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A *p*-benzyne to *m*-benzyne conversion through a 1,2-shift of a phenyl group. Completion of the benzyne cascade

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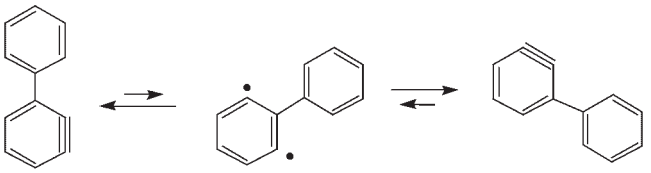
ABSTRACT: Pyrolysis of 1,6-diphenylhexa-1,5-diyne-*cis*-3-ene at 800–1000 °C leads to a mixture of 1- and 2-phenylbiphenylene, along with triphenylene. Formation of the two biphenylenes is taken as strong evidence of the rearrangement of a *p*-benzyne into a *m*-benzyne through a shift of one of the phenyl groups. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: *m*-benzyne; *p*-benzyne; pyrolysis; phenylbiphenylenes

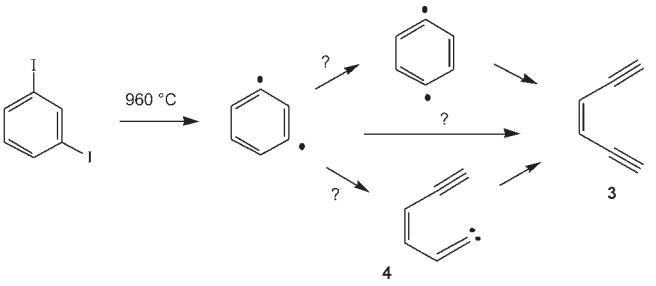
In 2003 we reported labeling evidence for the rearrangement of a phenyl-substituted *m*-benzyne (**1**) to the related *o*-benzyne (**2**) through shift of a phenyl group. In this paper we complete the phenylbenzyne cascade by demonstrating that a phenylsubstituted *p*-benzyne forms the meta isomer at high temperature.[1]



2 1 2

Theory and experiment agree that in the family of benzynes, the stability order is *ortho* > *meta* > *para*.[2,3] There is also agreement on the magnitude of the energy difference: 13–16 kcal mol^{-1} for each step (1 kcal = 4.184 kJ). Why, then, are rearrangements of the less stable isomers to the more stable versions not common? There have been a few experiments that might be so interpreted, but in most cases other mechanisms are now seen as more plausible or, at the very least, possible. The problem is the usual one; there are substantial kinetic barriers separating the three isomers of benzyne. Those barriers owe much of their magnitudes to the necessity of moving a hydrogen atom in a 1,2 fashion, a most difficult process indeed. For example, it is estimated (BP/DN**)[4a] that the barrier to a simple 1,2-shift in a phenyl radical is a formidable 58.4 kcal mol^{-1}. Barriers in the 56–60 kcal mol^{-1} range have been calculated for the hydrogen shifts interconverting benzynes.[4b] Benzyne to benzyne rearrangement could benefit from the exothermicity of the reaction, but migration of hydrogen must still be a difficult process. In the earlier work,[1] and here we use a phenyl ring as the migrating group in order to reduce the kinetic barrier. Phenyl migrations can make use of the π system, and are well known in radical systems, in sharp contrast to the all but unknown 1,2-hydrogen migrations.[4a,5]

As early as 1963, Fisher and Lossing isolated enediyne **3** from pyrolysis of *m*-diiodobenzene at 960 °C and suggested that it might have been formed by a *m*- to *p*-benzyne rearrangement, followed by ring opening. As the authors made clear, however, there were other, attractive mechanisms possible, such as the formation of vinylidene **4** or perhaps even concerted formation of **3**.[6] In Fisher and Lossing's example, it would surely not be surprising if the combination of the endothermic *meta* to *para* rearrangement and/or the necessity of overcoming a high barrier made an alternative concerted or stepwise mechanism viable.



More convincing is the experiment of the Bergman group in the late 1970s.[7] An enediyne, substituted on one end with a *tert*-butyl group, and on the other with a trimethylsilyl group (**5**), was pyrolyzed at 530 °C in a

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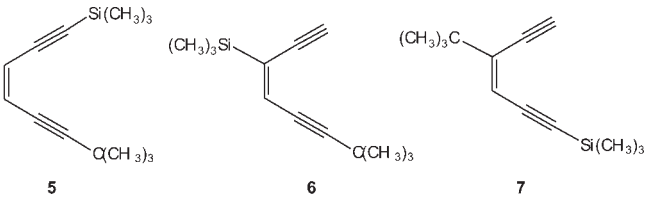
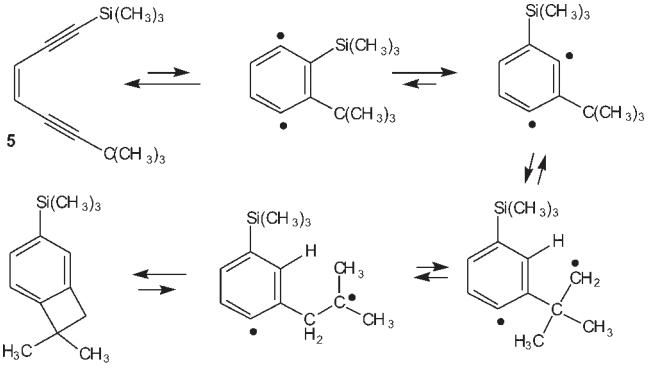
flowing system. Isomeric compounds **6** and **7** were also pyrolyzed at 450 °C.



5 **6** **7**

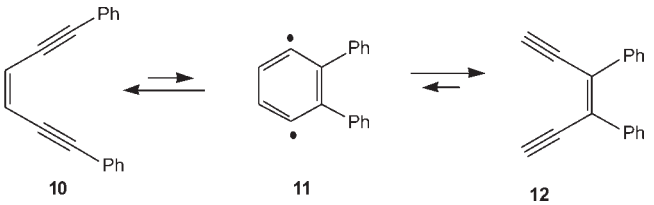
All three starting materials gave similar end products, which can be conveniently rationalized through a *p*- to *m*-benzyne rearrangement. For example, benzocyclobutene **8** is nicely explained through the sequence shown, in which the *para* to *meta* rearrangement is followed by hydrogen migrations and ring closure.



