Intermolecular Transfer and Elimination of Molecular Hydrogen in Thermal
Reactions of Unsaturated Organic Compounds

by

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GENERAL INTRODUCTION

During the past decade, the Trahanovsky research group has been actively investigating the thermal reactions of a number of simple organic molecules which model various structural features of coal. Two reactions which may be important in coal liquefaction processes are the intermolecular transfer and the elimination of two hydrogen atoms. We have designed several model reactions to probe the viability of several hydrogen transfer and elimination pathways. The two papers in this thesis describe our studies of bimolecular hydrogen transfer and unimolecular hydrogen elimination reactions utilizing the techniques of sealed-tube and flash vacuum pyrolysis (FVP). In the first paper, studies of the transfer of two hydrogen atoms in concert as a group, an example of a pericyclic reaction, are presented. Our purpose has been to look for well-behaved bimolecular model reactions of 1,4 hydrogen transfer which would allow us to evaluate whether the transfer proceeds by a concerted or stepwise pathway. In the second paper, studies of unimolecular hydrogen elimination from non-substituted *o*-xylene and highly methylated hydrocarbons are presented.

Explanation of thesis format

This thesis consists of two different papers. Each paper has its own numbering system, detailed experimental section, and reference section following the text. A generalized summary follows the second paper of this thesis.

THE INTERMOLECULAR TRANSFER OF TWO HYDROGEN ATOMS IN THERMAL REACTIONS OF UNSATURATED ORGANIC COMPOUNDS

A paper to be submitted to the Journal of Organic Chemistry

Sabartanty Suria and Walter S. Trahanovsky

INTRODUCTION

The reduction of one molecule by another involving the overall intermolecular transfer of two hydrogen atoms without a catalyst has been well documented.^{1,2a} H-transfer reactions play a well recognized role in bond cleavage during thermal coal hydroliquefaction.^{3,4,5d} Most of the observed hydrogen exchange reactions occur in aromatic hydrocarbon structures and have been reported to involve the stepwise transfer of hydrogen atoms;^{3,5} however, the concerted transfer of two hydrogen atoms has also been proposed.^{4c,6,7,8}

The special case of concerted group transfer reactions in which two hydrogen atoms are transferred in a process suprafacial on both reactants was first recognized by Woodward and Hoffmann.⁶ The reaction is thermally symmetry-allowed for ground state reactants when $m + n = 4q + 2$, where m and n are the number of π electrons involved in the transfer and q is an integer.⁶

One of the few hydrocarbon examples of the concerted 1,2-intermolecular hydrogen transfer is the dehydrogenation of *cis*-9,10-dihydronaphthalene with 1,2-dimethylcyclohexene, where $m = 0$ and $n = 2$.⁸ The reaction is supported by well described experimental results.⁸

An example of a concerted 1,4-intermolecular transfer of two hydrogen atoms was reported by Dowd, Flemming, and Schaffner for the transfer of hydrogen from 1,4-dihydrobenzene (6) to anthracene (5) where $m = 2$, $n = 4$.^{6,7} However, no experimental details of this study have been published.

The only well-supported concerted 1,4 transfer of two hydrogen atoms found in the literature is an intramolecular one. The study was described by Grimme who reported that the molecular hydrogen migration in compound 9 involves $4\sigma + 6\pi$ electrons and proposed that it is an example of a concerted 1,4-intramolecular hydrogen transfer.⁹

Thus, evidence for a concerted 1,4 hydrogen transfer process is very limited.¹⁰ Our research effort was directed toward finding well-behaved prototype reactions of 1,4-intermolecular hydrogen transfers which would allow us to attempt to establish whether the process is concerted or not. We thought that the reactive molecule *o*-xylylene (**12**) would be a good 1,4 hydrogen acceptor (HA) which could participate in concerted 1,4-intermolecular hydrogen transfers. Presumably the driving force for the reaction would be formation of the stable

aromatic ring upon addition of two hydrogen atoms to the diene. In our search for systems free of competitive side reactions, we investigated several reactions of *o*-xylylene and other likely 1,4 hydrogen acceptors and eventually found that 9,10-dihydroanthracene (**7**) cleanly transfers two hydrogen atoms to 2-methylantracene (**32**). The results of this study are reported in this paper.

RESULTS

Several 1,4 hydrogen transfer reactions of non-aromatic dienes

In our first attempt to find a good model reaction of 1,4-intermolecular hydrogen transfer, we utilized *o*-xylylene (**12**) as the potential hydrogen acceptor (HA). The method employed to generate **12** was thermal ring opening of benzocyclobutene (**11**).¹¹ Compound **11** was conveniently prepared by the FVP of *o*-methylbenzyl chloride at 800 °C, *ca.* 9×10^{-3}

torr.¹¹ The percentages reported here are the percentages of the total area of the peaks of all products and starting materials in a reaction mixture that are detected by GC.

*Reaction of *o*-xylene (12) with 2,3-dimethyl-2-butene (13):*

A mixture of **13** (3.47 mmol, 0.30g) and **11** (0.72 mmol, 0.075 g) was dissolved in 0.5 mL of phenyl ether and heated to 180 °C for 48 h. in an evacuated Pyrex sealed tube.¹² GC and GC-MS (EI mode) analyses showed that there were two significant products: a dimer of *o*-xylene (**12**) which we assume is **16** ($M^+ = 208$, *ca.* 13%), the most stable dimer,¹³ and an unidentified dimer of **12** ($M^+ = 208$, *ca.* 1%). In addition to these products, there were *ca.* 26% unidentified minor products and recovered starting materials, 6% **11** and 54% **13**. None of the 1,4 hydrogen transfer products, *o*-xylene (**14**) and 2,3-dimethyl-1,4-butadiene (**15**) was observed.

*Reaction of *o*-xylene (12) with 9,10-dihydroanthracene (7) or 1,4-dihydrobenzene (6):*

A mixture of **11** (0.55 mmol, 0.057 g) and **7** (2.05 mmol, 0.37 g) was dissolved in 1 mL of phenyl ether and heated to 180°C for 48h in a sealed tube.¹² GC and GC-MS analyses showed that the major product (*ca.* 6%) has a molecular weight of 282 and we propose that it has structure **18**. The 1,4 hydrogen transfer products, *o*-xylene (**14**, *ca.* 2%) and anthracene

(5, *ca.* 3%), were detected along with 16, the most stable dimer of *o*-xylylene ($M^+ = 208$, *ca.* 2%), and 17, a compound with a molecular weight of 210 which we assume is the dimer of *o*-methylbenzylic radical (*ca.* 0.7%). GC also showed *ca.* 5% unidentified minor decomposition products and recovered starting materials, 7 81% and 11 0.04%.

When *o*-xylylene (12) was allowed to react with 1,4-dihydrobenzene (6), presumably a better hydrogen donor than 7, the yields of 1,4 hydrogen transfer products were not significantly improved.

Reactions of 3,5-di-tert-butyl-o-benzoquinone (19) with 2,3-dimethyl-2-butene (13) and isobenzofuran (22) with 9,10-dihydroanthracene (7):

In order to reduce competition from dimerization, 19 and 22 were tried as 1,4 hydrogen acceptors. Reaction mixtures were dissolved in 1 mL of phenyl ether and heated to 180° C for 48h in a sealed tube.¹² GC and GC-MS analyses showed that the products of reaction of 19 (0.5 mmol, 0.11 g) with 13 (2.0 mmol, 0.18 g) were 3% of 2,3-dimethyl-1,3-butadiene (15), 0.7% of 3,5-di-*tert*-butyl-1,2-dihydroxybenzene (20, $M^+ = 222$), 10% of an unidentified product which has a molecular weight of 272, and *ca.* 26% of other unidentified minor decomposition products. GC analysis also showed that 60% of 13 but no 19 was recovered.

b: sealed tube at 180 °C, 48h.,
1 mL phenyl ether

Compound **22** was prepared by the FVP of 1,4-epoxy-1,2,3,4-tetrahydronaphthalene (**21**, 2 mmol) at 650 °C and pressure of 0.005 torr.¹⁴

A mixture of **22** (1.0 mmol, 0.12 g) and **7** (4.0 mmol, 0.72 g) was dissolved in 1.5 mL CD₂Cl₂ + 0.5 mL phenyl ether and heated in a sealed tube at 180 °C for 48 h.¹² GC analyses showed only anthracene (**5**, 4%) and naphthalene (**3**, 2%), a possible impurity of **22**, but no phthalan (**24**), the 1,4 hydrogen transfer product; there was 93% recovery of **7** but none of **22**; *ca.* 1% minor products were not identified.

c: sealed tube at 180 °C, 48h.,
1.5 mL CD₂Cl₂ + 0.5 mL phenyl ether

Reactions of 2,3-dimethyl-1,3-butadiene (15), 2,5-biphenylfuran (25), trans,trans-1,4-diphenyl-1,3-butadiene (26) as HA's with 9,10-dihydroanthracene (7):

A mixture of **15** (0.78 mmol, 0.064 g) and **7** (0.3 mmol, 0.054 g) was heated to 225 °C for 24h in a sealed tube. The reaction mixture dissolved in 1 mL of CD₂Cl₂/tms was analyzed by GC, GC-MS, and ¹H NMR. GC and mass spectral analyses showed the following results: 2.5% anthracene (**5**), 4% minor unidentified products, and recovered starting materials, 87.5% **7**, and 6% **15** (eq. 10).

