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Mechanochemistry of Some Hydrocarbons[‡]

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Abstract: Aromatic hydrocarbons (biphenyl, naphthalene, anthracene and phenanthrene) were subjected to ball milling (SPEX® 8000) with approximately ten-fold weight of inorganic materials (alumina or silica). After about 24 h all of the hydrocarbons were converted largely to carbon (graphite), but at intermediate stages disproportionation products (tetralin, phenylcyclohexane, bicyclohexyl, 9,10-dihydroanthracene, 1,2,3,4-tetrahydroanthracene, 1,2,3,4,4a,9,9a,10-octahydroanthracene, 1,2,3,4,5,6,7,8-octahydroanthracene, 9,10-dihydrophenanthrene, 1,2,3,4-tetrahydrophenanthrene, 1,2,3,4,4a,9,9a,10-octahydrophenanthrene, 1,2,3,4,5,6,7,8-octahydrophenanthrene) were also obtained in significant yields. © 1997 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Mechanochemistry[1] (sometimes referred to as Tribochemistry) has been postulated by Ostwald[2] as early as 1919 as a source of energy for chemical reactions, but systematic studies have been scattered and largely confined to engineering and physics aspects.[1]

Of most chemical interest have been some observations about mechanical treatment of polymers[3], wet reactions of lignin model compounds[4] and a recent report[5] concerning the "destruction" of toxic chlorinated compounds by mechanical processes.

We have carried out a number of investigations in mechanochemistry in the course of which we have made the surprising discovery that aromatic hydrocarbons treated mechanically with apparently non-reactive matrices (alumina and silica) were also "destroyed" ie. converted to carbon. Even more surprising was the observation that the reaction in the alumina matrix generated significant amounts of products arising from partial reduction of aromatic substrates.

RESULTS AND DISCUSSION

In connection with a systematic study of the mechanochemistry[1,4,5] of organic compounds, we have examined the mechanochemical reactions of a number of simple aromatic hydrocarbons (Tables 1-4 and Figures 1-3) by observing the effect of ball milling in a SPEX® 8000 Mixer Mill in the presence of two inorganic matrices (alumina and silica) at ambient temperatures. Data in Tables 1-4 refer to runs of 24 h

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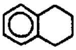
[‡] This work is dedicated to the memory of the late Professor Arthur J. Birch, FRS, FAA, who was an Honours graduate of this Department and later the Professor of Organic Chemistry in it. Arthur was also a personal mentor to one of us (SS).

Table 1. Mechanical Treatment of Naphthalene with Alumina or Silica over 24 Hours

Entry	 (mg)	Alumina (mg)	 as C (%)	 as C (%)	Carbon (%)	Carbon Balance (%)
1	199.3	2392[a]	1.4	38.5	58.8	98.7
2	217.7	2347[a]	9.9	13.2	na	na
3	174.6	2247[b]	2.9	34.4	62.6	99.9
4	206.7[c,d]	2319[a]	2.0[d]	61.0[d]	na	na
5	203.0	2458[e]	7.9[d]	34.4[d]	62.7	105.0
6	196.4	2311[f]	0.0	0.0	97.2	97.2

a: Alumina was baked at 250°C for at least twelve hours then stored in a desiccator. b: Alumina contains approximately 10% w/w H_2O. c: Naphthalene is 74.0% deuterated. d: See text. e: Alumina contains approximately 10% w/w D_2O. f: Silica.