8 **9**

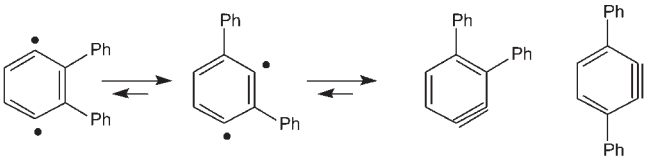
However, more circuitous routes are possible. For example, Bergman and co-workers pointed out that a sequence of hydrogen abstractions and aryl migrations starting from **5** can also lead to diradical **9**.[7] To be sure, economy favors the benzyne to benzyne rearrangement process but, at a minimum, further evidence is desirable.

Given Blake *et al.*'s evidence that benzynes could be interconverted through a phenyl shift[1] and the Bergman group's idea of using enediyne chemistry to generate *p*-benzynes thermally, we settled on 1,6-diphenylhexa-1,5-diyne-*cis*-3-ene (**10**) as starting material. [The use of enediyne chemistry was suggested to one of us (M. J.) in Nara, Japan, in September 2001, by W. T. Borden. Borden's suggestion was dismissed for a reason now unknown, but doubtless compelling at the time.] Although this material is known[8] and easily made, a formidable pyrolysis temperature seemed likely to be necessary, given the calculation of a 41.6 kcal mol^{-1} barrier for the cyclization, and an energy difference of 32.1 kcal mol^{-1} between starting material and cyclized *p*-benzyne product (**11**).[9]



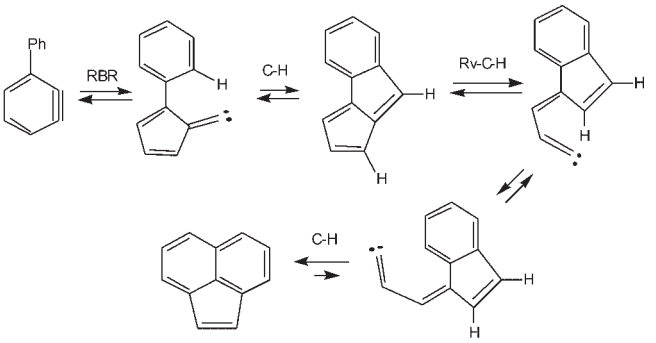
10 **11** **12**

Before reviewing the actual results, it is worth anticipating what might happen. First, surely Bergman–Sondheimer chemistry[10,11] in which the 1,6-diphenylenediyne **10** and the 3,4-diphenylenediyne **12** are equilibrated is to be expected. Phenyl migration in **11** can generate phenyl-substituted *m*-benzyne **13**. Further migration of a phenyl, according to Blake *et al.*,[1] can produce two *o*-benzynes, **14** and/or **15**.

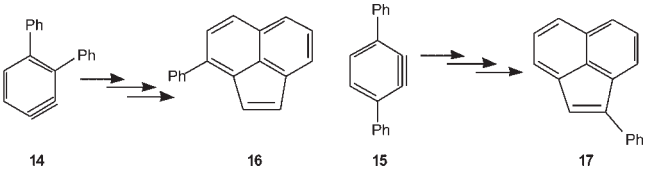


11 **13** **14** **15**

The mechanism first outlined by Brown and co-workers[12,13] and slightly elaborated by Blake *et al.*,[1] begins with the formation of a vinylidene through a Roger Brown rearrangement (RBR), followed by a sequence of forward and reverse carbon–hydrogen insertions (C–H, Rv-C–H).



This sequence predicts the formation of phenylacenaphthylenes **16** and/or **17** from **14** and **15**, respectively. Initially, we hoped to use the formation of one or both of these phenylacenaphthylenes as a diagnostic for formation of the *o*-benzynes **14** and **15**, and thus for the whole benzyne cascade, *para* → *meta* → *ortho*.

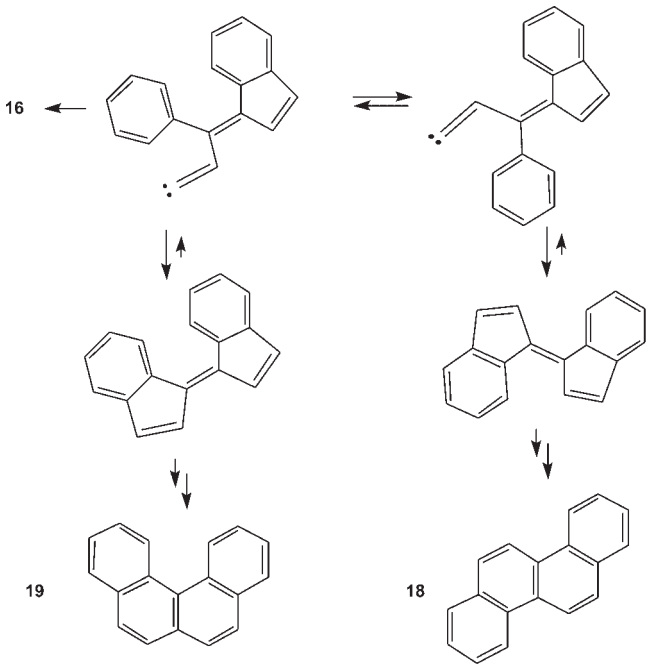


14 **16** **15** **17**

In fact, neither of these acenaphthylenes is formed in more than trace amounts when **10** is pyrolyzed at temperatures between 800 and 1000 °C. 1-Phenylacenaphthylene (**17**) was synthesized through the method of O'Brien and Smith[14] and the unknown **16** through a route starting from 3-nitroacenaphthene.[15] With authentic samples in hand, it was easy to verify that these anticipated compounds were not formed.