A mixture of **25** (0.6 mmol, 0.13 g) and **7** (0.53 mmol, 0.096 g) was heated to 225 °C for 24h in a sealed tube. The reaction mixture dissolved in 1 mL of CD₂Cl₂/tms was analyzed by GC, GC-MS, and ¹H NMR. GC and mass spectral analyses showed only 0.36% **5**, and recovered starting materials, 46.5% **7**, and 53.2% **25** (eq. 11).

A mixture of **26** (0.53 mmol, 0.11 g) and **7** (0.54 mmol, 0.097 g) was heated to 225 °C for 24h in a sealed tube. The reaction mixture dissolved in 1 mL of CD₂Cl₂/tms was analyzed by GC, GC-MS, and ¹H NMR. GC and mass spectral analyses showed the following results: 5.4% **5**, 8% minor unidentified products, and recovered starting materials, 65.2% **7**, and 21.5% **26** (eq. 12).

Reaction of 1,2,3,4-tetrahydro-2,3-naphthylidene (30) with 9,10-dihydroanthracene (7):

The preparation of compound **30** was accomplished in three steps as outlined in scheme I. In the first step, 2,3-dicarbomethoxytetralin (**28**) was prepared by the Diels-Alder reaction of *o*-xylene (using 1.15 mmol of **11** as the precursor) with dimethyl fumarate (**27**, 1.42 mmol). Diester **28** was reduced by LiAlH₄ followed by treatment with acetic anhydride to yield 2,3-di(acetoxymethyl)tetralin (**29**); excess LiAlH₄ was destroyed by addition of acetic acid. Compound **30** (45% calculated yield) was then prepared by the FVP of **29** at 675 °C and pressure of 2.8 x 10⁻⁴ torr.

Scheme I

A mixture of compound **30** (0.03 mmol, 4.68 mg) and **7** (0.09 mmol, 16.2 mg) was heated in a sealed tube at 225 °C for 24 h. GC analysis of the reaction mixture indicated *ca.*

0.5 % of 2,3-dimethyl-1,4-dihydronaphthalene (31) and *ca.* 10% of anthracene (5); there were also *ca.* 1% unidentified minor products and 88% of 7, the only starting material recovered.

d: sealed tube at 225 °C, 24h., Neat

1,4 bimolecular hydrogen transfer reactions between arenes and dihydroarenes

Reaction of 2-methylananthracene (32) with 9,10-dihydroanthracene (7):

A mixture of 32 (1.0 mmol, 0.19 g) and 7 (1.0 mmol, 0.18 g) was heated to 225 °C in a sealed tube for 24 h. The reaction mixture, solid at room temperature, was dissolved in 1.5 mL of CD₂Cl₂/TMS for GC and ¹H NMR analyses the product mixture. GC analysis of the reaction mixture indicated 6% of 2-methyl-9,10-dihydroanthracene (33), 6% of anthracene (5), and recovered starting materials, 47% of 32 and 41% of 7. When the furnace temperature was raised to 350 °C, the composition of the product mixture showed 26% of 5, 16% of 33, 27% of 32, and 16% of 7.

Reaction of 2-methylphenanthrene (35) with 9,10-dihydrophenanthrene (34):

A mixture of 35 (0.089 mmol, 0.016 g) with 34 (0.073 mmol, 0.014 g) was heated to 225 °C in a sealed tube for 24h. GC analysis showed 0.7% of 2-methyl-9,10-dihydro-

phenanthrene (37), 0.6% of phenanthrene (36), and recovered starting materials, 34% 35 and 62% 34.

Reaction of 2-methylanthracene (32) and 2-methylphenanthrene (35) with 9,10-dihydroanthracene (7) and 9,10-dihydrophenanthrene (34):

In order to determine whether the 1,4 intermolecular hydrogen transfer of 32 and 7 mixture is faster than that of 34 and 35 (1,2 H-transfer), a mixture of all four compounds (32, 7, 34, 35 = 1:1:1:1 moles ratio; 0.16 mmol each) was heated in a sealed tube at 225 °C for 24h. GC analyses indicated that all four products were formed with greater amounts of the 1,4 H-transfer products (5 and 33).

Reaction of 2-methylanthracene (32) with deuterated 9,10-dihydroanthracene (7):

In an attempt to gain additional insight into the mechanism of the hydrogen transfer between 32 and 7, a deuterium labeled experiment was pursued. The preparation of 9,9',10,10'-tetradeuterio-9,10-dihydroanthracene (7- d_4) is outlined in eq. 17.^{15a} The reaction was performed under an inert atmosphere. Upon mixing the three reactants (7 = 4.1 mmol;

Na = 16.7 mmol; ethan[D]ol = 15 mL), the suspension immediately turned a clear pale yellow; after being heated to reflux for 10h, it formed a clear brownish solution. Upon cooling to room temperature, the deuterated product crystallized along with sodium methanolate which was removed by the addition of D₂O (stirring for 5 mins).

GC-MS (using CI mode with NH₄ as carrier gas) was the only effective analysis technique that could be utilized to characterize the deuterium products obtained. The intensities of MNH₄⁺ peaks are reported as percentages of base peaks and utilized to analyze the compositions of deuterated dihydroanthracenes produced and recovered; however, no MNH₄⁺ peak was observed for the anthracene compounds so no deuterated anthracene specie was fully identified.

GC-MS analysis of the deuterium labeled 7 showed 7-*d*₄ (MNH₄⁺ = 202, 31%) and 7-*d*₃ (17%); no starting material, 7-*d*₀, was retained (figure A4-23 and 24). The deuterated (0.21 mmol, 0.038 g) and undeuterated 7 (0.2 mmol, 0.037 g) were then combined with 32 (0.41 mmol, 0.078 g) and heated to 225 °C in a sealed tube for 24 h. The experiment was pursued to distinguish between the hydrogen transfer products formed by a concerted molecular and the ones formed by a stepwise pathway. GC analysis showed 4% of anthracene (5), 4% of 2-methyl-9,10-dihydroanthracene (33-[*d*₀+*d*₁+*d*₂]), and recovered starting materials, 49% 7 and 43% 32.

d: sealed tube at
225 °C, 24h., Neat

The reported GC-MS % intensities of deuterated dihydroanthracene compounds were corrected for % intensities of ^{13}C isotope contributions (relative to the molecular ion peaks). GC-MS analysis of the deuterium reaction mixture showed 60.61% $33-d_0$, 34.43% of $33-d_1$, and 5.48% of $33-d_2$ ($\text{MNH}_4^+ = 214$) (figure A4-30). Beside these products, mass spectra also showed deuterium scrambling of recovered starting material **7**: 16% of $7-d_0$ ($\text{MNH}_4^+ = 198$), 9.49% of $7-d_1$, 9.54% of $7-d_2$, 20.91% of $7-d_3$, and 13.40% of $7-d_4$; figure A4-29). The deuterated anthracene product, **5**, and recovered anthracene starting material, **32**, did not give rise to MNH_4^+ peaks; thus, the deuterium composition could not be determined for these anthracene compounds. NOE analysis to determine the stereochemistry of the deuterium atoms of $33-d_2$ could not be accomplished due to some complicated splitting patterns of other deuterated products.

DISCUSSION

1,4 hydrogen transfer reactions of non-aromatic dienes

The reaction of *o*-xylene (**12**) with 9,10-dihydroanthracene (**7**) gave the H-transfer products, *o*-xylene (**14**) and anthracene (**5**), along with **18**, the major product, **16**, a dimer of *o*-xylene (**12**), and **17**, a dimer of *o*-methylbenzylic radical (**38**). We believe that the formation of **18** and **17** strongly supports the interpretation that the dominant mode of formation of *o*-xylene (**14**) and anthracene (**5**) is a stepwise H-transfer process (Scheme II). We propose

that the 1,4 intermolecular H-transfer process is initiated by the transfer of hydrogen atom of **7** to the terminal end of the double bond of **12** to give species, **38** and **39**.¹⁶

Scheme II

In the reaction of *o*-xylylene (**12**) with **13**, the competing dimerization of **12** supercedes the H-transfer reaction (eq. 5). Thus, competitive reactions such as dimerization must be minimized in order to observe the H-transfer reaction.