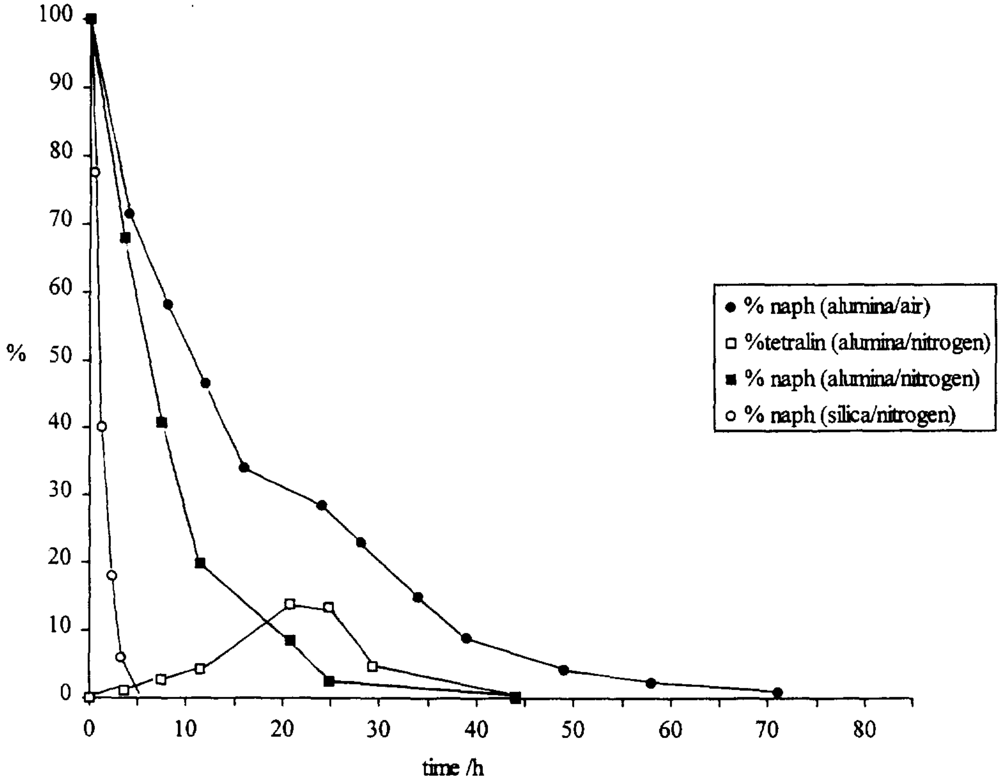
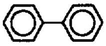
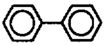


Figure 1. Yields of naphthalene and tetralin after mechanochemical treatment of naphthalene.

duration and show the distribution of carbon in the products. The results (columns 4-7, Tables 1 and 2 and columns 4-10, Tables 3 and 4) are expressed as percentages of carbon in the original substrate. Clearly the last column should be theoretically 100 % and indeed whenever the "carbon balance" was obtained the experimental figure was, with one exception (Table 3, Entry 4), within 7.4 % of theory and generally much closer.

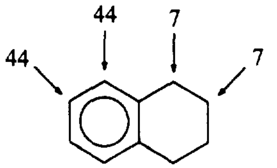
While the "destruction", ie. the complete conversion to carbon and chloride of chlorinated aromatics under similar conditions, but using more obviously chemically active inorganic matrices, has been recently reported[5], it is surprising to observe that simple aromatic *hydrocarbons*, such as naphthalene (Table 1), biphenyl (Table 2), anthracene (Table 3) and phenanthrene (Table 4) are largely converted to carbon under our conditions in relatively short time. Even more surprising is the observation that, while the eventual fate of carbon in all these substances is graphite (the residual elementary carbon was identified as graphite by powder X-Ray crystallography[6]), at intermediate stages one observes significant quantities of partly hydrogenated derivatives.

Table 2. Mechanical Treatment of Biphenyl with Alumina over 24 Hours

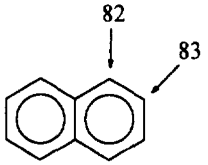
Entry	 (mg)	Alumina (mg)	 as C (%)	 as C (%)	Carbon (%)	Carbon Balance (%)
1	223.2	2313[a]	13.8[d]	31.5	51.6	96.9
2	198.4	2215[a]	8.4	26.7	64.5	99.6
3	195.7	2477[a]	17.0	18.8	63.0	98.8
4	195.1	2814[b]	1.7	10.5	90.0	102.2
5	198.5	2785[c]	1.6	84.4	14.0	100.0

a: Alumina was baked at 250°C for at least twelve hours then stored in a desiccator. b: Alumina was baked at 600°C for at least twelve hours then stored in a desiccator. c: Alumina contains approximately 10% w/w H_2O. d: A trace (0.1-0.5 %) of bicyclohexyl was detected.