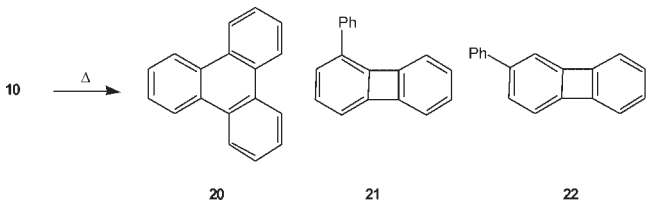
The presence of the second phenyl group allows a branching point in the Brown mechanism,[12,13] as one of the vinylidene intermediates has a 'choice' of benzene rings. Insertion can take place to give the missing

phenylacenaphthylenes or, after further rearrangements through '6–5' interconversions,[16] to give chrysene (**18**) or its cisoid isomer **19**. Neither of these compounds is formed in the pyrolysis in more than trace amounts.



So now we are in a difficult position–none of the anticipated products appears in the pyrolysis. Instead of these compounds, the major products are 1- and 2-phenylbiphenylene (**21** and **22**). Both biphenylenes were independently synthesized from commercial sources, and there can be no doubt about their structures.[17] Let us now explore how they are probably formed and why the conventional products, phenylacenaphthylenes **16** and **17**, and perhaps **18** and **19**, are not.

At 800–1000 °C, the major product distribution is shown below and in Table 1. Traces of biphenylene and, perhaps, chrysene are also found, and there is some starting material recovered (along with the *trans* isomer of **10**) at the lower temperatures. The structure of compound **X** is unknown, but it is not significantly formed at the lower temperature, and appears to be a secondary product, as does triphenylene (**20**), because they grow in at the expense of the primary products, biphenylenes **21** and **22**. Pyrolysis of **21** at 900 °C under the reaction conditions does result in about 8% of **20** as well as smaller amounts of **X**.



The non-formation of the 'expected' products and the appearance of **20** and **21** as the major products are connected in our view. The routes to acenaphthylenes

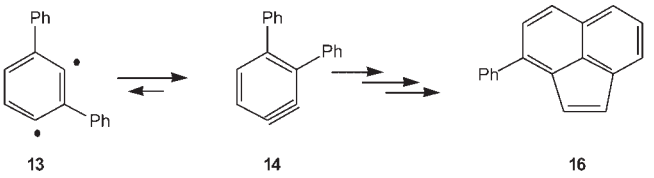
Table 1. Product distribution from the pyrolysis of **10** as a function of temperature

Temperature (°C)	**10**[a]	**20**	**21**	**22**	**X**
800	24	8	37	31	1
900	11	18	35	25	12
1000	tr	33	18	16	32

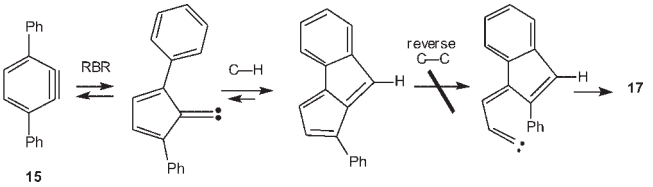
[a] Includes *trans*-**10**.

16 and **17** are cut off, and new reactions, leading to **20** and **21**, appear.

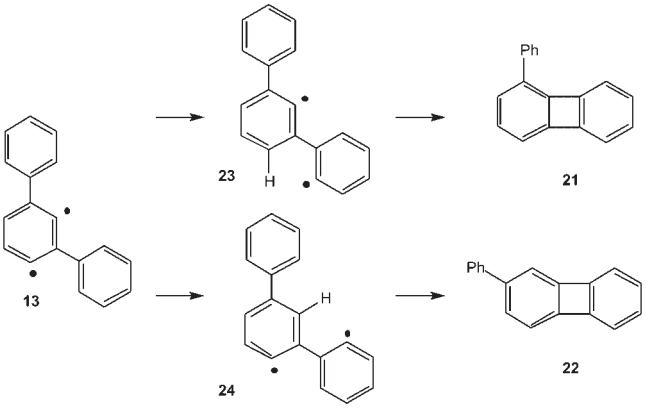
Formation of **16** requires that *m*-benzyne **13** re-establishes a destabilizing 1,2-diphenyl steric interaction in **14**. A similar difficulty attends the putative formation of **18** and **19**. *o*-Benzyne **14** must be an intermediate in each reaction, and the difficulty of its formation presumably blocks those pathways.



No such difficulty attends formation of **17**, but there is another problem. The pathway from *o*-benzyne **15** is shown. In this reaction, the reverse C—H insertion of the RBR mechanism[12,13] is transformed into a reverse C—C insertion. Carbon–carbon insertions are far more difficult that the corresponding C—H insertions. Indeed, the intermolecular C—C insertion is still unknown.[18] Perhaps the lack of **17** is due to the difficulty of this step.

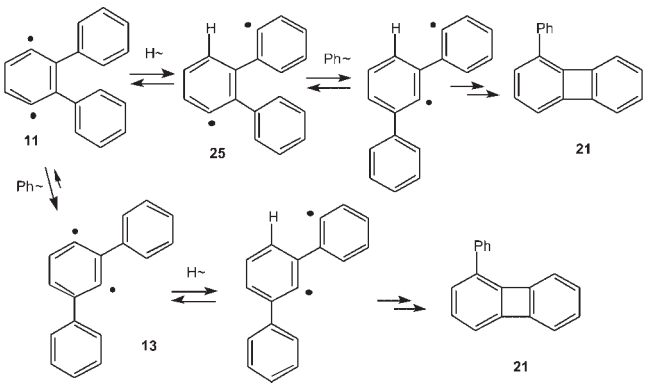


With the usual pathways difficult, the way is open for other things to happen in intermediate **13**. In particular, there are two possible hydrogen abstractions to give diradicals **23** and **24**. Closure leads to the two observed biphenylenes, **21** and **22**.