The reactions of 3,5-di-*tert*-butyl-*o*-benzoquinone (**19**) and isobenzofuran (**22**) with **7** was pursued because it was thought that **19** and **22** would be less likely to dimerize than *o*-xylylene (**12**) (eq. 7 and 9). However, these compounds did not give significant yields of 1,4 H-transfer products (eq. 7 and 9); the reactions were again complicated by competitive side

reactions. The parent of *o*-benzoquinone was not studied because of its instability in a concentrated solution, undergoing both polymerization and Diels-Alder dimerization.^{17,18}

In attempts to search for a good representative diene that would provide a clean H-transfer reaction, several other compounds were investigated: 2,3-dimethyl-1,3-butadiene (**15**), 2,5-biphenylfuran (**25**), *trans,trans*-1,4-diphenyl-1,3-butadiene (**26**), and 1,2,3,4-tetrahydro-2,3-naphthylidene (**30**). The result of the reaction mixture of **15** with **7** showed very small amount of anthracene (**5**) and no 2,3-dimethyl-2-butene (**13**) as the other H-transfer product was obtained. It is important to note that the reagents of H-transfer bimolecular reaction should be in the same liquid phase during the period of heating because it is impossible for the two reagents to react if they are in two different phases. We found that in the reaction of **15** with **7**, reagent **15** is very volatile; when the reaction was heated to 225 °C, **15** was very likely in gaseous phase while **7**, the hydrogen donor, which has low vapor pressure, was in liquid phase. Thus, the reaction mixture could not proceed under the circumstances. In addition to this, the two adjacent methyl groups of diene **15** were suspected to sterically distort the planar conformation of the diene and inevitably become a barrier for the H-transfer reaction to occur. As for the other diene systems (**25** and **26**), **5** was the only H-transfer product detected on GC and no corresponding H-transfer products of the dienes were indicated. It was previously reported that these dienes with phenyl substituents would form stabled benzylic radicals and undergo "molecule-induced" radical formation process.¹⁹ Thus, again these competitive side reactions of phenyl substituents might suppress the 1,4 H-transfer reactions. Compound 1,2,3,4-tetrahydro-2,3-naphthylidene (**30**) as another potential non-aromatic diene was synthesized (Scheme I) to facilitate the H-transfer reaction. This prototype diene was customized in a way to evade all possible obstacles that might have prevented previous hydrogen transfer reactions to occur. Diene **30** was made to have a cisoid conformation and low vapor pressure to accomodate the transfer of hydrogen. Similar to the previous systems, however, the reaction of **30** with **7** also experienced somewhat competing side reactions

(eq. 10) that caused very low yields of H-transfer products, **31** and **5**. Thus, the system could not be applied as a good model reaction for 1,4-intermolecular hydrogen transfer study.

1,4 bimolecular hydrogen transfer reactions between arenes and dihydroarenes

Our aromatic H-transfer reactions were investigated at 225 °C without any solvent. A similar study of H-transfer pathways in aromatic/dihydroaromatic mixture was reported but the reactions were carried out at temperatures above 380 °C.³ It was concluded that the formation of 1,2,3,4-tetrahydroanthracene (AnH₄) occurred *via* a series of radical hydrogen-transfer (RHT) steps.³ The radical stepwise process has been reported to be the main pathway that is most likely involved in aromatic H-transfer reactions at high temperatures.^{3,5} Thus, we were interested in finding out whether the aromatic H-transfer reactions at lower temperatures (225 °C) form different products that could be interpreted as coming from a concerted process. The mixture of 2-methylanthracene (**32**) with 9,10-dihydroanthracene (**7**) presents a well-behaved 1,4 H-transfer reaction which would allow us to further determine the type of H-transfer process involved. The reaction cleanly gave two hydrogen transfer products, **33** and **5**, in comparable amounts (eq. 14). As for 1,2 hydrogen transfer, the reaction of 9,10-dihydrophenanthrene (**34**) with 2-methylphenanthrene (**35**) again gave comparable amounts of phenanthrene (**36**) and 2-methyl-9,10-dihydrophenanthrene (**37**) (eq. 15). To further investigate the rate of 1,4 versus 1,2 hydrogen migration, a reaction of anthracene and phenanthrene (**32**, **7**, **34**, **35**) mixture was attempted. The results showed that the yields of 1,4 H-transfer products (**33** and **5**) were greater than the products of 1,2 H-transfer (**36** and **37**) (eq. 16). Thus, the finding suggests that 1,4 H-transfer reaction indeed proceeds at a faster rate than the 1,2 H-transfer system.

The deuterium labeled experimental results gave 2-methyl-9,10-dihydroanthracene (**33-d₀**) as the major product while more **33-d₁** was obtained than **33-d₂**. It was believed that the unexpected large amount of **33-d₀** was presumably due to a kinetic isotope effect.

Formation of the H-transfer products could be interpreted by two possible pathways, a concerted or a stepwise one. It is presumed that had the reaction proceeded by a concerted pathway, $33-d_2$ obtained would have predominated over the amount of $33-d_1$ produced. The observation of $7-d_1$ and $7-d_2$, in addition to $7-d_0$, $7-d_3$, and $7-d_4$, in the recovered starting material, **7**, indicated a deuterium scrambling process (Scheme III) which presumably occurred in the reaction mixture. The formation of deuterium scrambling is consistent with the stepwise pathway since the transfer of hydrogen atom from **7**, the hydrogen donor, to **32**, the hydrogen acceptor, would generate radical $39-d_0$ which then is involved in the deuterium scrambling process. In brief, the abundance of $33-d_1$ produced and the finding of deuterium-scrambling in recovered starting material, **7**, leads us to believe that the 1,4 hydrogen transfer products obtained were indeed formed by a stepwise process (Scheme IV).

Scheme III

Postulated Deuterium Scrambling Process

Scheme IV

Postulated Stepwise Hydrogen Transfer

CONCLUSION

The formation of **17**, a dimer of *o*-methyl benzylic radical (GC-MS $M^+ = 210$), and **18** ($M^+ = 282$) from the reaction of *o*-xylylene (**12**) with 9,10-dihydroanthracene (**7**) supports the idea that *o*-xylylene (**14**) and anthracene (**5**), the H-transfer products, are indeed formed by a stepwise process. In addition, the deuterium experimental result showed that more **33-*d*₁** was produced than **33-*d*₂**. Thus, the abundance of **33-*d*₁** formed and the finding of deuterium-scrambling in the recovered starting material, **7**, conclude that the reaction would be more appropriately explained by a stepwise H-transfer. As of this point in time, there is no experimental reaction model that provides supportive evidence for a concerted 1,4-intermolecular hydrogen transfer process.

EXPERIMENTAL SECTION

Methods and Materials. Gas Chromatographic analyses were performed on a Hewlett-Packard 5890-Series II Plus instrument utilizing a 30 m DB-5 (methylsilicone fluid) fused silica capillary column, helium carrier gas, and a flame ionization detector. Combined gas chromatographic/ mass spectra (GC-MS) analyses were performed on a Finnigan 4000 GCMS with an Incos 2500 data system and Finnigan 9610 GC. ^1H and ^{13}C NMR spectra were recorded on Nicolet NIC-300 and Varian VXR-300 spectrometers, respectively. Chemical shifts are recorded in parts per million (δ) relative to tetramethylsilane (tms). The percentages reported here, unless indicated otherwise, are the percentages of the areas of the peaks of all products detected by GC. When flash chromatography was used to purify products, the standard method²⁰ was used with Merck grade 60, 230-400 mesh silica gel, which was purchased from Aldrich. All chemicals, except those indicated, were commercially available and used as received.

General flash vacuum pyrolysis (FVP) procedure.²¹

The pyrolysis oven was equilibrated at the desired temperature before pyrolysis. A weighed sample (*ca.* 10-25 mg) was placed in a 50 mL 24/40 round-bottomed flask and connected to the pyrolysis apparatus fitted with a right angle sample adapter (40/35 outer 90 ° to 24/40 inner). The entire system was flushed with N₂ gas and the sample was frozen to -196 °C (liquid N₂) prior to pulling vacuum. The system was evacuated with the roughing pump to *ca.* 0.03 torr and the pyrolysis trap was cooled by liquid N₂. If the diffusion pump was used, the system was then evacuated to 10⁻⁵ torr. The sample was warmed to the desired temperature with an appropriate bath. After the pyrolysis was completed, the system was filled with N₂ and the trap was allowed to warm to near room temperature. An appropriate solvent was transferred into the trap containing the frozen pyrolysate at the conclusion of each pyrolysis. To the trap was added 1.0 mL of *ca.* 2 mg mL⁻¹ solution of biphenyl in CH₂Cl₂ (for some runs that were quantified) and an additional 1.0 mL of CH₂Cl₂. Using a long needle syringe, the pyrolysate was then transferred to other vessels for further studies. Pyrolysates were immediately analyzed by GC.

General sealed tube procedure.¹²

The reactions were studied in a static system. The reaction vessel, an evacuated Pyrex cylindrical tube of 10 mL, was heated in a metal cylinder-type furnace, which was controlled with a thermoelectric regulator. The reactions involved three steps: degassing, sealing, and pyrolysing. Degassing cycle: the sample mixture had to be frozen to -78 or -196 °C (in isopropanol/dry ice slurry or liquid nitrogen) before the system was evacuated to *ca.* 0.03 torr for *ca.* 5 min; vacuum line was closed and the sample was brought back to room temperature. Next, it was frozen and evacuated again. After the pressure reached the same level as previously obtained, argon gas was bled into the system to dissolve any trapped gas in the system and then, it was evacuated again. The freeze and thaw cycle was repeated for two more times before the frozen sample tube was sealed. While the sample was being degassed, the furnace which was connected to a thermocouple had to be set

up and equilibrated at the desired temperature. The frozen sample was allowed to liquify. The sealed tube was wrapped with aluminum foil, attached to the thermoelectric coil, and inserted into a metal cylinder-type furnace. At the end of reaction, the products were dissolved in an appropriate ^1H NMR solvent (CDCl_3 , CD_2Cl_2 , or phenyl ether and CD_2Cl_2 mixture).