In the mechanochemical treatment of biphenyl up to 14 % of biphenyl is converted to phenyl*cyclo*hexane (Table 2, Entry 3) and up to 17 % of naphthalene (Figure 1) is converted to tetralin. By substituting partly deuterated naphthalene (Table 1, Entry 4) for naphthalene, one can demonstrate directly that the extra hydrogen indeed comes from naphthalene. Thus mechanochemical treatment of naphthalene deuterated to 74 % at the α position and 74 % at the β position, in the presence of carefully dried alumina, gave tetralin (Table 1, Entry 4) with the deuterium content indicated in structure (1) while the residual naphthalene has the deuterium content indicated in structure (2) (Numbers on structures 1-4 are % of ^2H at the relevant position).

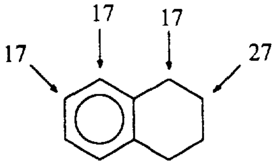


1



2

However, an apparently alternative source of hydrogen is also possible (Table 1, Entry 5), because using alumina "wetted" with D_2O, also results in deuterated tetralin (structure 3) and deuterated residual naphthalene (structure 4). This experiment is not, however, conclusive because one can postulate that naphthalene might first undergo H/D exchange with alumina and then a hydrogen (or deuterium) transfer reaction takes place as in the experiment summarised in Table 1, Entry 4.



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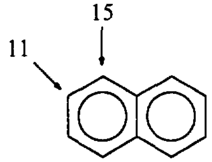

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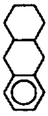
Table 3. Mechanical Treatment of Anthracene with Alumina over 24 Hours

Entry	 (mg)	Alumina[a] (mg)	 as C (%)	 as C (%)	 as C (%)	 as C (%)	 as C (%)	C (%)	Balance (%)
1	209.9	2239	4.0	1.4	0.0	0.0	15.5	74.9	95.7
2	188.3	2261	3.9	1.9	0.0	0.0	13.1	73.7	92.6
3	149.0	2229	3.6	1.3	0.0	0.0	9.9	na	na
4[b]	196.8	2532	2.8	6.3	0.8	9.9	1.4	64.4	85.6

a: Alumina was baked at 250°C for at least twelve hours then stored in a desiccator b: This reaction was performed under a nitrogen atmosphere.

The most extaordinary feature of this hydrogen-transfer reaction is its extent. Stoichiometry requires that three molecules of naphthalene could theoretically yield two molecules of tetralin and 10 carbon atoms. Thus the highest (but undoubtedly not maximum) yield of tetralin observed (17 %) corresponds to approximately 25 % of theory. We have also obtained isolated results at somewhat more elevated temperatures which gave up to a 39 % yield of tetralin, corresponding to 58 % of theory, but these reactions have so far proved to be poorly reproducible.

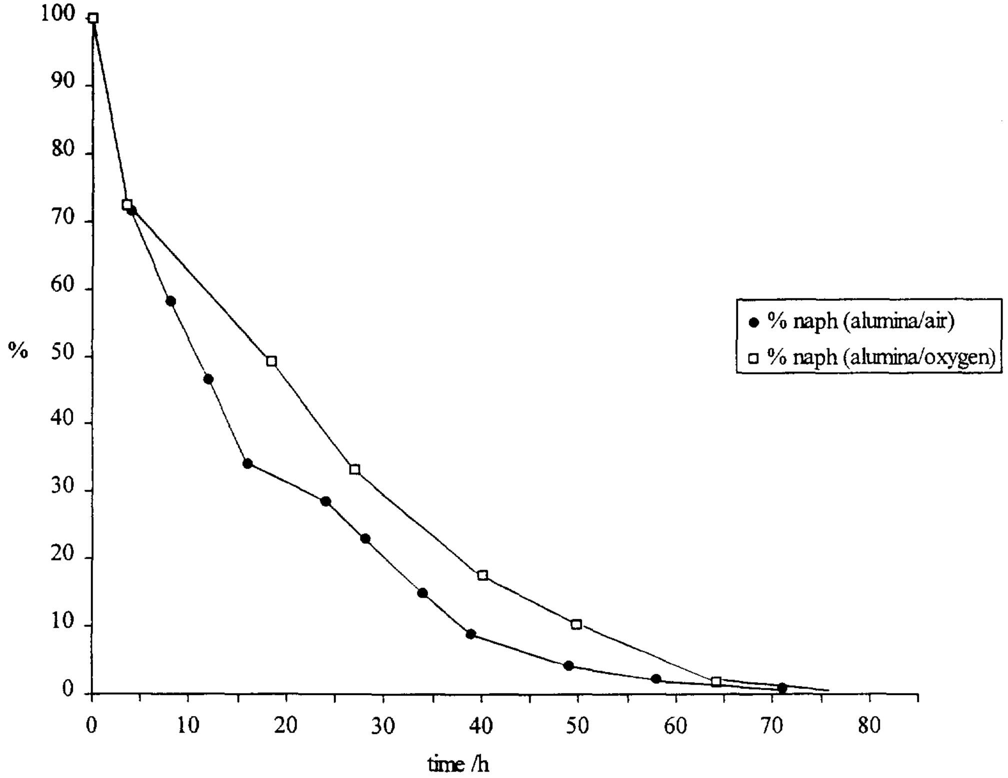
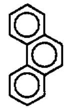
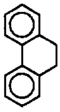
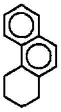
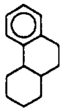
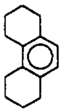
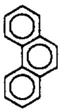