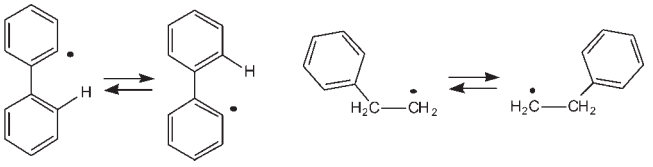


Even though the anticipated acenaphthylenes are not formed, the isolation of **21** and **22** is strongly indicative of the presence of **13**, and thus of the *p*- to *m*-benzyne rearrangement, completing the *para* → *meta* → *ortho* cascade.

Of course, one must consider other mechanistic possibilities. No mechanism is ever proved–every mechanistic proposal lives in peril of the next experiment or of an alternative proposal. In particular, we might circumvent our postulated phenyl migration directly converting *p*-benzyne **11** into *m*-benzyne **13** with the sequence of a hydrogen abstraction followed by a phenyl shift shown, forming biphenylene **21**. Formation of isomer **22** is more difficult to rationalize, but the point remains that we are essentially in the position of Bergman and coworkers.[7] We must argue that our path is more plausible than this alternative. To that end, we note that the alternative mechanism begins with abstraction of a hydrogen atom to form diradical **25**, not with the phenyl migration to **13**. The basic difference is only in the order of steps. Therefore, we might profitably ask which step, hydrogen abstraction or phenyl migration, is likely to be easier?



We take as models hydrogen abstraction in a biphenyl radical and the 1,2-phenyl migration in the β-phenethyl radical. Calculations at the UBLYP/6–311G** level yield



a barrier to the hydrogen abstraction of 23.6 kcal mol^{-1}.[19] The phenyl migration in phenethyl is calculated to be 14.1 kcal mol^{-1} at the UB3PW91/6–31G(d,p) level.[20] The almost 10 kcal mol^{-1} difference in favor of phenyl migration does not take into account the substantial exothermicity of the *p*- to *m*-benzyne rearrangement and therefore is certainly too low. Accordingly, we see the phenylbenzyne cascade as far more likely than any mechanism that must start with hydrogen abstraction.

EXPERIMENTAL

General. Chemicals were obtained from commercial sources unless noted otherwise and used as received without additional purification. GC–MS analysis was run on a Hewlett-Packard 5890 gas chromatograph equipped with a Hewlett-Packard 5971 mass spectrometric detector, with a 30 m HP-1701 fused-silica capillary column. High-resolution mass spectrometry was performed with a Kratos MS 50 instrument. ^{1}H and ^{13}C NMR spectra were acquired on Varian Mercury 300 MHz and Varian Inova 400 and 500 MHz instruments, and certain high-resolution ^{1}H spectra of pyrolysates were acquired on Varian Inova 500 and 600 MHz instruments. Melting-points were obtained on a Thomas Hoover Uni-Melt Capillary Melting Point Apparatus, using benzoic acid as a standard, and are uncorrected.

*Preparation of 1,6-diphenylhexa-1,5-diyne-cis-3-ene (**10**).*[9] In a typical run, copper iodide (0.387 g, 2.0 mmol), tetrakis(triphenylphosphine)palladium (0.496 g, 0.43 mmol), *cis*-1,2-dichloroethylene (1.125 ml, 16 mmol) and butylamine (4.50 ml, 50 mmol) were dissolved in 60 ml of undistilled benzene in a 100 ml two-necked round-bottomed flask under an argon atmosphere at room temperature. To the resulting dark-green solution, phenylacetylene (3.50 ml, 32 mmol) in 5.0 ml of undistilled benzene was added dropwise. The solution turned a pale peach color, then darkened a second time. Following completion of the addition, the reaction mixture was stirred under an argon flow at room temperature. After 3 h of stirring, the reaction mixture was extracted into 30 ml of diethyl ether and the organic layer was washed with saturated ammonium chloride solution (2 × 50 ml), dried over anhydrous $MgSO_4$, filtered and concentrated to yield 6.8 g of crude product. This material was further purified by chromatography over a 60 × 4.5 cm i.d. silica gel column. Elution began with 1 l of hexanes, then acetone was added in increasing concentrations (1% in hexanes for 500 ml, 2% in hexanes for 1.5 l, 3.5% in hexanes for 1 l, 4% in hexanes until the last fraction). A pale-yellow band was collected, concentrated and recrystallized from methanol to yield 1.62 g of pale-yellow crystals (44% yield, m.p. 31.5–32.5 °C, lit.[9] 33–34 °C).

Preparation of 1-acenaphthenone. The oxidation of acenaphthene to produce acenaphthenone was performed according to the procedure of Perumal and Bhatt.[21] To a 100 ml two-necked round-bottomed flask fitted with a condenser were added acenaphthene (1.03 g, 6.7 mmol), copper(II) sulfate pentahydrate (0.347 g, 1.4 mmol) and potassium persulfate (3.51 g, 13 mmol). This mixture was dissolved in acetonitrile (35 ml) and heated to reflux. After 45 min, 35 ml of deionized water were added to the beige–brown reaction mixture. Three hours after the addition of water, the mixture was taken off reflux and

washed three times with 50 ml of deionized water. The clear brown organic layer was swirled over decolorizing carbon, dried over anhydrous magnesium sulfate and filtered through a plug of silica gel. The filtrate was condensed and purified by chromatography over a 20×1.5 cm i.d. silica gel column. The column was eluted with hexanes (175 ml), followed by 700 ml of 2.5% acetone in hexanes. Concentration of the second band yielded pure acenaphthenone (0.302 g, 27% yield, m.p. 113–117 °C, lit.[22] 119–119.5 °C).