Preparation of benzocyclobutene (11).¹¹ *o*-Methylbenzyl chloride (8.97 mmol, 1.26 g) was placed in a sample head and pyrolyzed at 800 °C, *ca.* 0.04 torr. Upon completion of the pyrolysis, the pyrolysate was taken up in pyridine (5 mL) and transferred to a round-bottomed flask with an attached reflux condenser; the contents were then heated to reflux at 50 °C for *ca.* 1 h. After the mixture was cooled to room temperature, the resulting precipitate was filtered out and the liquid was drained into a separatory funnel containing 10% HCl (20 mL + 5 mL 37% HCl) to remove any unreacted starting material and styrene (minor product). Pentane (10 mL) was added to the mixture. This extraction process was repeated 3 more times; then, 10% CuSO_4 solution (3 x 10 mL) was substituted to remove pyridine from the solution. Excess HCl was neutralized with saturated NaHCO_3 (3 x 20 mL). The pentane solution was then dried over MgSO_4 . Finally, the pentane was removed by distillation using a vigreux column to yield benzocyclobutene (11). After work-up, the calculated yield was 80% (biphenyl was an internal standard).²² Compound 11 was used with no further purification. ^1H NMR (CDCl_3 ; 300 MHz): δ 7.02 (m, 4H), 3.16 (s, 4H); [lit.²³ ^1H NMR δ 7.05 (m, 4H), 3.15 (s, 4H)]; IR (cm^{-1} , neat-film) 3085 (m), 2980 (s), 2945 (s), 1465 (m).

Reactions of benzocyclobutene (11) with 2,3-dimethylbutene (13), 9,10-dihydroanthracene (7), and 1,4-dihydrobenzene (6). Compound 11 (0.73 mmol, 0.076 g) with 13 (3.57 mmol, 0.3 g) was dissolved in 1 mL of phenyl ether and heated to 180 °C for 48 h in a sealed tube. GC and GC-MS analyses of the cloudy pale yellowish reaction mixture indicated the following products: dimer 16 with GC-MS (70 eV) *m/e* [EI, quadrupole mode, (% base peak)] 208 (60.5), 130(46.5), 115 (30.2), 104 (100), 91 (26.2), 78 (23.8) and

unidentified dimer of **12** with GC-MS (70 eV) m/e (% base peak) 208 (74.6), 193 (100), 178 (29.3), 115 (20.9), 104 (30.2), 91 (10), 77 (11.4).

Compound **11** (0.55 mmol, 0.057 g) and **7** (2.05 mmol, 0.37 g) were dissolved in 1 mL phenyl ether and heated to 180 °C for 48 h in a sealed tube. GC, GCMS, and ¹H NMR (CDCl₃/tms) analyses showed that **18** was the major product along with *o*-xylene (**14**), anthracene (**5**), and dimers **16** and **17**. The products were not isolated. Their mass spectra were distinguished and assigned individually. For **18**: GC-MS (70 eV) m/e [EI, quadrupole mode, (% base peak)] 282 (15.6), 178 (100), 104 (6). For **14**: GC-MS (70 eV) m/e (% base peak) 106 (70.4), 91 (100), 77 (14.7), 63 (6), 51 (23), 39 (20.5). For **5**: GC-MS (70 eV) m/e (% base peak) 178 (100), 151 (6), 88 (27), 76 (25.6). For **17**: GC-MS (70 eV) m/e (% base peak) 21 (14.2), 105 (100), 77 (11.1).

Reaction of **11** with **6** was performed under the same condition as the one with **7**. Compound **6** is very volatile and easily converted to benzene so the addition of reagents was carried out under an inert atmosphere.

Reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone (19**) and isobenzofuran (**22**) with **13** and **7**.** A mixture of **19** (0.5 mmol, 0.11 g) with **13** (2.0 mmol, 0.18 g) was heated to 180° C for 48h in a sealed tube. The dark green color of starting material mixture in 1 mL phenyl ether turned to a clear brownish solution at the end of reaction. For 3,5-di-*tert*-butyl-1,2-dihydroxybenzene (**20**): GC-MS (70 eV) m/e [EI, ion trap mode (% base peak)] 222 (30), 207 (100), 57 (48), 41 (35). For 2,3-dimethyl-1,3-butadiene (**15**): GC-MS (70 eV) m/e (% base peak) 82 (46), 67 (92), 53 (12.7), 39 (100).

Compound **22** was prepared following the published procedure with a slight modification (using CD₂Cl₂ in spite of CCl₄).¹⁴ 1,4-Epoxy-1,2,3,4-tetrahydronaphthalene (**21**; 2.0 mmol, 0.3248 g) was pyrolyzed at 650°C, *ca.* 0.003 torr to give **22**. The pyrolysate was dissolved in 1 mL CD₂Cl₂. Compound **22** had to be generated immediately before used. ¹H NMR (CD₂Cl₂/tms; 300 MHz): δ 8.00 (s, 2H), 7.39 (dd, *J* = 9.6, 3 Hz, 2H), 6.84 (dd, *J* =

9.6, 3 Hz, 2H); [lit.¹⁴ ¹H NMR singlet at δ 7.80 ppm. (CCl₄), attributed to the 2 furanoid protons; an AA'BB' pattern centred around δ 7.22 and 6.70 ppm due to the protons of the other ring]; GCMS (EI) m/e (% base peak): 118 (20, M⁺), 91 (100), 65 (23), 51(12).

A mixture of **22** (1 mmol, 0.12 g) and **7** (4 mmol, 0.72 g) was dissolved in 1.5 mL CD₂Cl₂ and 0.5 mL phenyl ether and heated to 180° C for 48h in a sealed tube. GC and GC-MS analyses show only anthracene (**5**) and naphthalene (**3**, M⁺ = 128)

Preparation of 1,2,3,4-tetrahydro-2,3-naphthylidene (30). Compound **11** (1.15 mmol, 0.12 g) was transferred to a Pyrex sample tube by using a long needle syringe and then, to the same tube 0.20 g (1.42 x 10⁻³ mol) of dimethyl fumarate (**27**) was added; no solvent was used. The tube was degassed as previously described and then sealed.¹² The mixture was heated to 225 °C for 24h in a sealed tube. The crude light yellow-brownish product, 2,3-dicarbomethoxytetralin (**28**), a solid at room temperature, was dissolved in 1 mL CD₂Cl₂/tms and flash-chromatographed using silica gel. The eluent mixtures for this flash-column were hexanes/ hexanes: chloroform (60:40)/ chloroform.^{10a} TLC and GC were used to monitor the product fractions which, were collected in a pear-shaped flask. The purified diester **28**: (slightly yellow oil; 45% calculated yield); ¹H NMR (CD₂Cl₂, 300 MHz): 7.13-7.11 (m, 4H), 3.7 (s, 6H), 3.15-3.01 (m, 6H).

2,3-Di(acetoxymethyl)tetralin (**29**) was prepared following the published procedure.²⁴ Some steps were modified since diester **28** was a pretty soluble liquid. Into a dry 50 mL round-bottomed flask fitted with a reflux condenser was added 0.1102 g (2.9 mmol) of LiAlH₄. A volume of 10 mL of dry diethyl ether (distilled from N₂/benzophenone) was added to the flask (through a septum) before 0.1473 g (0.60 mmol) of **28** which was dissolved in some portions of diethyl ether was slowly added. The ether in the reaction flask was heated to reflux for 24h; an additional 8 mL of ether had to be added as the reaction progressed. The flask was fitted with a short-path still-head, and 6 mL of n-butyl ether was placed on portions with the distillative removal of the diethyl ether. The butyl ether solution was allowed to cool

to room temperature and 0.35 mL of glacial AcOH was added dropwise to the reaction mixture to decompose excess LiAlH_4 . The reaction solution was heated to about $100\text{ }^\circ\text{C}$ and 3.5 mL of acetic anhydride was slowly added. The reaction solution was held at $110\text{ }^\circ\text{C}$ under N_2 for another 24h. The reaction solution was allowed to cool, and the gray solid suspended in the solution was removed by vacuum filtration. Removal of the n-butyl ether by rotavaporization in $40\text{ }^\circ\text{C}$ H_2O bath left 0.17 g of a yellow-brown thick liquid. Analysis of the final products by capillary GC showed *ca.* 84 %. For the preparation of diacetate **29**, this percentage represents purified and isolated yield of product. ^1H NMR (CD_2Cl_2) δ 7.08 (s, 4 H), 4.3–4.04 (m, 4H), 2.9–2.67 (m, 4H), 2.05 (s, 6H); GCMS *m/e* (CI) 276 (M^+), 156 (86), 141 (100), 128 (72), 115 (15), 43 (87).

