then reduces the carbonyl group in the usual manner. Second, with respect to stereochemistry, the cyclohexane-1,2-diol produced in this reaction was found by NMR spectroscopy to be a mixture of cis and trans isomers. These isomers were carried through the remaining steps of the synthesis as a mixture without complication.

The final aromatization step f also deserves a brief explanation. This reaction was conducted as a normal acetate pyrolysis except that the initially formed product (presumably cyclohexadiene) was made to pass through a short plug of palladium on carbon just before exiting from the hot tube. Spectroscopic analysis (see below) demonstrated that no scrambling of the labels occurred during this step; the benzene-$^{13}C_2$ produced was exclusively ortho. From 5.0 g of KCN we obtained 2.5 g of benzene (41% overall yield). The synthetic benzene was purified by preparative gas chromatography prior to thermolysis.

Thermolysis. The labeled benzene was slowly evaporated into a stream of dry nitrogen gas that carried the vapors through a conventional quartz pyrolysis oven and into a cold trap. The contact time of the benzene in the hot zone was controlled by varying the nitrogen flow rate. To minimize the possibility of bimolecular reactions, the concentration of benzene in the hot zone was kept low by cooling the starting material so that the rate of evaporation never exceeded more than 0.5 mg/min.

Spectroscopic Analysis. Since the two ^{13}C nuclei in benzene-*o*-$^{13}C_2$ are magnetically equivalent by symmetry, they should give rise to a ^{13}C NMR spectrum comprised of only a single line at 129 ppm downfield from tetramethylsilane. By the same reasoning, benzene-*m*-$^{13}C_2$ and benzene-*p*-$^{13}C_2$ should likewise give

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(4) (a) Scott, L. T.; Jones, M., Jr. *Chem. Rev.* **1972**, *72*, 181–202. (b) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981. (c) Cotton, F. A.; Hanson, B. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, Chapter 12.

(5) Scott, L. T.; Agopian, G. K. *J. Am. Chem. Soc.* **1977**, *99*, 4506.

(6) (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. (c) Zeller, K.-P. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 440.

(7) Scott, L. T.; Kirms, M. A.; Berg, A.; Hansen, P. E. *Tetrahedron Lett.* **1982**, *23*, 1859.

(8) Scott, L. T.; Tsang, T.-H.; Levy, L. A. *Tetrahedron Lett.* **1984**, *25*, 1661.

(9) Garratt, P. J. *Aromaticity*; Wiley: New York, 1986.

(10) Scott, L. T. *Acc. Chem. Res.* **1982**, *15*, 52.

(11) (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. (c) For related calculations on one portion of the C_6H_6 energy surface, see: Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1975**, *97*, 2932–2933.

(12) For the azulene-to-naphthalene rearrangement, see ref 6a and 6b; see also: (a) Scott, L. T.; Kirms, M. A.; Minton, M. A. *Croat. Chem. Acta* **1980**, *53*, 643. (b) Scott, L. T.; Kirms, M. A.; Earl, B. L. *J. Chem. Soc., Chem. Commun.* **1983**, 1373. (c) Scott, L. T. *J. Org. Chem.* **1984**, *49*, 3021 and references cited therein.

(13) Crow, W. D.; Wentrup, C. *Tetrahedron Lett.* **1968**, 3111–3114.

(14) Scott, L. T.; Highsmith, J. R. *Tetrahedron Lett.* **1980**, *21*, 4703.

(15) Barry, M.; Brown, R. F. C.; Eastwood, F. W.; Gunawardana, D. A.; Vogel, C. *Aust. J. Chem.* **1984**, *37*, 1643–1657.

rise to ^{13}C NMR spectra comprised of only a single line at 129 ppm. Thus, conventional ^{13}C NMR spectroscopy would appear inadequate as a method to detect scrambling of the label.

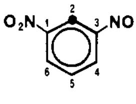
This cursory view of the problem, however, overlooks the fact that the two ^{13}C nuclei in benzene-*o*-$^{13}C_2$ occupy magnetic environments that are intrinsically different from those of the ^{13}C nuclei in benzene-*m*-$^{13}C_2$ and benzene-*p*-$^{13}C_2$. In the ortho isomer, each ^{13}C nucleus has one ^{12}C neighbor and one ^{13}C neighbor; the ^{13}C nuclei in the meta and para isomers, on the other hand, each have two ^{12}C neighbors and no ^{13}C neighbors. Thus, the ^{13}C nuclei in benzene-*o*-$^{13}C_2$ should resonate at slightly higher field than those in the meta and para isomers, owing to the isotope shift[16] caused by an attached ^{13}C. It was hoped that the isotope shift would be measurable by ^{13}C NMR spectroscopy at very high field strength, and this proved to be the case.