*Preparation of 1-phenylacenaphthylene (**17**).* This synthesis was carried out according to the procedure of O'Brien and Smith.[14] Acenaphthenone (106 mg, 0.63 mmol) and 10 ml of anhydrous diethyl ether were added to an oven-dried, hot, 25 ml pear-shaped flask under an argon atmosphere. To a second 25 ml pear-shaped flask was added phenylmagnesium bromide as a 1 M solution in tetrahydrofuran (1.1 ml, 1.1 mmol) under an argon atmosphere. The acenaphthenone solution was transferred dropwise into the phenylmagnesium bromide solution to form a cloudy yellow reaction mixture, which was stirred under argon for 1.5 h at room temperature. The resulting pale-yellow suspension was poured into 50 ml of ice–water and concentrated hydrochloric acid was added dropwise until the solution pH reached 2. The organic layer was separated and the aqueous layer extracted a second time with 50 ml of diethyl ether. The two organic extracts were combined and the resulting solution was washed with 50 ml of 10% hydrochloric acid. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated to yield a bright-yellow oil. The oil was dissolved in glacial acetic acid (10 ml), transferred to a 25 ml pear-shaped flask fitted with a condenser and refluxed for 1 h 45 min. Diethyl ether (20 ml) and water (20 ml) were then added to the orange reaction mixture and the organic layer was washed with water (3×20 ml) and 10% sodium bicarbonate solution (3×20 ml, vigorous bubbling!), dried over anhydrous $MgSO_4$, concentrated and purified on two 20×20 cm, 1000 μm thick silica gel TLC plates, using 10% acetone in hexanes as eluent. Scraping off the center of the yellow band and washing with deuterochloroform or diethyl ether yielded pure 1-phenylacenaphthylene (**17**) as a bright yellow–orange solid; 15 mg were purified in total, m.p. 55–57 °C, lit.[14] 57–58 °C. ^{1}H NMR ($CDCl_3$), δ: 7.19 (s, 1H), 7.40 (dd, $J = 7.4$, 7.3 Hz, 1H), 7.51 (dd, $J = 7.6$, 7.2 Hz, 2H) 7.58 (dd, $J = 8.2$, 6.9 Hz, 1H), 7.62 (dd, $J = 8.2$, 7.0 Hz, 1H), 7.71 (d, $J = 6.5$ Hz, 1H), 7.81 (m, 3H), 7.87 (d, $J = 8.1$ Hz, 1H), 7.96 (d, $J = 7.0$ Hz, 1H). ^{13}C NMR ($CDCl_3$), δ: 123.86, 124.43, 125.53, 127.00, 127.49, 127.58, 127.61, 127.93, 127.94, 128.76. MS (ESI), calculated for $C_{18}H_{12}$: 228.09390. Found: 228.09456.

Preparation of 3-aminoacenaphthene. The reduction of 3-nitroacenaphthene[15] to yield the amine was performed according to the procedure of Pascal *et al.*[15] In a typical run, 3-nitroacenaphthene (5.0 g, 0.025 mol) and 10% palladium on activated carbon (0.57 g, 11.4 wt%) were added to a 500 ml, thick-walled glass hydrogenation flask and suspended in 200 proof ethyl alcohol (250 ml). The suspension was agitated under 50 psi of hydrogen gas in a Parr Hydrogenator apparatus and a rapid reduction in H_2 pressure to 38 psi indicated that the reaction was in progress. After 4 h of agitation, no solid was visible in the dark-green reaction mixture. The solution was filtered twice under vacuum through a Celite plug and concentrated to yield 3.73 g of crude 3-aminoacenaphthene, which was assayed by GC–MS and NMR spectroscopy. Various chromatographic systems were attempted for purification, but none produced satisfactory results and the crude product was not purified further.

Preparation of 3-bromoacenaphthene.[23] In a typical run, the crude 3-aminoacenaphthene from the synthesis described above (7.0 g, 41 mmol) and deionized water (83 ml) were added to a 250 ml Erlenmeyer flask. The resulting suspension was stirred and chilled in an ice bath. To the stirred grayish white suspension at 2 °C were added concentrated HBr (20 ml) and sodium nitrite (2.90 g, 42 mmol). The solution color turned a deep forest green. To this reaction mixture was added a cold solution of $ZnBr_2$, previously prepared by gradually dissolving Zn dust (10.5 g) in 60 ml of concentrated HBr (**Caution**: vigorous exotherm). On addition of the $ZnBr_2$ solution, a reddish green, frothy paste was formed above the liquid phase, and occasional mechanical stirring with a glass rod was performed to homogenize the reaction mixture. Following stirring for 30 min at 1 °C, the reaction mixture was filtered under vacuum and the isolated green–blue solid was washed with 400 ml of cold 50:50 diethyl ether–ethanol and dried under suction. The solid was then transferred to a 250 ml round-bottomed flask fitted with a condenser, dissolved in 80 ml of toluene and the solution refluxed overnight. The reaction mixture was combined with 400 ml of glacial acetic acid and concentrated to yield crude 3-bromoacenaphthene (6.0 g) as a dark-brown amorphous solid, almost perfectly pure by NMR analysis (61% yield). A portion of the crude product was purified further by vacuum distillation to yield white crystals, m.p. 59–62 °C. The product was characterized by GC–MS and NMR spectroscopy. GC–MS analysis shows a single peak with parent ion masses of 234 and 232. ^{1}H NMR ($CDCl_3$), δ: 3.39 (br m, 4H), 7.31 (d, $J = 6.9$ Hz, 1H), 7.46 (dd, $J = 8.2$, 7.6 Hz, 1H), 7.49 (d, $J = 8.7$ Hz, 1H), 7.52, (d, $J = 8.7$ Hz, 1H), 7.58 (d, $J = 8.2$ Hz, 1H).