Compound **30** was prepared by a slightly modified procedure than that was previously used to make a similar product.²⁴ A quantity of 22.3 mg (0.081 mmol) of diacetate **29** (without any further purification) was pyrolyzed (furnace: $675\text{ }^\circ\text{C}$; sample chamber: $50\text{ }^\circ\text{C}$; 3×10^{-4} torr) to give **30**. After about 3 to 4 h most of the starting diacetate was gone from the sample compartment (*ca.* 8 mg of a brown sticky residue was left behind) and a white band of frozen material had been deposited in the trap. The system was isolated from the diffusion pump and reopened to the roughing pump. A volume of 1.6 mL of CD_2Cl_2 was transferred into the trap via a sidearm. The system was brought back up to atmospheric pressure with N_2 gas. The material in the trap was slowly allowed to warm to room temperature under nitrogen atmosphere. To remove all of the AcOH which was formed as a by-product, the solution was washed in saturated NaHCO_3 and then dried over anhydrous MgSO_4 . The absolute yield of **30** was found by comparison of GC integration. A quantity of 10.1 mg of biphenyl (this was about the same calculated amount as the expected diene produced) was dissolved in 2 mL of CD_2Cl_2 ; 1 μL of this solution was inserted to a GC syringe followed by another μL of the pyrolysate solution. GC trace indicates 62% area of biphenyl solution and 31% area of the diene solution so it means that the diene pyrolysate produced was 5.05 mg (36% calculated yield).

GC-MS (70 eV) m/e [EI, ion trap mode (% base peak)] 156 (5), 104 (58), 76 (100), 50 (23);

^1H NMR (CD_2Cl_2 , 300 MHz): δ 7.06 (s, 4H), 5.31 (s, 2H), 4.87 (s, 2H), 3.46 (s, 4H).

Reaction of 2,3-dimethylene-1,2,3,4-tetrahydronaphthalene (30) with 7. The concentrated compound 30 (0.03 mmol, 5 mg) was transferred into a sample tube and then 16.5 mg (0.09 mmol) of 7 was added. The reaction was heated to 225 °C for 24h in a sealed tube. No solvent (except a trace of CD_2Cl_2 from the pyrolysis of 29) was added. For 2,3-dimethyl-1,4-dihydronaphthalene (31): GC-MS (70 eV) m/e [EI, ion trap mode, (% base peak)] 158 (7), 141 (100), 128 (12), 115 (27), 40 (25). For 5: GC-MS (70 eV) m/e (% base peak) 178 (100), 152 (50), 88 (17), 76 (26).

Reaction of 2-methylantracene (32) with 9,10-dihydroanthracene (7).

A mixture of 0.19 g (1.0 mmol) of 7 and 0.18 g (1.0 mmol) of 32 was heated to 225 °C for 24h, neat in a sealed tube. The slightly off-white starting material color changed to yellow-brownish solid crystal. GC and GC-MS analyses showed the two products: 6% of 2-methyl-9,10-dihydroanthracene (33) and 6% of anthracene (5). For 33: ^1H NMR ($\text{CD}_2\text{Cl}_2/\text{tms}$) δ 7.46 (m, 7 H), 3.87 (s, 2 H), 2.32 (s, 2 H), 1.52 (s, 3 H); GC-MS (70 eV) m/e [EI, ion trap mode, (% base peak)] 194 (18), 178 (100), 165 (6), 76 (3). For 5: ^1H NMR δ 8.31–8.38 (m, 8 H), 7.76 (s, 2 H); GC-MS (70 eV) m/e (% base peak) 178 (100), 152 (22), 76 (4).

Reaction of 9,10-dihydrophenanthrene (34) with 2-methylphenanthrene (35).

Compound 34 (0.2 mmol, 35 mg) and 35 (0.6 mmol, 0.12 g) were heated to 225 °C for 24 h, neat. GC and GC-MS showed the two products: 0.7% of 2-methyl-9,10-dihydrophenanthrene (37) and 0.6% of phenanthrene (36). For 36: ^1H NMR ($\text{CD}_2\text{Cl}_2/\text{tms}$) δ 8.52 (m, 8 H), 7.71 (s, 2 H); GC-MS (70 eV) m/e [EI, ion trap mode, (% base peak)] 178 (100), 152 (51), 89 (18), 76 (23), 63 (17), 50 (12). For 37: ^1H NMR ($\text{CD}_2\text{Cl}_2/\text{tms}$) δ 7.69 (m, 4 H), 7.52 (m, 3 H), 2.8 (s, 2 H), 2.75 (s, 2 H), 2.51 (s, 3 H); GC-MS (70 eV) m/e (% base peak) 194 (5), 182 (100), 178 (68), 165 (72), 153 (87), 141 (35), 115 (5), 76 (7).

Reaction of 32 + 7 + 34 + 35. The yellow liquid 34 (0.16 mmol, 0.029 g) was mixed with (0.16 mmol, 0.03 g) of white crystalline 35. Next, white crystalline 7 (0.16 mmol, 0.029 g) and brownish powder 32 (0.16 mmol, 0.031 g) were also added into the same sample tube; no solvent was added. The mixture was heated to 225 °C for 24 h; CD₂Cl₂/tms was used as a solvent for GC, GC-MS, and ¹H NMR analyses.

Preparation of 9,9',10,10'-tetradeuterio-9,10-dihydroanthracene (7-*d*₄).

The previously published procedure was followed with a few experimental modifications.^{15a} Under an inert argon atmosphere (in a glove bag), 15 mL ethan[D]ol was transferred to a dry three-necked round bottom flask and then 0.3838 g (0.017 mol) of sodium and 0.7297 g (4.05 mmol) of 9,10-dihydroanthracene (7) were added. After all three compounds were combined the flask was taken out of the glove bag. The reaction was heated to reflux for 10h. Upon cooling to room temperature, the deuterated product crystallized along with sodium methanolate as a by-product. Into the cooled solution, 2 mL D₂O was added and stirred for 5 min to dissolve sodium methanolate. The product was filtered using suction filtration and washed with 2 mL ethan[D]ol. Next, the crude product was recrystallized in 5 mL ethan[D]ol under argon. The melting point of the dried and purified coral needle crystals was 108-109 °C with *ca.* 60% calculated yield. No undeuterated material, 7-*d*₀ was detected by GC-MS. ¹H NMR (300 MHz, CD₂Cl₂): δ = 3.912 (br, s, 0.2H, CH₂), 7.175 (m, 4H, aryl-H), 7.278 (m, 4H, aryl-H); GC-MS [CI, *m/z* (% base intensity)]: 202 (31, M[7-*d*₄]NH₄⁺), 201 (17, M[7-*d*₃]NH₄⁺), 185 (10), 184 (73), 183 (100), 182 (75), 181 (40), 180 (20), 168 (13), 154 (5).

Reaction of 2-methylantracene (32) with deuterated and undeuterated

9,10-dihydroanthracene (7). 2-methylantracene (0.41 mmol, 0.078g), 9,10-dihydroanthracene (0.2 mmol, 0.037 g) and 7-*d*₄ (0.21 mmol, 0.038 g) were weighed directly into a sample tube and heated to 225 °C for 24 h in a sealed tube (neat). At the end of reaction the crystallized product was analyzed by GC, GC-MS [CI (NH₃ gas), quadrupole mode] and ¹H NMR (CD₂Cl₂/tms).

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APPENDIX: SUPPLEMENTARY FIGURES

Figure A-1. Schematic diagram of the flash vacuum pyrolysis apparatus

Figure A-2.

^1H NMR spectrum of crude compound 11 (CD_2Cl_2 , 300 MHz)

Figure A-3. GC trace of crude compound 11

Figure A-4. ^1H NMR spectrum of reaction mixture of **11** + **13** (CDCl_3 , 300 MHz)

Figure A-5. ¹H NMR spectrum of reaction mixture of **11** + **7** (CDCl₃, 300 MHz)

Figure A-6. EI mass spectrum of 16 (70 eV)

Figure A-7. GC trace of reaction mixture of **11** (0.27M) with **7** (1M)

Figure A-8.

GC trace of reaction mixture of 11 (0.5M) with 7 (2M)

Figure A-9. GC trace of reaction mixture of 19 with 13

Figure A-10. EI mass spectrum of 20 (70 eV)

Figure A-11. GC trace of starting material, 22 and 7

Figure A-12. GC trace of reaction mixture of 22 with 7

Figure A-13. ¹H NMR spectrum of compound 22 (CD₂Cl₂, 300 MHz)

Figure A-14. GC trace of reaction mixture of 32 with 7

Figure A-15. ¹H NMR of reaction mixture of **32** with **7** (CD₂Cl₂, 300 MHz)

Figure A-16. ^1H NMR of purified compound 28 (CD_2Cl_2 , 300 MHz)

Figure A-17. ^1H NMR of purified compound **29** (CD_2Cl_2 , 300 MHz)

Figure A-18. ^1H NMR of the crude pyrolysate **30** (CD_2Cl_2 , 300 MHz)

Figure A-19. ^1H NMR spectrum of reaction mixture of **30** + **7** (CD_2Cl_2 , 300 MHz)

Figure A-20.