Before proceeding with the product analysis, it is important first to look at the analysis of the starting material. The benzene used in these experiments was synthesized from KCN that was claimed by the manufacturer to be 90% ^{13}C enriched. Accordingly, the synthetic benzene would be expected to be approximately 81% di-^{13}C labeled, 18% mono-^{13}C labeled, and 1% unlabeled if the four "unlabeled" positions were all purely ^{12}C. Of course, the contributions of natural abundance ^{13}C at these four positions changes these numbers slightly. By mass spectrometric analysis, the percentages of tri-, di-, mono-, and non-labeled benzene were actually found to be 0.13%, 75.66%, 20.04%, and 4.17%, respectively. These experimental values agree with the theoretical values obtained by calculations that include all sources of ^{13}C, i.e., 86.5% enrichment at two positions and 1.1% natural abundance at the other four. The small amount of tri-^{13}C-labeled material should be a mixture of isomers and henceforth will be ignored. The meta- and para-di-^{13}C-labeled material are each calculated to constitute less than 0.5% of the molecules in the synthetic benzene and can also be ignored. Most importantly, the high-field (125 MHz) ^{13}C NMR spectrum of the synthetic benzene showed two well-resolved peaks at 129.04 and 129.06 ppm with relative areas 89:11, respectively, thus demonstrating that this spectroscopic method can indeed distinguish between benzene-*o*-$^{13}C_2$ (129.04 ppm) and other benzenes lacking nearest-neighbor ^{13}C nuclei (129.06 ppm). Taking into account the fact that benzene-*o*-$^{13}C_2$ has two ^{13}C nuclei contributing to the signal intensity at 129.04 ppm, the relative areas of 89:11 correspond to a molar ratio of ortho-di-^{13}C- to mono-^{13}C-labeled benzene of 77:19. The agreement between the mass spectral and NMR analyses (76:20 vs. 77:19) confirmed our assumption that the benzene-$^{13}C_2$ obtained by synthesis had the labels located essentially all ortho.

The benzene recovered from thermolysis likewise gave two well-resolved peaks at 129.04 and 129.06 ppm in its 125-MHz ^{13}C NMR spectrum. Under relatively mild thermolysis conditions, the integrated ratio of these two peaks remained the same as that in the starting material (89:11), and this ratio did not change even in samples heated under fairly severe conditions (1050 °C oven, 2.0 s contact time). More forcing conditions (1096 °C oven, 5.0 s contact time), however, finally produced a growth in the low-field peak at the expense of intensity in the high-field peak. From the change in the relative areas of these two peaks (75:25) we calculate that 16% of the benzene-*o*-$^{13}C_2$ must have rearranged to the meta and/or para isomers.

Unfortunately, this method of analysis does not distinguish between meta and para benzene-$^{13}C_2$, so it was not possible to tell whether both were formed in equal amounts or whether one predominated over the other. To solve this problem, we decided to derivatize the benzene. Nitration with nitric acid and trifluoromethanesulfonic acid at room temperature was found to be quite straightforward on a small scale and cleanly stopped at the *m*-dinitrobenzene stage. Carrying out this reaction on the rearranged sample, of course, would be expected to give all possible *m*-dinitrobenzene products of each of the three benzene-$^{13}C_2$s present as well as all possible *m*-dinitrobenzene products of the mono-^{13}C-labeled benzene, i.e., up to 13 compounds in all. Fortunately, the task of analyzing the ^{13}C NMR spectrum of this bewildering mixture is not nearly as formidable as it might appear at first sight.

The proton-decoupled natural-abundance ^{13}C NMR spectrum of *m*-dinitrobenzene consists of four signals: 133.39, 130.69, 128.86, and 119.09 ppm. Note that the highest field signal, which corresponds to the resonance of the carbon nucleus at position 2, is well separated from the other three signals. The key to simplifying the analysis of the spectrum of the nitrated thermolysis mixture is to recognize that only four of the 13 compounds (**1**–**4**) will have a ^{13}C at the 2-position that can contribute to the signal centered at 119 ppm; the other nine compounds will have a ^{12}C at the 2-position. Thus, if the relative contributions of the four compounds **1**–**4** to the signals centered at 119 ppm can be determined, then the relative abundances of all four compounds in the mixture can be established.