Figure 2. Yields of naphthalene after mechanochemical treatment of naphthalene with alumina.

Table 4. Mechanical Treatment of Phenanthrene with Alumina over 24 Hours

Entry	 (mg)	Alumina[a] (mg)	 as C (%)	 as C (%)	 as C (%)	 as C (%)	 as C (%)	C (%)	Balance (%)
1	189.2	2282	4.4	5.0	0.0	0.0	31.1	54.9	95.4
2	195.7	2313	0.0	1.1	0.0	0.0	39.8	56.0	96.9
3	204.5	2215	0.0	0.1	0.0	0.0	41.1	53.1	94.3
4[b]	191.4	2457	0.0	6.7	4.5	14.0	11.6	na	na

a: Alumina was baked at 250°C for at least twelve hours then stored in a desiccator b: This reaction was performed under a nitrogen atmosphere.

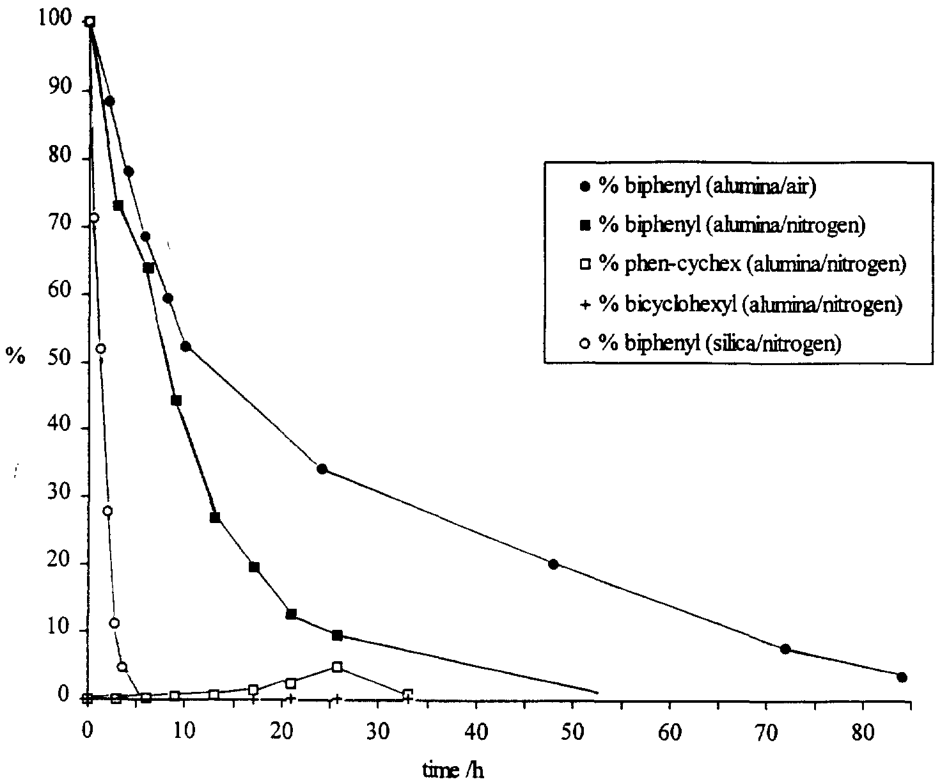


Figure 3. Yields of biphenyl and phenylcyclohexane after mechanochemical treatment of biphenyl.