GC trace of reaction mixture of 30 with 7

Figure A-21. GC trace of reaction mixture of 32 + 7 + 34 + 35

Figure A-22. ¹H NMR spectrum of reaction mixture of 30 + 7 + 34 + 35 (CD₂Cl₂, 300 MHz)

Figure A-23. GC trace of reaction mixture of 34 with 35

Figure A-24. ¹H NMR spectrum of reaction mixture of 34 with 35 (CD₂Cl₂, 300 MHz)

Figure A-25. GC-Mass spectrum deuterium labeled 7 (CI mode; NH₃ gas)

Figure A-26. GC-Mass spectrum of 7-d₀ (CI mode, NH₃ gas)

Figure A-27. ^1H NMR spectrum of 7- d_0 (CD_2Cl_2 , 300 MHz)

Figure A-28. ^1H NMR spectrum of anthracene, 5 (CD_2Cl_2 , 300 MHz)

Figure A-30. GC trace of reaction mixture of deuterated+undeuterated-7 with 32

Figure A-31. GC-Mass spectrum 7-d_x in the reaction mixture (x = 0, 1, 2, 3, 4; CI mode; NH₃ gas)

Figure A-32. GC-Mass spectrum of product 33- d_y ($\gamma = 0, 1, 2$; CI mode; NH_3 gas)

Figure A-33. GC-Mass spectrum of standard 33-d₀ (CI mode; NH₃ gas)

Figure A-34. GC-Mass spectrum of 5-d₀ in the reaction mixture ($\mu = 0, 1, 2$; CI mode; NH₃ gas)

Figure A-35. GC-Mass spectrum 32-d₀ in the reaction mixture ($v = 0, 1, 2$; CI mode; NH₃ gas)

THE ELIMINATION OF MOLECULAR HYDROGEN IN THERMAL REACTIONS OF UNSATURATED HYDROCARBONS

A paper prepared for submission to the Journal of Organic Chemistry

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INTRODUCTION

The unimolecular noncatalytic dehydrogenation of unsaturated hydrocarbons has been well documented.¹ A couple of thermal reactions of concerted 1,4-elimination of molecular hydrogen have been reported in the conversion of 1,4-cyclohexadiene (1) to benzene (2), and 9,10-dihydroanthracene (3) to anthracene (4).^{1e,f}

There is an enormous amount of research reported on the generation of benzocyclobutene and its derivatives from *o*-xylene derivatives involving derivatives of *o*-xylylene intermediates.^{2,3} One example is the formation of 1,2-dibromobenzocyclobutene (7) which is suggested to proceed *via* dibromo-*o*-xylylene (6) intermediate in the conversion of tetrabromide 5 to dibromide 7.^{2a}

Another example is the thermal reaction of *o*-methylbenzyl chloride (**11**) which proceeds by 1,4-elimination of hydrogen chloride from adjacent benzylic positions, followed by ring closure of the resulting *o*-xylylene (**9**) to give benzocyclobutene (**10**).^{2b}

Pyrolysis of *p*-xylene (**14**) is known to form *p*-xylylene (**31**), which has been exploited as a monomer to form the polymer "perylene", is proposed to proceed by a stepwise pathway.⁶

However, non-substituted *o*-xylene (**8**) has never been reported as a possible precursor of benzocyclobutene (**10**). In this study, we were interested in finding out whether flash vacuum pyrolysis (FVP) of *o*-xylene (**8**) produces **10**. The formation of **10** would be evidence for formation of *o*-xylylene (**9**) proposed to result from the 1,4-elimination of hydrogen from **8**.

As part of our effort to find good evidence for the 1,4-elimination of hydrogen from non-aromatic systems, we also investigated several other more methylated hydrocarbons. The results of these studies are reported herein.

RESULTS

Flash vacuum pyrolysis (FVP) of *o*-xylene (8) and *p*-xylene (14)

A known quantity of biphenyl was added as a standard to determine the amount of pyrolysate produced (in mass unit). Percent yield is reported as the amount of pyrolysate obtained relative to the amount of starting material consumed and based on weights. Products were identified by comparison with authentic samples and/or by GC retention time and GC-MS analyses. Percent conversion is total moles of starting material minus moles of recovered starting material divided by total moles of starting material. Percent recovery is moles of recovered material divided by moles of starting material originally used.

GC analyses of the FVP of *o*-xylene (8) at 950 °C, 10^{-3} torr showed two significant products: 3.1% yield of styrene (13) and 1.5% yield of benzocyclobutene (10) along with several minor unidentified products; there was 47.5% recovery of 8 (Table A-1).

Mass spectral confirmed the identities of **13** and **10** ($M^+ = 104$) by comparison with the GC-MS of the standard samples (Figure A-2 and A-3). GC analyses of the FVP of *o*-xylene (**8**) at 1000 °C indicated the percent yields of **13**, **10**, and phenylacetylene to be 16.5%, 1.64%, and 1.3%, respectively; three other minor products, naphthalene, anthracene, and phenanthrene were also observed (<1% yield); 33% of **8** was recovered (Table A-1).

The pyrolysis of *p*-xylene (**14**) at 1018 °C, 0.003 torr produced mostly styrene and polymers which were observed as a dry thin layer covering the inside wall of a cold trap. Other minor products obtained were: benzocyclobutene, anthracene, and phenanthrene (<0.2 mg; Table A-2). The co-pyrolysis of *o*- and *p*-xylene gave no significant different products.

FVP of hexamethylbenzene (**15**)

Compound **15** was pyrolyzed to gain additional insight into whether more methylated hydrocarbon (more steric hindrance) would be more prone to 1,4-dehydrogenation. If the 1,4-elimination of hydrogen occurred, the expected product would be tetramethylbenzocyclobutene (**16**). GC and GC-MS analyses of the FVP of **15** at 910 °C showed 8.3% yield of **16**. Other minor rearrangement products detected by GC are: tetramethylstyrene (**17**, 3.5% yield), pentamethylbenzene (**19**, 8.0%), trimethylstyrene (**22**, 1.7%), and naphthalene (**25**, 1.2%); 44.2% recovery of **15** (Table A-5). FVP of **15** at 1000 °C showed that naphthalene was the major product observed (*ca.* 21% yield) while **16** and **17**, the H₂-loss products, were the predominant products (*ca.* 12%) at 900 °C (Table A-6). GC analyses of FVP of **15** at 750 and 800 °C showed much lower similar product conversions than the pyrolysis at 900 °C (Table A-3).

FVP of pentamethylbenzene (19)

Compound 19 required heating to 50 °C to make it sufficiently volatile to traverse the hot zone of the FVP apparatus. GC and GC-MS analyses of FVP of 19 at 900 °C showed 12% yield of CH_2 -loss products (21), 9% H_2 -loss products (20 and 22), and 2% naphthalene (25) (Table A-6). FVP of 19 at 1000 °C, CH_2 -loss (2.12%) and H_2 -loss (1.16%) products became less significant with the increase of naphthalene produced (11%) (Table A-6).

FVP of 1,2,4,5-tetramethylbenzene (29) and 1,2,3,4-tetramethylbenzene (30)

According to GC analyses, in each pyrolysis only starting material was observed at 900 °C. GC analysis of FVP of 29 at 1000 °C showed 6% yield of CH₂-loss product, 4% H₂-loss product, and 0.8% naphthalene while FVP of 30 at 1000 °C gave 6.9% CH₂-loss product, 6.3% H₂-loss product, and 3.2% naphthalene (Table A-6).

DISCUSSION

FVP of *o*-xylene (8) and *p*-xylene (14)

The conversion of 9,10-dihydroanthracene (3) to anthracene (4) is reported to proceed readily by 1,4-dehydrogenation process due to the formation of a stable aromatic ring. In our first attempt to probe the 1,4 H-elimination on a non-aromatic system, *o*-xylene (8) was utilized. The hydrogens that were eliminated in the cases of 9,10-dihydroanthracene and 1,4-dihydrobenzene were locked in a strained-aromatic ring position while in the *o*-xylene system, the hydrogens that were expected to be eliminated were part of the aliphatic methyl groups. FVP of 8 at 950 °C gave 1.5% yield of benzocyclobutene (10) and 3.1% of styrene (13). It was quite surprising that at 1000 °C the yield of 13 produced was increased to 16.5% but only about the same 1.6% 10 was obtained (Table A-1). It was suspected that the significant amount of 13 formed was the result of decomposition of 10 at high temperature. This result would lead to a conclusion that more 10 was indeed generated in the pyrolysis of 8 but due to its instability at high temperature, some of 10 rearranged to 13.^{4,5} A simplest mechanism that might clarify the rearrangement of 10 to 13 is previously reported by breaking a bond adjacent to the aromatic ring with subsequent hydrogen transfer (Scheme I). However, this pathway has a potential draw-back due to the unfavorable first step, generation of intermediate 34; the more favorable step would be the opening of 10 to *o*-xylylene (9) (route A).^{4,5}