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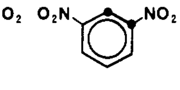

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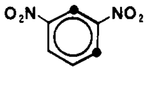

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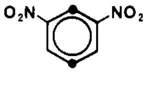

4

The *m*-dinitrobenzene obtained from nitration of the starting benzene gave a singlet at 119 ppm in the ^{13}C NMR spectrum (for compound **1**) flanked by a doublet ($^1J_{CC}$ = 70 Hz, for compound **2**). The integrated ratio of the doublet to the singlet (77:23) provided yet another measure of the ratio of ortho-di-^{13}C-labeled:mono-^{13}C-labeled benzenes in the synthetic material.

A $^1J_{CC}$ of 70 Hz is about what one would expect for ortho ^{13}Cs in a benzene ring.[17] From the literature values of long-range CC coupling constants in other aromatic compounds, a meta coupling constant ($^2J_{CC}$) of 0–2 Hz and a para coupling constant ($^3J_{CC}$) of 5–8 Hz would be expected.[17] This means that any production of benzene-*m*-$^{13}C_2$ during the thermolysis would be manifest in the ^{13}C NMR spectrum of the nitration product as a growth (and possibly broadening) in the singlet centered at 119 ppm. Any production of benzene-*p*-$^{13}C_2$ during the thermolysis would be manifest as a new doublet with a J = 5–8 Hz centered at 119 ppm. Thus, after correcting for the contribution of mono-^{13}C-labeled benzene to the central peak at 119 ppm, one should be able to determine the ratio of ortho:meta:para benzene-$^{13}C_2$s directly from the integration of the peaks centered at 119 ppm. Since the peaks being compared all arise from ^{13}C nuclei at the 2-position of *m*-dinitrobenzene, the analysis should not suffer from the complications usually associated with the integration of ^{13}C NMR signals.

The thermolysis of benzene-*o*-$^{13}C_2$ was repeated at an oven temperature of 1110 °C with a contact time of 2.0 s, and the recovered benzene was nitrated as described above. The ^{13}C NMR spectrum of the *m*-dinitrobenzene thus obtained showed a singlet and two doublets (J = 5.6 and 70 Hz) centered at 119 ppm in the high-field region. We ascribe these peaks to the resonances of the ^{13}C nuclei at position 2 in compounds **1** (singlet), **2** (doublet, J = 70 Hz), **3** (singlet), and **4** (doublet, J = 5.6 Hz). The ratio of the integrated areas of the 70-Hz doublet to the singlet to the 5.6-Hz doublet was determined to be 59:38:3. Correcting the area of the singlet for the known amount of mono-^{13}C-labeled material gives a ratio of **2**:**3**:**4** of 72:24:4. Assuming no kinetic isotope effect in the nitration step, which seems quite safe, these data imply that this thermolysis of benzene-*o*-$^{13}C_2$ gave 24% benzene-*m*-$^{13}C_2$ and 4% benzene-*p*-$^{13}C_2$.

Mass spectroscopic analysis of the automerized benzene (as its dinitro derivative) showed that there had been no disproportionation of di-^{13}C-labeled benzenes to tri- and mono-^{13}C-labeled benzenes, i.e., that there had been no *inter*molecular scrambling of the atoms.

Finally, it should be noted that the first benzene thermolysis (1096 °C, 5.0 s contact time) gave only 16% rearrangement,

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(16) Porwoll, J. Ph.D. Dissertation, University of Minnesota, Minneapolis, MN, 1984.

(17) Hansen, P. E. *Org. Magn. Reson.* **1978**, *11*, 215.

whereas the second one (1110 °C, 2.0 s contact time) gave 28% rearrangement. This difference seems too large to ascribe solely to the change in temperature and presumably reflects also the change in apparatus between the two experiments: the first thermolysis was conducted in a 1.0 cm diameter tube with a hot zone volume of 13.6 mL, and the second thermolysis was conducted in a 3.0 cm diameter tube with a hot zone volume of 80 mL. Both results were reproducible; however, the larger volume tube appears to have been more efficient at heating the sample, even over a shorter contact time. This observation emphasizes the need for caution when comparing quantitative thermolysis data obtained with different apparatuses.