Results on biphenyl (Table 2), anthracene (Table 3) and phenanthrene (Table 4) show that the hydrogen transfer reaction is general and can lead to more extensively hydrogenated products than tetralin, including in the case of biphenyl (Table 2, Entry 1) trace amounts of the fully reduced bicyclohexyl.

In an attempt to obtain an indication of the kinetics of the destruction of naphthalene and biphenyl, we have followed their disappearance (Figures 1-3) under a variety of conditions. In these runs we monitored only substances soluble in ethyl acetate (see Experimental), ie. the substrates and the reduced products. The limited data from these experiments indicate that:

1. Silica is far more effective matrix for the destruction than alumina.
2. The presence of air (oxygen) slows down the reaction(s) leading to the disappearance of the hydrocarbons. This is entirely reasonable as numerous scattered studies of mechanochemical reactions[2] indicate the presence of free radicals. Thus oxygen could act as a radical trap.

3. By apparent contrast, the presence of oxygen leads to the elimination of the intermediate hydrogenated materials which is faster than the destruction of the original substrate. This is unexceptional, as the benzylic positions in the newly produced partially hydrogenated hydrocarbons are susceptible to direct oxygenation. In the 24 hour runs, the amount of oxygen present in the vessel is apparently insufficient for this effect to be conspicuous, but it may contribute to the wide range of yields of the partly hydrogenated materials observed by us (Tables 1-4).

Conclusions : We have shown that a number of aromatic hydrocarbons (biphenyl, naphthalene, anthracene and phenanthrene) react readily at room temperature under our conditions with apparent half-lives (Figures 1-3) of between 1 hour and 20 hours. The products were carbon (as graphite) and a variety of partly hydrogenated materials. These were tetralin, phenyl-cyclohexane, bicyclohexyl, di-, tetra- and octa-hydroanthracenes and -phenanthrenes. Silica was shown to be a more effective matrix than alumina (see Figures 1 and 3) and oxygen slows down the rate of reactions.

EXPERIMENTAL

General : Gas chromatographic-mass spectroscopic (GC-MS) analyses were performed on a Hewlett-Packard 5890 Series II GC-MS system with a Supelco BPX5 capillary column interfaced with a 5971 mass selective detector. Ionisation was by 70 eV electron impact and masses were reported in units of mass over charge (m/z). The molecular ion is indicated by M^+, the base peak by B^+ and intensities are calculated as a percent of the base peak intensity. Gas chromatographic (GC) analyses were performed on a Hewlett-Packard 5890A GC system with a Hewlett-Packard 3393A integrator and a Supelco BPX5 capillary column. For both GC-MS and GC, injector and detector temperatures were set to 270°C. The temperature program for the GC was 60°C, held constant for 2 min; a gradient of 15°C per minute until 245°C; an increased gradient of 70°C per minute until the final temperature of 300°C. All analyses involved splitless injections; the purge valve was switched off prior to injection, then 30 seconds after injection, it was switched back on. All injections were approximately 1µl. The responses corresponding to the analytes were expressed as fractions of the area due to the analyte over the area due to the 2,3-dimethylnapthalene internal standard.

High performance liquid chromatography (HPLC) was performed on a Waters system, consisting of a Model 510EF pump, U6K injector, a Model 481 u.v. detector and a Model R403 differential refractometer. The analytical normal phase chromatography was done on a Whatman Partisil 10 column (22 mm i.d. x 50 cm). The flow rate was 13.5 ml per minute, the mobile phase de-aromatised distilled light petroleum. Reverse phase HPLC required a Dupont ZORBAX (8 µm) column (21.2 mm i.d x 25 cm). A composite eluant consisting of 10% methanol and 90% water at a flow rate of 11.25 ml/min was employed to effect separation.