Preparation of 3-bromoacenaphthylene. 3-Bromoacenaphthene was oxidized to 3-bromoacenaphthylene according to the procedure of Chen.[24] In a typical run, purified crystalline 3-bromoacenaphthene (1.43 g, 6.1 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2.5 g,

11 mmol) were added to a 500 ml round-bottomed flask fitted with a condenser and dissolved in dry toluene (150 ml). The resulting mauve solution was refluxed under an argon atmosphere for 17 h and the reaction progress was monitored by GC–MS. The red product mixture was filtered through a 3.5 × 6.5 cm i.d. column of Celite in a sintered glass crucible; the Celite plug was washed with excess toluene (150 ml). The red–brown solution was concentrated and the residue was chromatographed through a 3.5 × 6.5 cm i.d. column of neutral alumina, which was eluted first with 200 ml of light petroleum, followed by 200 ml of toluene. The filtrate was concentrated and chromatography was repeated through a 3.5 × 6.5 cm i.d. neutral alumina column, this time using only light petroleum as eluent. The bright-yellow eluate was concentrated to yield 3-bromoacenaphthylene (564 mg, 40% yield) as a red–orange solid. The product was analyzed by GC–MS and NMR spectroscopy, and no further purification was performed. GC–MS analysis showed a single peak with parent ion masses of 232 and 230. ^{1}H NMR ($CDCl_3$), δ: 7.07 (d, $J = 5.2$ Hz, 1H), 7.11 (d, $J = 5.3$ Hz, 1H), 7.53 (dd, $J = 8.2$, 6.9 Hz, 1H), 7.60 (d, $J = 8.6$ Hz, 1H), 7.66 (d, $J = 8.6$ Hz, 1H), 7.69 (d, $J = 6.8$ Hz, 1H), 7.77 (d, $J = 8.2$ Hz, 1H).

*Preparation of 3-phenylacenaphthylene (**16**).* The coupling of 3-bromoacenaphthylene and phenylboronic acid was performed according to the procedure of Miyaura *et al*.[25] In a typical run, 3-bromoacenaphthylene (634 mg, 2.7 mmol), phenylboronic acid (401 mg, 3.3 mmol), tetrakis(triphenylphosphine)palladium (191 mg, 0.16 mmol) and sodium carbonate monohydrate (814 mg, 6.6 mmol) were added to a 250 ml round-bottomed flask fitted with a condenser. This mixture was dissolved in toluene (130 ml) and absolute ethyl alcohol (13 ml) and heated gradually to 80 °C under an argon atmosphere while stirring. Once at 80 °C, deionized water (11.0 ml) was added to the pale-yellow suspension to commence the reaction. Ten minutes following addition of water, the reaction mixture changed color from yellow to red–orange and finally to dirty brown ~30 min. later. Reaction progress was monitored by GC–MS. Three hours after the initial addition of water, the reaction mixture was poured into 120 ml of deionized water while hot and allowed to cool to room temperature. The product mixture was extracted into 200 ml of diethyl ether. The organic layer was washed with 5% $NaHCO_3$ (1 × 200 ml) and with saturated NaCl solution (2 × 200 ml). A black emulsion that formed during the extractions was kept with the organic layer until the final wash. The yellow–brown organic layer was dried over anhydrous magnesium sulfate and filtered through a 4 × 7 cm diameter pad of Celite in a sintered-glass crucible. Removal of solvent yielded 336 mg of a yellow–brown amorphous solid, which was further purified by chromatography over a 57 × 4.5 cm i.d. silica gel column. Elution with hexane, isolation of the first yellow band and removal of solvent yielded 3-phenylacenaphthylene as a bright-yellow solid (198 mg, 32% yield), m.p. 74.5–76 °C. GC–MS showed a single peak with a parent ion mass of 228. ^{1}H NMR ($CDCl_3$), δ: 7.13 (d, $J = 5.3$ Hz, 1H), 7.23 (d, $J = 5.3$ Hz, 1H), 7.43 (tt, $J = 7.4$, 1.36 Hz, 1H), 7.53 (m, 3H), 7.69 (m, 4H), 7.83 (d, $J = 8.2$ Hz, 1H), 7.89 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 124.43, 126.98, 127.49, 127.65, 127.94, 128.72, 128.85, 128.89, 129.46, 129.79. MS (ESI), calculated for $C_{18}H_{12}$: 228.09390. Found: 228.09363.

Preparation of biphenylene. The synthesis of biphenylene was adapted from that of Pascal *et al.*[26] In a typical run, isoamyl nitrite (3.75 ml, 28 mmol) and 1,2-dichloroethane (250 ml) were added under argon purge to a 2 L, three-necked round-bottomed flask fitted with a pressure-equalized 500 ml addition funnel and a condenser. This solution was stirred and heated to reflux under an argon flow. Anthranilic acid (1.95 g, 14 mmol) and 1,2-dichloroethane (750 ml) were added to a 1 l round-bottomed flask and stirred until dissolution was complete. The solution of anthranilic acid was added dropwise to the refluxing solution of isoamyl nitrite over 3.5 h and the combined mixture was stirred at reflux for an additional 3 h. The reaction mixture was quenched while hot with 200 ml of absolute ethyl alcohol, followed by 400 ml of 2% aqueous NaOH. The mixture was then extracted into chloroform (1.5 l) and separated into two equal portions. The organic layer of each portion was washed twice with 500 ml of saturated $NaHCO_3$ and once with 500 ml of deionized water. The organic layers were combined and the resulting solution was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by chromatography over a 40 × 3 cm i.d. silica gel column, using hexanes as eluent. The first band to elute (colorless) was concentrated to yield biphenylene (60 mg, 11% yield) as white crystals, m.p. 107–109 °C, lit.[27] 110–112 °C.

Preparation of 1-lithiobiphenylene.[28] Biphenylene (500 mg, 3.28 mmol) was added to a hot, oven-dried 100 ml round-bottomed flask and immediately dissolved in distilled diethyl ether (40 ml). The flask was sealed with a wired-on rubber septum and the solution was purged with argon while stirring for 10 min. To this solution was added 2.5 M butyllithium in hexane (13.9 ml, 32.8 mmol). Vigorous gas evolution was observed upon addition, and the combined solution was stirred for 5 h under a slow flow of argon. Once the flow was stopped, the top of the septum was sealed with electrical tape to minimize solvent evaporation, and the red solution was stirred in the dark at room temperature for 1 week, at which point it was ready for use in the iodination reaction described below.