Discussion

Our results clearly reveal that the atoms of benzene interchange positions at temperatures on the order of 1100 °C in a quartz flow system. The absence of disproportionation means that the molecules must not be flying apart to smaller fragments (e.g., acetylene) that recombine randomly. It also means that benzene molecules must not be coming together to form dimers in which atoms are swapped from ring to ring. Such dissociative and associative processes are incompatible with the experimental data. Our results are consistent with, but do not demand, a unimolecular process involving only C_6H_6 species. Unfortunately, we cannot absolutely exclude the possibility of a radical chain reaction involving, for example, species such as $^{\bullet}C_6H_7$. Such processes are considered improbable, however, at the low concentrations of benzene employed in our experiments.

The fact that benzene-*o*-$^{13}C_2$ gives both benzene-*m*-$^{13}C_2$ and benzene-*p*-$^{13}C_2$, with the former predominating at low conversion, implies that the primary automerization process must involve a "1,2-switch" of atoms (no mechanism yet implied); from benzene-*o*-$^{13}C_2$, 1,3-switches can give only benzene-*p*-$^{13}C_2$ (never benzene-*m*-$^{13}C_2$), and 1,4-switches can give only meta (never para). This conclusion remains valid even if the molecules suffer an arbitrarily large number of 1,*n*-switches, as long as *n* does not vary.

Another point worth noting is that of the six possible 1,2-switches in benzene-*o*-$^{13}C_2$, only the two that switch a ^{13}C with a ^{12}C can produce a new isomer (*meta*) while the other four possible 1,2-switches would be invisible. Therefore, assuming a negligible kinetic isotope effect for this process, the total number of 1,2-switches that actually occurred must be three times the amount actually seen. The detection of 28% scrambling thus indicates that at least 3 × 28% or 84% of the benzene molecules must have suffered automerization under the conditions of our experiment.

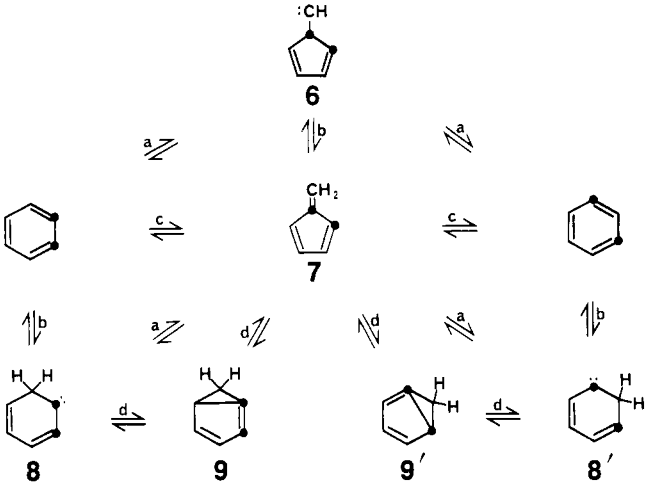
What is the mechanism of this 1,2-switch? Several possibilities deserve consideration. One of the simplest is the reversible formation of benzvalene, **5** (eq 4).

(4)

5

Benzvalene was first isolated many years ago by Wilzbach et al., who showed that aromatization to benzene occurs thermally with great ease.[18] A theoretical analysis of that process showed it to be symmetry allowed.[11c] From the kinetic and thermodynamic parameters measured for the aromatization of benzvalene[19] ($\Delta H^{\ddagger} = 25.9$ kcal/mol; $\Delta H_{rxn} = -67.5$ kcal/mol), one can calculate for the valence isomerization of benzene back to benzvalene a $\Delta H^{\ddagger} = 93.4$ kcal/mol. Since a unimolecular reaction with an activation enthalpy of this magnitude should have a half-life of less than 1.0 s at 1100 °C, eq 4 is reasonable on energetic grounds. Benzvalenes have previously been proposed as intermediates in the *photochemical* scrambling of atoms in substituted benzenes.[20] The first excited singlet state of benzene lies 110 kcal/mol above the ground state.[21]

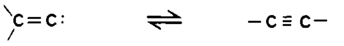
Scheme II[a]



[a] (a) Carbon 1,2-shift. (b) Hydrogen 1,2-shift. (c) C,H-dyotropic rearrangement. (d) 6-Electron electrocyclic reaction.