^{1}H n.m.r. spectra were acquired on a Bruker AMX 400 spectrometer, or a Bruker AC 200F spectrometer using 5-mm sample tubes and the solvent stated under the preparation of individual compounds at concentrations of about 5 % w/v at 300 K. Where no details are given, the solvent was deuterochloroform. Tetramethylsilane ($SiMe_4$) was used as internal standard. Each signal is described in terms of chemical shift in ppm downfield from $SiMe_4$. Abbreviations used for multiplicities are s, singlet; d, doublet; t, triplet; q, quartet; aa'bb', AA'BB' quartet; m, multiplet; br, broad; quint, quintet.

Mechanochemical reactions were carried out using a SPEX® 8000 Mixer Mill purchased from the SPEX® corporation, 203 Norcross Avenue, Metuchen, NJ 08840, USA. A dry mixture of substrate (~200 mg) and inorganic matrix (~2300 mg) were placed in the cylindrical steel SPEX® 8001 vessel (~50 cm^3) with four chromium steel balls (12 mm diameter) which was mechano-reacted over a measured time interval.

The fixed time reactions were carried out over 24 h. The solid reaction product was sonicated (50 kHz) in ethyl acetate for fifteen minutes, the graphite-containing insoluble component was collected on a 45μm filter (Supelco Membrane 66). An internal standard solution of 2,3-dimethyl naphthalene (~500 mg) in ethyl acetate (100 ml) was prepared. The filtrate was made up to 250.0 ml with 10.0 ml of the internal standard solution. Standard solutions of the substrate and reaction products (tetralin, phenyl-cyclohexane etc.) were prepared (250.0 ml) with internal standard solution (10.0 ml). These solutions were injected in duplicate (< 2.0 % RSD) onto the capillary GC column. The masses of the analytes were calculated by direct comparison to standard responses.

The insoluble component was dried under high vacuum at 50°C for 2 h and accurately weighed. An aliquot was boiled in aqueous hydrochloric acid (3N, 40 ml) for three hours. The bulk of the HCl was decanted, the remainder centrifuged, and the residue was washed with water (until pH neutral) and dried to give a black solid which was accurately weighed. The solid was placed in a furnace overnight (800°C), the weight loss being equal to the mass of carbon in the aliquot.

Kinetic runs were carried out over a variable time frame depending on the speed of the mechanochemical degradation of the substrate. At selected intervals, the mixer mill was stopped, and an accurately weighed portion (~150 mg) was removed from the reaction vessel and placed in a 25.00 ml volumetric flask. The remaining reaction mixture was further mechano-reacted over subsequent time intervals and sampled.

A few millilitres of ethyl acetate were added to the 25.00 ml volumetric flask, the mixture was then sonicated (50 kHz) for fifteen minutes. An internal standard solution of 2,3-dimethylnaphthalene (~120 mg) in ethyl acetate (250 ml) was prepared. The analytical solution was made up to 25.00 ml including 5.00 ml of the internal standard. The solution was injected in duplicate (< 2% RSD) onto a capillary GC, the mass of compound was determined by referencing to a prepared calibration GC response curve. At each time interval, the amount of substrate remaining (and, if required, the amounts of other products generated) could be determined as a percentage of the initially present substrate.

Mechanochemical reactions performed under an oxygen or nitrogen atmosphere were carried out in an Aldrich Atmos-Bag. The bag was flushed with the selected gas, sealed, then evacuated and re-filled twice. When the mechano-reaction vessel was being prepared initially, a gauze mat was placed over the top of the vessel prior to evacuation of the chamber so as to minimise any interference from the bag walls.

Bicyclohexyl[7] : Phenylcyclohexane (Aldrich) (2.8 g) was dissolved in glacial acetic acid (20 ml) and Adam's catalyst (50 mg) was added to the solution. The mixture was placed in a high pressure chamber and hydrogen gas was admitted so that at 250°C, the hydrogen pressure was 250 kPa. The mixture was allowed to stir for 8 h at 250°C then the pressure was released, the catalyst filtered and the solvent removed to yield a clear liquid (2.9 g, 100 %). ^{1}H n.m.r. (400 MHz) : δ 0.9 - 1.25, mult. ^{13}C n.m.r. : δ 43.5, 2CH; δ 30.2, 4CH$_2$; δ 26.9, 6CH$_2$ (Relative intensities conformed by quantitative ^{13}C n.m.r.). GC-MS (m/z, %) : 166, (M$^+$, 20), 82 (B$^+$), 67 (30), 55 (40).