Preparation of 1-iodobiphenylene.[28] Iodine (4.0 g, 16 mmol) in distilled diethyl ether (25 ml) was added to

a solution of 1-lithiobiphenylene prepared as described above. A slight exotherm was generated upon addition. The resulting dark-red solution was stirred at room temperature under an argon atmosphere, exposed to light, for 2 h. The solution was then transferred to a 125 ml separating funnel, the reaction flask was rinsed with diethyl ether (20 ml) and the rinse was added to the product mixture. The resulting solution was washed with saturated $NaHSO_3$ (2×30 ml) and deionized water (2×30 ml). The red–orange organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated to yield ca 3 ml of a dark-red oil, which by GC–MS contained 1-iodobiphenylene (parent ion mass 287) as the major product, with unreacted starting material and several other impurities as minor constituents. This material was chromatographed through a 60×3.5 cm diameter silica gel column using hexanes as eluent. The product appeared as the third overall band (colorless), immediately following a yellow–green band that gradually turned purple after isolation. Only fractions that were pure by TLC were combined and concentrated into solid 1-iodobiphenylene (0.23 g, 26% yield). The product was characterized by GC–MS and ^{1}H NMR spectroscopy. GC–MS analysis shows a single peak with parent ion mass of 287. ^{1}H NMR ($CDCl_3$), δ: 6.47 (dddd, $J = 8.2$, 6.8, 0.6, 0.6 Hz, 1H), 6.59 (dd, $J = 6.8$, 0.6 Hz, 1H), 6.67 (br ddd, $J = 6.7$, 3.5, 0.6 Hz, 1H), 6.82 (m, 3H), 6.96 (dd, $J = 8.6$, 0.6 Hz, 1H).

*Preparation of 1-phenylbiphenylene (**21**).*[17] The coupling of 1-iodobiphenylene with phenylboronic acid as described below was performed according to Miyaura *et al*.[25] To a 100 ml two-necked round-bottomed flask fitted with a condenser were added phenylboronic acid (77 mg, 0.68 mmol), sodium carbonate monohydrate (156 mg, 1.3 mmol), tetrakis(triphenylphosphine)palladium (37 mg, 0.032 mmol), and 1-iodobiphenylene (151 mg, 0.52 mmol). This mixture of solids was immediately dissolved in toluene (25 ml) and absolute ethyl alcohol (2.5 ml). The bright-yellow suspension was warmed to 80 °C over 2 h while stirring under an argon atmosphere. Once the warm-up was complete, deionized water (2.3 ml) was added to the yellow–orange suspension and the mixture was stirred under an argon atmosphere for 10 h, at which point the hot reaction mixture was quenched with 50 ml of cold deionized water. No significant change in color was observed over the course of the reaction. The resulting mixture was stirred until cool and extracted into diethyl ether (60 ml). The organic layer was washed with 5% sodium bicarbonate solution (1×70 ml) and saturated NaCl solution (2×70 ml). Drying over anhydrous $MgSO_4$ and removal of solvent yielded 0.173 g of crude product. This material was separated into two equal fractions and each was purified by preparative TLC on a 20×20 cm, 1000 μm thick silica gel plate. Elution with hexane, isolation of the middle band (yellow, dark under UV light) from a total of five bands and washing with acetone yielded 1-phenylbiphenylene (0.123 g, ~100% yield) as a pale-yellow, low-melting oil (lit.[17] m.p. 46.5 °C). The product was analyzed by GC–MS, ^{1}H,^{1}H COSY and ^{13}C NMR spectroscopy and high-resolution mass spectrometry. GC–MS shows a single peak with a parent ion mass of 228. ^{1}H NMR ($CDCl_3$), δ: 6.62 (dd, $J = 6.8$, 0.7 Hz, 1H), 6.68 (m, 1H), 6.77 (m, 3H), 6.86 (dd, $J = 8.5$, 6.8 Hz, 1H), 7.01 (dd, $J = 8.5$, 0.7 Hz, 1H), 7.35 (dd, $J = 7.4$, 7.4 Hz, 1H), 7.46 (dd, $J = 7.4$, 7.2 Hz, 2H), 7.60 (dd, $J = 8.4$, 1.3 Hz, 2H). ^{13}C NMR ($CDCl_3$), δ: 116.12, 117.30, 117.80, 126.42, 126.95, 127.69, 128.20, 128.43, 128.78, 129.26. MS (ESI), calculated for $C_{18}H_{12}$: 228.09390. Found: 228.09472.

Preparation of 2-bromobiphenylene.[29] 2-Bromobiphenylene was synthesized according to the method of Baker *et al*.[29] Biphenylene (250 mg, 1.6 mmol) was added to a 100 ml round-bottomed flask. A solution of bromine (0.5 ml, 9.8 mmol) in carbon tetrachloride (25 ml) was prepared and 4.5 ml of this solution were added to the flask containing biphenylene. The resulting blood-red mixture was placed under an argon atmosphere and two drops of pyridine were added while the mixture was stirred at room temperature. A cloud of yellow–orange vapor was generated immediately upon pyridine addition. The mixture was stirred at room temperature for 10 min. Next, an additional 2.5 ml of the bromine–CCl_4 solution was added, the reaction flask was immersed in a 90 °C oil bath and stirring under argon at the elevated temperature was continued for an additional 15 min, after which almost all solvent had evaporated through the gas outflow. The remaining yellow–red residue was dissolved in 30 ml of CCl_4 and washed with saturated $NaHCO_3$ solution (1×30 ml), followed by 5% $NaHCO_3$ solution (1×30 ml). The pale-yellow organic layer was dried over anhydrous $MgSO_4$ and removal of solvent yielded 0.71 g of pale-yellow crude product. This material was spotted on to two 20×20 cm, 1000 μm thick silica gel plates, which were eluted with hexanes. Following development, the top bands were cut out from each plate, washed with acetone and concentrated to yield 2-bromobiphenylene as a white–yellow solid (70 mg), slightly contaminated with starting material by NMR but appearing clean by GC–MS. ^{1}H NMR ($CDCl_3$), δ: 6.50 (d, $J = 7.3$ Hz, 1H), 6.66 (m, 2H), 6.77 (t, $J = 0.8$ Hz, 1H), 6.78 (m, 2H), 6.91 (dd, $J = 7.3$, 1.5 Hz, 1H).