Scheme II depicts a family of alternative mechanistic possibilities that could account for the 1,2-switch of atoms in benzene. Reaction a is nothing more than a 1,2-shift of carbon to interconvert a carbene with an "alkene" (eq 5). Carbenes are well-known to give alkenes by such a 1,2-shift;[22] however, the reverse process has never been documented for hydrocarbons, except from the photochemically excited state of simple olefins.[23] In the more highly unsaturated analogue (eq 6), the thermal 1,2-shift has actually been demonstrated in both directions.[24] Thus, there is no reason to assume that the reaction in eq 5 should not also be reversible at sufficiently high temperatures.

$$-\overset{|}{\underset{|}{C}}-\ddot{C}- \rightleftharpoons {>}C{=}C{<} \quad (5)$$



$$>C{=}C: \rightleftharpoons -C{\equiv}C- \quad (6)$$

Ring contraction of benzene-*o*-$^{13}C_2$ by a 1,2-shift of a ^{12}C from a ^{12}C to a ^{13}C would generate the cyclopentadienyl carbene **6** (Scheme II). Ring expansion by a 1,2-shift of ^{13}C would then yield benzene-*m*-$^{13}C_2$. Another cycle of carbon 1,2-shifts could yield benzene-*p*-C_2 as a secondary product. This is one alternative to the benzvalene mechanism that can equally well explain the results.

There is, however, also a hydrogen 1,2-shift available to the carbene **6** (Scheme II, reaction b), the product of which would be fulvene **7**. This would simply represent an unproductive side reaction if benzene were able to automerize directly through carbene **6**, but there are other pathways in Scheme II that include fulvene **7** as an obligatory intermediate. For example, the ring contraction by a carbon 1,2-shift could begin as described above, but the hydrogen 1,2-shift could then begin before the carbene (**6**) were fully developed. Processes of this sort, in which atoms swap ends of a bond by pair-wise 1,2-shifts in a single step without intermediates, have been termed "dyotropic rearrangements".[25]

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(18) (a) Wilzbach, K. E.; Ritscher, J. S.; Kaplan, L. *J. Am. Chem. Soc.* **1967**, *89*, 1031–1032. (b) Katz, T. J.; Wang, E. J.; Acton, N. *J. Am. Chem. Soc.* **1971**, *93*, 3782–3783.

(19) Turro, N. J.; Renner, C. A.; Katz, T. J.; Wiberg, K. B.; Connon, H. A. *Tetrahedron Lett.* **1976**, 4133–4136.

(20) Bryce-Smith, D.; Gilbert, A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Chapter 19.

(21) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; p 181.

(22) Jones, W. M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 3.

(23) Kropp, P. J.; Reardon, E. J., Jr.; Gaibel, Z. L. F.; Williard, K. F.; Hattaway, J. H., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 7058–7067. See also ref 22 and references cited therein.

(24) Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J.; McMullen, G. L. *Aust. J. Chem.* **1974**, *27*, 2393. See also ref 22 and references cited therein.

(25) (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.

The dyotropic conversion of benzene to fulvene **7** with the carbon 1,2-shift leading the hydrogen 1,2-shift would be classified as a "concerted but nonsynchronous" reaction in Dewar's terminology.[26] Reversible dyotropic rearrangement of benzene to fulvene **7** (Scheme II, path c) thus represents a third possible mechanism for the automerization of benzene.

Fulvene could also be formed from benzene in two steps via carbene **8** (Scheme II).[27] In this sequence, the hydrogen 1,2-shift precedes the carbon 1,2-shift. A "concerted but nonsynchronous" dyotropic variation of this two-step process can likewise be envisioned.

Finally, as an alternative to the direct conversion of **8** to **7** by a carbon 1,2-shift, **8** could undergo a pair of successive 6-electron electrocyclic reactions to give **7** via the bicyclic diene **9**. Dewar and Merz have suggested structures analogous to **9** and **9′** as possible intermediates in the automerization of naphthalene.[11]

Still other mechanistic schemes may well be put forth in the future, but for now, it will be sufficient to focus on the possibilities presented above. How can one decide which mechanism is the most reasonable? Obviously, neither benzvalene nor any of the other high-energy intermediates in Scheme II (even fulvene) would ever accumulate during the course of the automerization, so it would be senseless to look for them as byproducts. Benzvalene and fulvene are already known to isomerize to benzene at temperatures well below 1100 °C,[19,28] and few chemists would doubt that intermediates **6**, **8**, and **9** would likewise aromatize at these temperatures, so the independent generation of these species would probably add little to our understanding of the benzene automerization mechanism.