Scheme I

When *p*-xylene (14) was pyrolyzed to compare product distributions between the ortho and para isomers, the fact that some styrene was also observed was quite surprising. Interestingly enough, this finding follows the published mechanism *via* the generation of *p*-xylylene (31) which undergoes equilibration with *p*-tolylmethylene (32) to give styrene.⁴

FVP of highly methylated hydrocarbons

Pyrolyses of more methylated hydrocarbons were pursued to see whether compounds with more methyl groups and therefore more steric hindrance would be more prone to 1,4-dehydrogenation process than *o*-xylene (8). FVP of hexamethylbenzene (15) at 910 °C gave significant yields of tetramethylbenzocyclobutene (16) and tetramethylstyrene (17), H₂-loss products, along with pentamethylbenzene (19), a CH₂-loss product. In addition, there were also naphthalene (25), trimethylstyrene (21), and some unidentified decomposition products observed. GC analyses of FVP of hexamethylbenzene (15) and pentamethylbenzene (19)

showed increasing formation of naphthalene as the furnace temperature was raised from 900 to 1000 °C while percent yields of the other two products, the H₂-loss and CH₂-loss products, decreased correspondingly (Table A-6). The amount of **16** as the 1,4 H-elimination product of FVP of hexamethylbenzene (**15**) obtained is greater than benzocyclobutene (**10**), the 1,4 H₂-loss product obtained from *o*-xylene (**8**). Thus, the more methylated hydrocarbon **15** is more likely to undergo 1,4-elimination of hydrogen than the less substituted hydrocarbon **8**. Moreover, the pyrolysis of **15** was always observed to give CH₂-loss products, a comparable competing process. The CH₂-loss products are significant ones from the highly methylated hydrocarbons; at this point in time, it is not clear how these products are formed.

CONCLUSION

The FVP of *o*-xylene (**8**) produces benzocyclobutene (**10**); however, the yield is low. The formation of styrene (**13**) supports the 1,4-dehydrogenation process since **10** is known to rearrange to **13** at high temperature. The formation of CH₂-loss products from pyrolyses of more highly methylated hydrocarbons is significant; a mechanism to explain this reaction is unclear.

EXPERIMENTAL SECTION

Methods and Materials. Gas Chromatographic analyses were performed on a Hewlett-Packard 5890 Series II Plus instrument utilizing a 30 m DB-1701 (methylsilicone fluid) fused silica capillary column, helium carrier gas, and flame ionization detector. Combined gas chromatographic/mass spectra (GC-MS) analyses were performed on a Finnigan 4000 GC-MS with an Incos 2500 data system and Finnigan 9610 GC (EI, quadrupole). ¹H and ¹³C NMR spectra were recorded on Nicolet NIC-300 and Varian VXR-300 spectrometer,

respectively; chemical shifts were recorded in parts per-million (δ) from tetramethylsilane (tms). Pyrolysate yield percentages were calculated by GC integration using biphenyl as an internal standard. The commercially available chemical reagents are listed in Table 1.

General pyrolysis procedure.^{7,8} A typical sample weighing about 20 to 120 mg was transferred to a round bottomed flask. The furnace was set up at a certain temperature ranging from 900 to 1000 °C. After purging the pyrolysis system with dry N₂ gas, cooling the sample head to -196 °C (in liquid N₂) was required for some materials. The system was evacuated; then, the sample head was gradually warmed back to room temperature and allowed to distill through the pyrolysis tube under ambient temperature. Some heavier materials, such as hexamethylbenzene, required heating due to its low vapor pressure. Upon completion of the pyrolysis, N₂ gas was slowly bleed into the system to facilitate removal of the trap. The cold trap was disconnected, stoppered, and kept under argon gas while it equilibrated back to room temperature before adding solvent (either CD₂Cl₂ or phenyl ether) for analyses. Quantitative GC analysis was done by adding a weighed amount of biphenyl standard to a solvent mixture which then, used to rinse the inside wall of the cold trap where the product was collected. Next, the pyrolysate solution was transferred to other vessels for further studies and kept in a refrigerator or at room temperature. Identification of individual components of the pyrolysate was based on molecular weight and fragmentation patterns determined by GCMS, co-injection with commercial samples, ¹H NMR and ¹³C NMR analyses. After each pyrolysis, FVP tube was cleaned by passing O₂ gas through the tube while it was heated to temperature > 800 °C.

FVP of *o*-xylene (8). Compound 8 was transferred to a round bottom flask and pyrolysed using the previously described method.⁹ Before the system was evacuated, the sample head temperature had to be lowered to -196 °C (liquid N₂). Once the system was under vacuum, the sample head temperature was gradually raised to -78 °C (isopropanol/ dry ice slurry), 0 °C (ice/ H₂O bath), and finally, remained at room temperature for the rest of

Table 1. Commercially available chemical reagents.

Compound	Source
2,3-dimethyl-2-butene	Aldrich
2,3-dimethyl-1,3-butadiene	Aldrich
9,10-dihydroanthracene	Aldrich
1,4-dihydrobenzene	Aldrich
1,4-epoxy-1,2,3,4-tetrahydronaphthalene	Janssen Chimica & Aldrich
Hexamethylbenzene	Aldrich
Pentamethylbenzene	Aldrich
1,2,3,4-tetramethylbenzene	Aldrich
1,2,4,5-tetramethylbenzene	Aldrich

pyrolysis time. The experiments were run at temperatures 900 and 1000 °C with sample weights of 30 and 120 mg, respectively. The FVP products were collected in a liquid N₂ cooled trap and isolated using CD₂Cl₂ and biphenyl added as an internal standard. The product was analyzed by GC, ¹H NMR and GCMS (mode: quadrupole, EI).

FVP of other hydrocarbons. They were all done using a FVP apparatus and methods that had been previously described.⁹ All the other hydrocarbons pyrolyzed for this experiment were hexamethylbenzene (15), pentamethylbenzene (19), 1,2,3,4-tetramethylbenzene (30), and 1,2,4,5-tetramethylbenzene (29). FVP of 15 were conducted at several different temperatures ranged from 750 to 1040 °C. Compound 15 (20-30 mg) required heating in 50 °C H₂O bath to make the compound sufficiently volatile to traverse the hot zone of FVP apparatus. Compound 30 (20 to 50 mg) was pyrolysed at 900 and 1000 °C. Compound 19 was

conducted with the apparatus evacuated to *ca.* 10^{-3} Torr and the oven set up at 900 and 1000 °C. As the overall result outline, all data were combined and calculated to explain the percent conversion of starting material, percent total loss of CH₂, and percent total loss of H₂ (Table A-6).

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APPENDIX 1: SUPPLEMENTARY FIGURES

Figure A-1. Schematic diagram of the FVP apparatus

Figure A-2. EI (70 eV) mass spectrum of benzocyclobutene (10)

Figure A-3. EI (70 eV) mass spectrum of styrene (13)

Figure A-4. GC trace of FVP of *o*-xylene (8)

Figure A-5. GC trace of *p*-xylene (14)

START

Figure A-6. GC trace of hexamethylbenzene (15)

Figure A-7. GC-Mass spectrum of hexamethylbenzene (15) (EI, 70 eV)

Figure A-9. GC-Mass spectrum of tetramethylstyrene (17) (EI, 70 eV)

Figure A-10.

Figure A-11. GC-Mass spectrum of naphthalene (25) (EI, 70 eV)

APPENDIX 2: SUPPLEMENTARY DATA TABLES

Table A-1. Products and recovered starting material from FVP of *o*-xylene (8) at 950 and 1000 °C

Experiment	TS-1-25-A					TS-1-15-O			
Furnace Temp., °C	950					1000			
System Pressure, torr	0.03					0.01			
Sample Temperature, °C	0					0			
Starting material	<i>o</i> -xylene					<i>o</i> -xylene			
Mass of sample, mg	30					120			
Biphenyl added, mg	2.26					3.04			
Solvent	Pentane					Methylene Chloride			
Entry	GC RT	Rel. RT	Mass, mg	% Yield		GC RT	Rel. RT	Mass, mg	% Yield
m/p-xylene									
<i>o</i> -xylene	6.85	0.408	14.26	47.5		6.96	0.412	40	33.33
phenylacetylene						7.018	0.416	1.07	1.34
styrene	7.043	0.419	0.485	3.08		7.159	0.425	13.36	16.7
benzocyclobutene	7.787	0.464	0.23	1.46		7.865	0.466	1.31	1.64
hexamethylbenzene									
tetramethylbenzocyclobutene									
tetramethylstyrene									
naphthalene						13.9	0.824	0.203	0.25
anthracene						23.241	1.378	0.16	0.2
phenanthrene						23.417	1.389	0.65	0.81
biphenyl (standard)						16.864	1		
(Corr. factor 0.90 for others)									

GC RT = actual GC retention time

Rel. RT = relative retention time

Table A-2. Products and recovered starting material from FVP of *p*-xylene (14), co-pyrolysis of 8 and 14, and hexamethylbenzene (15) at 1000 °C