9,10-dihydroanthracene[8] : Anthracene was sublimed under high vacuum and stored in the dark prior to reaction. Sodium metal was washed repeatedly with distilled light petroleum and then the surface of the metal was removed. Anthracene (900 mg) was dissolved in amyl alcohol (100 ml) and the solution was brought to the boil. Sodium (5.27 g) was added in pieces over a period of five minutes and the reaction allowed to boil under reflux for 3 h. Water (100 ml) was added to the system, and after cooling, this aqueous layer was removed. The organic layer was washed with brine (3 x 30 ml) and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure. The product was passed down a silica column and then sublimed to give 9,10-dihydroanthracene (890 mg, 93 %). ^{1}H n.m.r. (200 MHz) : δ 7.1-7.4, aa'bb', 8H; δ 3.9, s, 4H. ^{13}C n.m.r. : δ 136.6, C, δ 127.4, CH, δ 126.1, CH, δ 36.1, CH$_2$. m.p. 112 - 113°C (lit.[9] 111 °C).

Dihydrotetrakis(triphenylphosphine)ruthenium(II), $RuH_2(PPh_3)_4$[10] : A mixture of benzene (60 ml) and methanol (100 ml) containing triphenylphosphine (6 g, 22.9 mmol) was placed in a 250 ml, round-bottomed, two necked flask under an argon atmosphere. After stirring under hydrogen for ~5 min $RuCl_2[P(C_6H_5)_3]_3$ (1.0 g, 0.87 mmol) was added through a side neck. Dry, finely ground sodium tetrahydroborate (1.5g, 0.04 mmol) was added in approximately five 0.3 g portions, over a period of 20 min, with rapid stirring. The solution was stirred for 1 h, during which time the initial red solution changed to brown and then yellow and the complex was precipitated as bright yellow microcrystals. Degassed methanol (100 ml) was added to the solution, and the product was collected on a sintered glass filter under argon, washed with argon purged methanol, and dried *in vacuo*. The yield based on ruthenium was 1.02 g (85 %).

1,2,3,4-Tetrahydroanthracene and 1,2,3,4,5,6,7,8-octahydroanthracene were prepared using a modified procedure of Grey, Pez and Wallo.[11] : Anthracene (1.63 g) and dihydrotetrakis(triphenylphosphine) ruthenium(II), $RuH_2(PPh_3)_4$ (62 mg) were dissolved under an argon atmosphere in ether (25 ml). This solution was transferred (while still under argon) to a high pressure reaction chamber. Hydrogen gas was admitted to the chamber so that at 100°C, there was a pressure of 620 kPa. The solution was allowed to stir for 12 h at 100°C, before the pressure was released and the reaction vessel allowed to cool. The catalyst and products were separated on a silica column using light petroleum as eluant, and light petroleum was removed to give a solid (1.5 g), which was heated in light petroleum (2 ml). Solubility differences between the starting material and products enabled the collection of some residual anthracene on a filter. The remaining solution was injected (1.8 µl) onto a normal phase preparative HPLC column. The 1,2,3,4,5,6,7,8-octahydroanthracene was collected (38 min - 45 min) with a relative (to anthracene) area of two. The 1,2,3,4-tetrahydroanthracene was collected (50 min - 65 min) with a relative area of six. Residual anthracene (73 min - 110 min) was not collected. As the procedure required multiple injections onto the HPLC column to attain adequate amounts, it was more time effective to 'overlap' injections whereby injections were made every fifty minutes so that the lead time (ie. time before the first compound eluted) and slow running anthracene (from a previous injection) overlapped each other. 1,2,3,4-Tetrahydroanthracene : ^1H n.m.r. (200 MHz) : δ 7.25, 7.75, aa'bb', 4H; δ 7.5, s, 2H; δ 2.95, br, 4H; δ 1.90, mult., 4H. ^{13}C n.m.r. : δ 137.0, C; δ 132.0, C; δ 126.9, CH; δ 126.6, CH; 124.9, CH; δ 29.8, CH_2; δ 23.4, CH_2. m.p. 103 - 105°C (lit.[9] 106 - 107°C). 1,2,3,4,5,6,7,8-Octahydroanthracene : ^1H n.m.r. (200 MHz) : δ 6.8, s, 2H; δ 2.7, br, 8H; δ 1.8, br, 8H. ^{13}C n.m.r. : δ 134.9, C; δ 130.2, CH; δ 30.4, CH_2; δ 24.2, CH_2. m.p. 79 - 80°C (lit.[9] 78°C).