One source of insight might come from theoretical calculations. To our knowledge, the portion of the C_6H_6 energy surface depicted in Scheme II has not yet been examined by theoreticians; however, Dewar and Merz have recently reported extensive calculations on the corresponding portion of the $C_{10}H_8$ energy surface in connection with their study of the automerization of naphthalene.[11] Extrapolation of their data back to the C_6H_6 energy surface suggests that benzvalene (**5**) should be the most accessible intermediate that could lead to automerization of benzene. For this reason, we tentatively favor the mechanism in eq 4 to explain the automerization of benzene.

Conclusions

It has been demonstrated that the atoms of benzene interchange positions *intra*molecularly (but not *inter*molecularly) at temperatures on the order of 1100 °C in a quartz flow system. The experimental results are consistent with, though they do not demand, a unimolecular process involving only C_6H_6 species. Radical chain reactions involving species such as $^{\bullet}C_6H_7$ are considered to be improbable at the low concentrations of benzene employed in these experiments. The data further point to a "1,2-switch" of atoms as the primary reaction pathway. Of the several mechanistic possibilities that could explain this automerization of benzene, the reversible formation of benzvalene (eq 4) appears to be the most reasonable at this time.

Experimental Section

General Methods. All chemicals were purchased from Aldrich Chemical Company, Inc. with the exception of ^{13}C KCN (90% ^{13}C) and deuteriated solvents which were purchased from MSD Isotopes, a division of Merck & Co. Solvents were purified prior to use by simple distillation. Specific handlings are detailed throughout the Experimental Section. Silica for column chromatography use was Baker 60–200 mesh; flash silica was purchased from Aldrich.

All IR spectra were recorded on a Perkin-Elmer IR 599 spectrophotometer: all ultraviolet–visible spectra were recorded on a Beckman 25 UV–vis spectrophotometer; and all melting points were determined on a Thomas-Hoover capillary melting point apparatus and are reported uncorrected. ^{1}H NMR were recorded on one of the following: (60 MHz, CW) Hitachi Perkin-Elmer Model R24B, Varian EM 360A; (80 MHz, FT) IBM AF 80; (100 MHz, FT) JEOL FX-100 with modified Varian HA-100 magnet; (500 MHz, FT) Nicolet NT-500 (located at The University of California, Davis). ^{13}C NMR were taken on one of the following: (20 MHz) IBM AF-80; (25 MHz) JEOL FX-100 (as above); (90 MHz) Nicolet NT-360. ^{19}F NMR (94.1 MHz) were recorded on a JEOL FX-100 (as above). All chemical shifts are reported relative to tetramethylsilane or 1,1,1,2-tetrafluoro-2,2-dichloroethane.

Computer calculations were performed on the University of Nevada—Reno CDC 6400 Series computer. The Hückel molecular orbital program was written by J. R. Howles and R. D. Gillion, revised for IBM 1620 (40K) by B. R. Gilson and J. E. Bloor. The Hückel program was modified for the University of Nevada—Reno system by James Herod.

Combustion analyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, Michigan 49951. Gas-chromatograph mass spectra were taken on a Finnigan 4023 GC-MS operated by Roger Scholl.

Pyrolyses were run in either a verticle dropping apparatus, which was constructed in house, or a horizontal flow apparatus purchased from Kontes Glass Inc.

1,6-^{13}C-Enriched Adiponitrile. A 10-mL solution of CH_3CN (containing 0.8 g of 18-crown-6) was added to a 250-mL round-bottom flask which contained 5.0 g (76 mmol) of 90% enriched $K^{13}CN$, and 4.79 g (38 mmol) of 1,4-dichlorobutane in 50 mL of CH_3CN was then transferred into the flask. The suspension turned from colorless to yellow upon addition of the dichloride. This solution was stirred at reflux for 16 h and then allowed to cool to room temperature. The solution was filtered through a 60-mL glass-fritted funnel with a 1-cm pad of silica gel. The residue was washed with CH_3CN (2 × 25 mL) and the filtrates combined. The solvent was removed under reduced pressure to yield 4.11 g (98.8%) of a faint yellow oil. The ^{1}H NMR and IR spectra were consistent with the literature values. The ^{13}C NMR ($DCCl_3$) showed a strong signal at 121.4 ppm.