Experiment	TS-1-17-P			TS-1-19-T			TS-1-19-S		
Furnace Temp., °C	1018			1001			1040		
System Pressure, torr	0.004			0.003			0.02		
Sample Temperature, °C	0			0			60		
Starting material	<i>p</i> -xylene			co-pyrolysis (<i>o</i> - & <i>p</i> -xylenes)			hexamethylbenzene		
Mass of sample, mg	111			59			20.6		
Biphenyl added, mg				2.16			2.08		
Corr. factor 0.90 for others									
Entry	GC RT	Rel. RT	Mass, mg	GC RT	Rel. RT	Mass, mg	RT	Rel. RT	Mass, mg
<i>m/p</i> -xylene	6.119	0.363	18.66	6.005	0.357	7.36			
<i>o</i> -xylene	6.99	0.415	0.999	6.836	0.407	5.59	6.923	0.412	0.157
phenylacetylene				6.94	0.413	0.82			
styrene	7.13	0.423	6.71	7.076	0.421	5.44	7.04	0.419	0.25
benzocyclobutene	7.852	0.466	0.24	7.805	0.464	0.24			
indene							10.934	0.651	0.849
naphthalene				13.847	0.824	0.191	13.847	0.824	3.26
trimethylstyrene							13.963	0.831	0.17
pentamethylbenzene							14.766	0.879	0.436
tetramethylstyrene							16.425	0.978	0.13
tetramethylbenzocyclobutene							16.498	0.982	0.173
biphenyl (standard)	16.857	1		16.814	1		16.799	1	
hexamethylbenzene							17.325	1.031	0.668
anthracene	23.271	1.378	0.165	23.149	1.377	0.152			
phenanthrene	23.443	1.388	0.12	23.319	1.387	0.212			

from 750°C to 900°C

Experiment	TS-1-21-X	TS-1-23-Z	TS-1-23-V
Starting material	hexamethylbenzene	hexamethylbenzene	hexamethylbenzene
Mass of sample, mg	22 mg	17 mg	15 mg
Eliphenyl added, mg	3.76	2.68	2.24
Corr. factor 0.90 for others			
Sample Temperature, °C	60	60	65
System Pressure, torr	0.003	0.03	0.002
Furnace Temp, °C	910	790	749
			TS-1-23-V
Name	GC RT	GC RT	GC RT
m/p-xylene	Rel. RT	Rel. RT	Rel. RT
o-xylene	Mass, mg	Mass, mg	Mass, mg
phenylacetylene			
styrene			
benzocyclobutene			
indene			
naphthalene	13.878	13.883	0.041
trimethylstyrene	14.018	14.022	0.085
pentamethylbenzene	14.812	14.814	0.521
tetramethylstyrene	16.472	16.474	0.18
tetramethylbenzocyclobutene	16.55	16.551	0.64
biphenyl (standard)	16.853	16.852	1
hexamethylbenzene	17.418	17.426	10.03
anthracene	1.034	1.034	17.45
phenanthrene	9.723	9.723	1.036
			9

Table A-4. Products and recovered starting material from FVP of 1,2,4,5-tetramethylbenzene (29), 1,2,3,4-tetramethylbenzene (30), and pentamethylbenzene (19) at 1000 °C

Experiment	TS-I-31-I					TS-I-29-I				TS-I-27-e		
Furnace Temp., °C	1000					1000				1000		
System Pressure, torr	0.004					0.025				0.02		
Sample Temperature, °C	0					0				50		
Starting material	1,2,3,4-tetramethylbenzene					1,2,4,5-tetramethylbenzene				Pentamethylbenzene		
Mass of sample, mg	51.4					24.4				21.3		
Bi phenyl added, mg	2.42					2.66				2.24		
Corr. factor	0.9					0.9				0.9		
Name	GC RT	Rel. RT	Mass, mg	% Yield		Mass, mg	% Yield			Mass, mg	Rel. RT	% Yield
m/p-xylene	6.023	0.357575	0.78	1.52								
o-xylene	6.852	0.407	0.43	0.84						0.14		0.66
phenylacetylene	6.97	0.414	0.29	0.56								
styrene	7.09	0.421	0.99	1.93		0.18	0.74					
benzocyclobutene										0.33		1.55
1,2,4-trimethylbenzene	9.379	0.557	1.72	3.35		1.05	4.3			0.17		0.80
1,2,3-trimethylbenzene	10.136	0.602	1.09	2.12								
1,4-dimethylstyrene	11.751	0.695	0.51	0.99								
1,2-dimethylstyrene	11.85	0.704	0.39	0.76								
2,3-dimethylstyrene	12.243	0.727	0.32	0.62		0.79	3.23					
1,4-dimethylbenzocyclobutene	12.391	0.736	1.15	2.24						0.19		0.89
1,2-dimethylbenzocyclobutene	12.621	0.749288	0.46	0.89								
1,2,4,5-tetramethylbenzene						5.1	20.9			0.093		0.44
1,2,3,4-tetramethylbenzene	12.715	0.755	5.8	11.3								
Trimethylstyrene *										0.11	0.831	0.52
Trimethylbenzocyclobutene										0.26	0.87	1.22
Naphthalene	13.882	0.824	1.38	2.68		0.147	0.6			1.98		9.30
Pentamethylbenzene	14.833									0.389	0.88	1.83
hexamethylbenzene	17.418										1.03	
bi phenyl (standard)	16.844											

Table A-5. Products and recovered starting material from FVP of hexamethylbenzene (15) and pentamethylbenzene (19) at 900 °C

Experiment	TS-1-21-X					TS-1-27-d			
Furnace Temp., °C	910					900			
System Pressure, torr	0.003					0.003			
Sample Temperature, °C	60					65			
Starting material	hexamethylbenzene					pentamethylbenzene			
Mass of sample, mg	22 mg					17.7 mg			
Biphenyl added, mg	3.76					2.08			
Corr. factor 0.90 for others									
Entry	GC RT	Rel. RT	Mass, mg	% Yield		GC RT	Rel. RT	Mass, mg	% Yield
m/p-xylene									
o-xylene									
phenylacetylene									
1,2,3,5-tetramethylbenzene						12.011	0.714	0.31	8.76
1,2,4,5-tetramethylbenzene						11.92	0.708	0.14	4
1,2,3,4-tetramethylbenzene						12.681	0.754	0.19	5.4
naphthalene	13.878	0.823	0.149	1.2		13.87	0.824	0.11	3.1
trimethylstyrene	14.018	0.832	0.211	1.7		14.011	0.832	0.62	17.5
pentamethylbenzene	14.812	0.879	0.983	8		14.833	0.881	14.16	
trimethylbenzocyclobutene						14.612	0.868	0.14	4
tetramethylstyrene	16.472	0.977	0.427	3.5					
tetramethylbenzocyclobutene	16.55	0.982	1.023	8.3					
biphenyl (standard)	16.853	1				16.827	1		
hexamethylbenzene	17.418	1.034	9.723						
anthracene									
phenanthrene									

GENERAL SUMMARY

In efforts to search for well behaved 1,4 H-transfer model reactions that would allow us to attempt to provide support for the occurrence of a concerted process, we investigated *o*-xylylene (12) with 9,10-dihydroanthracene (7) as a hydrogen donor (HD); also utilized 2,3-dimethyl-2-butene (13), and 1,4-dihydrobenzene (6). All thermal reactions were carried out in sealed pyrex tubes utilizing a metal cylinder-type furnace. The formation of 17, a dimer of *o*-methylbenzylic radical (GC-MS $M^+ = 210$), and 18 ($M^+ = 282$) from the reaction of *o*-xylylene (12) with 9,10-dihydroanthracene (7) supports that *o*-xylene (14) and anthracene (5), the H-transfer products, are indeed formed by a stepwise process. Several other potential dienes were also investigated as hydrogen acceptors (HA's); however, there were always some competitive reactions that complicated hydrogen transfer studies. A well-behaved prototype system was found in the reaction of 2-methylantracene (32) with 7. The two expected hydrogen transfer products were 2-methyl-9,10-dihydroanthracene (33) and anthracene (5) and these were obtained in comparable amounts. In an attempt to gain insight into the reaction mechanism, deuterium labeled experiments were pursued. From the results of these experiments, it was concluded that the reaction would be more appropriately explained by a stepwise hydrogen transfer. At this time, there is no model reaction that provides support for a concerted 1,4-intermolecular hydrogen transfer process.

In the second paper, the 1,4-elimination of molecular hydrogen from systems that do not produce aromatic rings was investigated utilizing flash vacuum pyrolysis (FVP). Non-substituted *o*-xylene (8) was first attempted as a model compound that was expected to undergo 1,4-dehydrogenation *via o*-xylylene (9) to give benzocyclobutene (10). The FVP of 8 at 950 and 1000 °C indeed yields 10 and styrene (13), a rearrangement product of 10; however, the products were always obtained in low yields. Several more highly methylated hydrocarbons were pyrolyzed and expected to be more prone to the elimination than *o*-xylene (8).

H₂-loss and CH₂-loss products were observed from the pyrolyses of these more sterically hindered hydrocarbons. The formation of CH₂-loss product from the pyrolyses of these hydrocarbons pyrolyses is interesting; the mechanism for the formation of the CH₂-loss products is still unclear.

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