*9,10-Dihydrophenanthrene and 1,2,3,4-*tetrahydrophenanthrene were prepared using a modified procedure of Jablonski.[12] : Phenanthrene (1.0 g) was dissolved in piperidine (100 ml) and the solution was brought to the boil. Sodium (1.29 g) was added over ten minutes and the system allowed to boil under reflux for 5 h. After cooling, hydrochloric acid (3M, 100 ml) was added. The products were extracted from this mixture with ether (4 x 50 ml), the extracts were combined and washed with 5% w/v sodium carbonate (4 x 50 ml). The ether was removed under reduced pressure, and the products passed down a flash silica column. The products were dissolved in light petroleum (2 ml) and injected onto a normal phase preparative HPLC column which yielded two major peaks. The second major peak eluted over a period of twenty-five minutes, beginning at the seventy-fifth minute. This peak consisted entirely of 9,10-dihydrophenanthrene. The first peak (50 min - 60 min) contained three compounds: 1,2,3,4-tetrahydropheanthrene, 1,2,3,4,5,6,7,8-octahydrophenanthrene and 1,2,3,4,4a,9,9a,10-octahydrophenanthrene. This mixture of products was dissolved in dichloromethane (0.5 ml) and injected onto a reverse phase HPLC column. The first compound to elute (28 min - 32 min; area, 0.83) was one of the octahydrophenanthrene isomers. The second compound (33.6 min - 37.2 min; area, 1.0) was the target compound, 1,2,3,4-tetrahydrophenanthrene and the final compound (45.2 min - 49.2 min; area, 0.11) was the second octahydrophenanthrene isomer. 9,10-Dihydrophenanthrene (810 mg): ^{1}H n.m.r. (200 MHz) : δ 7.75, d, 2H; δ 7.1 - 7.4, m, 6H; δ 2.9, s, 4H. ^{13}C n.m.r. : δ 137.3, C; δ 134.5, C; δ 128.1, CH; δ 127.4, CH; δ 126.9, CH; δ 123.7, CH; δ 29.0, CH_2. GC-MS (m/q, %) : 180 (M^+), 89 (40). 1,2,3,4-Tetrahydrophenathrene (115 mg): ^{1}H n.m.r. (200 MHz) : δ 8.0, d, 1H; δ 7.8, d, 1H; δ 7.6 d, 1H; δ 7.5, m, 2H; δ 7.3, d, 1H; δ 3.2, t, 2H; δ 2.9, t, 2H; δ 1.9, m, 4H. GC-MS (m/q, %) : 182 (M^+), 154 (90), 89 (20), 76 (35).

Aluminium tris-trifluoroacetate[13] : Trifluoroacetic acid (5.57 g) was added dropwise to aluminium chloride (1.0 g). A vigorous reaction ensued with liberation of hydrogen chloride. After complete addition of trifluoroacetic acid (TFA), the mixture was allowed to stand, protected from moisture, for a further thirty minutes after which the excess TFA was removed at room temperature (reduced pressure) to yield a free flowing powder (624 mg, 78 % yield). No chloride ion could be detected with aqueous silver nitrate.

Deuteronaphthalene[14] : D_2O (6.0 g) was added slowly to a mixture of naphthalene (750 mg), trifluoroacetic anhydride (102.0 mg) and aluminium tris-trifluoro acetate (3.61 g). This mixture was boiled for 48 hours then allowed to cool. Ethyl acetate (100 ml) was added to the solution followed by water (100 ml). The organic and aqueous layers were separated, with the water being further extracted with ethyl acetate (3 x 50 ml). The organic phases were combined, the solvent removed under reduced pressure and the brown solid sublimed to give a clear, white powder (650 mg, 82 % yield). The total deuterium content (74.0 %) and the relative amounts of deuterium at the α (74 %) and β (74 %) positions were determined by ^{1}H n.m.r. using 1,3,5-trinitrobenzene as internal standard.

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