1,6-^{13}C-Enriched Diethyl Adipate. The entire amount of [1,6-$^{13}C_2$]-adiponitrile (4.11 g) was transferred into a 100-mL round-bottom flask. To this flask was added 65 mL of a 10% solution of H_2SO_4 in 1:1 absolute ethanol–toluene. The flask was fitted with a Dean-Stark trap, and the solution was heated to reflux for 8 h. The solution was allowed to cool to room temperature and extracted with benzene (3 × 30 mL). The solvent was removed under reduced pressure. The crude product was purified by vacuum distillation (0.8 mm, bp 70–72 °C) to yield 5.14 g (75.6%) of diethyl adipate. Spectral data were consistent with the literature; ^{13}C NMR ($CDCl_3$) showed a strong signal at 177.6 ppm.

1,2-^{13}C-Enriched 1,2-Disilyloxycyclohexene. Into a 500-mL round-bottom three-neck flask was added 200 mL of freshly distilled toluene and 3.7 g of sodium metal. The flask was fitted with a mechanical stirrer, a condenser, and a 125-mL pressure equalizing dropping funnel. The mixture was brought to reflux with continued stirring under dry nitrogen gas. Upon melting of all the sodium (1 h) a solution containing 25 mL of freshly distilled chlorotrimethylsilane, 5.14 g of 1,6-^{13}C-enriched diethyl adipate, and 25 mL of dry toluene was added dropwise via the addition funnel over a 1.5-h period to the refluxing mixture. A purple precipitate began to form upon addition. The solution was allowed to reflux an additional 5 h under nitrogen and then allowed to cool to room temperature. The reaction mixture was filtered through a 60-mL fritted funnel and washed with dry toluene (3 × 25 mL). The filtrate fractions were combined, and the solvent was removed under reduced pressure to yield 5.98 g of crude product (91.2%): ^{13}C NMR ($DCCl_3$) 127.4 ppm.

1,2-^{13}C-Enriched 1,2-Cyclohexanediol. The crude 1,2-disilyloxycyclohexene (5.98 g) was dissolved in 5 mL of tetrahydrofuran (THF) and then transferred into a 100-mL round-bottom flask containing 3.9 g of $NaBH_4$, 45 mL of THF, and 25 mL of 5% NaOH, cooled to 0 °C. This deep yellow mixture was stirred and allowed to warm to room temperature. After 3 h the mixture was poured into a 125-mL separatory funnel and the layers were separated. The aqueous layer was returned to the separatory funnel and extracted with diethyl ether (6 × 25 mL). The organic layers were combined, dried with $MgSO_4$, and filtered, and the solvent was removed under reduced pressure. The residual white solid (2.65 g; mp 70–75 °C; 98.6% yield) gave spectra consistent with literature data. The ^{13}C NMR ($CDCl_3$) showed two strong signals at 76.6 and 74.7 ppm (relative intensities 7:5) consistent with a mixture of the cis and trans diols labeled at the carbinol carbons.

1,2-^{13}C-Enriched 1,2-Diacetoxycyclohexane. To a 10-mL round-bottom flask was added 0.38 g of 1,2-^{13}C-enriched 1,2-cyclohexanediol dissolved in 5.0 mL of pyridine. To this solution was added 2.0 mL of freshly distilled acetic anhydride with stirring. The flask was fitted with a reflux condenser, and the mixture was heated to reflux for 1 h. The solution was allowed to cool to room temperature, and the solvent was removed under reduced pressure. This yielded 5.9 g of a crude brown

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

[27] An analogous carbene has been mentioned as a possible intermediate in the thermal isomerization of benzfulvene to naphthalene: Brown, R. F. C.; Gream, G. E.; Peters, D. E.; Solly, R. K. *Aust. J. Chem.* **1968**, *21*, 2223.

[28] Heffernan, M. L.; Jones, A. J. *Chem. Commun.* **1966**, 120.

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 ^1H 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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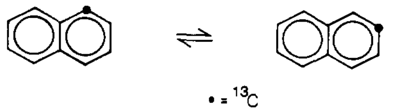
Abstract: The predicted interconversions of the title compounds (**11**, **13**, and **15**) at high temperatures have been verified (Table I) and represent the first examples of thermal rearrangements of aromatic hydrocarbons in which one benzenoid skeleton is transformed into another benzenoid skeleton. 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 aromatic hydrocarbons, e.g., pyrene,[3] azulene,[4] benz[*a*]-



(1)

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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