*Preparation of 2-phenylbiphenylene (**22**).*[17] The coupling of 2-bromobiphenylene with phenylboronic acid was performed according to Miyaura *et al*.[25] To a 100 ml two-necked round-bottomed flask fitted with a condenser were added 2-bromobiphenylene as obtained in the previous synthesis (49 mg, 0.21 mmol), phenylboronic acid (31 mg, 0.25 mmol), sodium carbonate monohydrate (63 mg, 0.51 mmol) and tetrakis(triphenylphosphine)palladium (18 mg, 0.016 mmol). This mixture of solids was

dissolved in toluene (10 ml) and absolute ethyl alcohol (1 ml) and heated to 80 °C over a period of 1 h while stirring under a slow flow of argon. Once at 80 °C, deionized water (0.8 ml) was added to the pale-yellow reaction mixture and stirring at this temperature was continued for 10.5 h, at the completion of which the solution color was a gray–brown. This mixture was quenched while hot by addition of 20 ml of deionized water and allowed to cool to room temperature. The resulting suspension was extracted into 30 ml of diethyl ether and the organic layer was washed with 5% sodium bicarbonate solution (1×40 ml) and with saturated NaCl solution (2×40 ml). The yellow–brown organic layer was dried over anhydrous $MgSO_4$ for 15 min, then filtered through a sintered-glass crucible containing a 2×3.5 cm in i.d. column of Celite, which was washed with an additional 50 ml of diethyl ether. The crude product was concentrated to $\sim$2 ml and chromatographed over a 20×20 cm, 1000 μm thick silica gel plate with hexanes as eluent. Isolation of the diffuse migrating yellow band yielded 2-phenylbiphenylene as a pale-yellow solid (30 mg, m.p. 114–117 °C, 63% yield assuming perfect purity of starting material). Note: two melting-points from two different preparations are reported in the literature.[17] The more reliable value appears to be 111–113 °C, although an alternative preparation led to products that melted at 125.5 °C. The product was analyzed by GC–MS, ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry. GC–MS shows a single peak with a parent ion of mass 228. ^{1}H NMR ($CDCl_3$), δ: 6.69 (br ddd, $J = 4.0$, 3.2, 1.0 Hz, 2H), 6.72 (dd, $J = 7.0$, 0.9 Hz, 1H), 6.79 (d, $J = 7.7$ Hz, 1H), 6.79 (dd, $J = 2.0$, 0.6 Hz, 1H), 6.92 (ddd, $J = 1.4$, 0.1 Hz, 1H), 6.99 (dd, $J = 7.2$, 0.4 Hz, 1H), 7.33 (dd, $J = 7.1$, 7.1 Hz, 1H), 7.42 (br dd, $J = 7.4$, 7.0 Hz, 2H), 7.52 (m, 2H). ^{13}C NMR ($CDCl_3$), δ: 116.79, 117.46, 117.50, 117.51, 126.49, 126.99, 127.26, 128.31, 128.46, 128.66. MS (ESI), calculated for $C_{18}H_{12}$: 228.09390. Found: 228.09436.

*Pyrolysis of 1,6-diphenylhexa-1,5-diyne-cis-3-ene (**10**) or 1-phenylbiphenylene (**21**).* In a typical reaction, 40–60 mg of starting material (0.18–0.26 mmol) were sublimed through a 40×1.5 cm i.d. quartz tube passing through a 30×2.0 cm i.d. ceramic tube furnace set to the appropriate temperature through a variable voltage controller. Pressures in the system were maintained below 20 mTorr (1 Torr = 133.3 pa) with a standard vacuum pump coupled to a diffusion pump and monitored with a Varian pressure sensor coupled to a Virtis logarithmic manometer gauge. Temperatures were measured with a K type thermocouple probe attached to a digital thermometer, and were maintained within 20 °C of the desired setpoint. Teflon tape and small amounts of Apiezon grease were used to seal tubing joints. If starting material volatilization was slow, first intermittent then more vigorous heating was applied to the starting material container with a heat gun. The outflow of the pyrolysis tube led into a 100 ml spherical vacuum trap partially immersed in liquid nitrogen, although most of the product condensed in a warmer region of the quartz tube itself just outside the oven. Pyrolyses were allowed to continue until most of the starting material had volatilized and passed through the hot tube (ranging from 1 to 5 h). Upon completion of the reaction, the vacuum was slowly broken and the oven turned off. The apparatus was allowed to cool to room temperature, after which the outflow region of the tube and the entirety of the cold trap were washed out with 25–30 ml of diethyl ether. Removal of solvent yielded the pyrolysate product mixture.

*Cis–trans isomerization of cis-1,6-bisphenyl-hex-3-ene-1,5-diyne (**10**).* The UV-induced isomerization of **10** to its *trans* counterpart was adapted from König *et al*.[30] 1,6-Diphenylhexa-1,5-diyne-*cis*-3-ene (**10**) (16 mg, 0.070 mmol) was dissolved in $CDCl_3$ (2.0 ml) and the solution was transferred to a 20×0.5 cm o.d. NMR tube. The tube was capped and irradiated at 365 nm with a Spectroline TLC visualizer for 3.5 h at a distance of 3 cm, at the completion of which the initially pale-yellow solution was colored orange–brown. ^{1}H NMR analysis of the contents showed a 54:46 mixture of *cis* and *trans* isomers. GC–MS analysis of the product mixture shows two peaks with parent ion mass 228. New peaks corresponding to the *trans* isomer in the ^{1}H NMR spectrum of the mixture are ($CDCl_3$) δ: 6.30 (s, 2H), 7.35 (m, 6H), 7.47 (m, 4H).

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