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An Oxidation Induced by Potassium Metal. Studies on the Anionic Cyclodehydrogenation of 1,1′-Binaphthyl to Perylene

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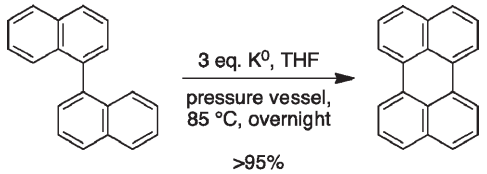

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Oxidative cyclization of 1,1′-binaphthyl (**1**) to perylene (**2**) can be achieved in essentially quantitative yield by the action of three or more equivalents of potassium metal in hot tetrahydrofuran. An overall reaction mechanism is proposed that accounts for all of the experimental observations reported by previous investigators and those from the present studies. The *trans*-6a,6b-dihydroperylene dianion ($\mathbf{6}^{2-}$) is believed to be the pivotal intermediate from which H_2 is lost. A radical chain reaction involving free hydrogen atoms ($H^{\bullet}$) in the two-step propagation cycle is proposed to explain the formation of H_2 from $\mathbf{6}^{2-}$. Anionic cyclodehydrogenations of this sort are complementary to those performed under strongly acidic/oxidizing conditions, photochemically, or thermally (flash vacuum pyrolysis), and a better understanding of how they occur, together with the optimized synthetic protocol reported here, should encourage their wider use in organic synthesis.

Introduction

Methods for the selective formation of unsymmetrical aryl−aryl bonds between reaction partners that require no functionality other than C−H bonds at the carbon atoms to be joined constitute some of the most exciting new advances in the field of transition metal catalyzed cross-coupling reactions.[1] The formation of symmetrical aryl−aryl bonds by homocoupling of unfunctionalized arenes, on the other hand, can often be achieved by the oxidative dimerization of electron-rich arenes, thanks to the pioneering work of Scholl, Kovacic, and others,[2,3] and intramolecular adaptations of these oxidative methods have been pushed to spectacular heights by Müllen et al. for the synthesis of very large graphene substructures.[4] Other noncatalytic, intramolecular methods include the oxidative photocyclization of stilbenes to phenanthrenes (the Mallory reaction)[5] and, in special circumstances, thermal cyclodehydrogenations by

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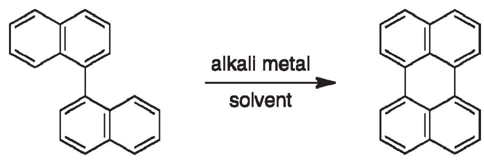

1 **2**

FIGURE 1. Anionic cyclodehydrogenation of 1,1′-binaphthyl (**1**) to perylene (**2**) by alkali metals.

flash vacuum pyrolysis.[6] Less well-known than all of these methods, however, is the anionic cyclodehydrogenation of aromatic hydrocarbons, for which the cyclization of 1,1′-binaphthyl (**1**) to perylene (**2**) by alkali metals serves as the classic example (Figure 1).[7,8]

None of the other methods mentioned above convert 1,1′-binaphthyl (**1**) to perylene (**2**) very efficiently, if at all, and this makes the anionic cyclodehydrogenation method unique, complementary, and worthy of attention.[9] Most intriguing is the seemingly incongruous fact that the starting material (**1** = $C_{20}H_{14}$) is being *oxidized* (**2** = $C_{20}H_{12}$), whereas the reagents used to induce this oxidation are alkali metals, which arguably qualify as some of the strongest *reducing agents* known. The alkali metal is also being *oxidized* during the course of this reaction, so what is being reduced? The inescapable conclusion is that the two lost hydrogen atoms *must* end up reduced to a lower oxidation state, either H_2 or hydride.

Almost nothing is known about the mechanistic details of this reaction.[10,11] Even the stoichiometry is uncertain, so the metal is generally just used in large excess. Because this reaction is so poorly understood and the yields rarely exceed 50%,[11] the method remains underutilized in synthesis. The most prominent application is probably the syntheses of rylenes by Müllen et al.,[12] in which potassium metal was used to "zip up" specifically designed oligomers of 1,4-linked naphthalenes. A knowledge of the mechanism operating, the intermediates involved, and the optimum conditions to use would allow chemists to tame this rather obstreperous reaction, making it available for a broader scope of substrates and facilitating its application. Herein, we describe studies on the archetypical system in Figure 1 that have provided deeper mechanistic insights and an optimized synthetic protocol.

Background

The cyclization of 1,1′-binaphthyl (**1**) to perylene (**2**) by alkali metals was discovered accidentally in 1967 by Solodovnikov et al. during their attempts to record the ESR spectrum of the 1,1′-binaphthyl radical anion in solution.[7,8] Because the work was published originally in Russian and the later English translation is not cited by *Chemical Abstracts*, the experimental data described therein, unfortunately, have been mostly overlooked for the last 40 years; the paper has been cited only three times. To rectify this situation, we summarize here some of the key findings that we have gleaned from our own translation of the early Russian paper; the summary in *Chemical Abstracts* is not entirely accurate.

Solodovnikov et al. reduced 1,1′-binaphthyl (**1**) in 1,2-dimethoxyethane (0.1 M) with an excess of potassium metal under vacuum at room temperature. The ESR signal for the 1,1′-binaphthyl radical anion ($\mathbf{1}^{\bullet-}$) grew in rapidly during the first hour but then began to diminish slowly, disappearing essentially completely over a period of 48 h. After 72 h, the contents of the ampule were exposed to oxygen, and perylene (**2**) was isolated in 39% yield. Some other hydrocarbon products, detected by TLC and tentatively identified as partially hydrogenated 1,1′-binaphthyl, were also obtained, but the amount of recovered 1,1′-binaphthyl, if any, was not specified. When the experiment was repeated and the reaction mixture was filtered to remove the potassium metal after 1 h, the point at which the ESR signal had reached its maximum intensity, immediate exposure of the filtrate to oxygen produced only a 0.3% yield of perylene (**2**). On the other hand, allowing the filtrate to stand at room temperature for 72 h, after removal of the potassium at the 1 h point, produced a 10% yield of perylene (**2**). These results indicate that the cyclization and rearomatization process is slow at room temperature and that it does not require the continued presence of potassium metal, once the solution contains a significant concentration of organic radical anions. The yield of perylene after 72 h was lower, however, if the solution was not left in contact with excess potassium after the first hour (10% vs 39%).

Solodovnikov et al. also report the formation of hydrogen gas in this reaction. They monitored the production of H_2 by GC analysis and the formation of perylene by UV−vis spectroscopy. Figure 2 reproduces the graph they published in 1968 that shows the percent yields of H_2 gas and perylene (**2**), as well as the growth and decline of the ESR signal, as a function of time. It is noteworthy that (i) the amount of H_2 detected was always significantly lower than the amount of perylene and (ii) the formation of both products leveled off with time; after 72 h, the yield of H_2 reached 24.6%, whereas the yield of perylene (**2**) reached 39%.

As the reaction proceeded, color changes were observed that gave a crude indication of the dominant species present. In the beginning, a green color developed that corresponded to the radical anion of 1,1′-binaphthyl ($\mathbf{1}^{\bullet-}$); the radical anion of naphthalene itself is also green. The solution then

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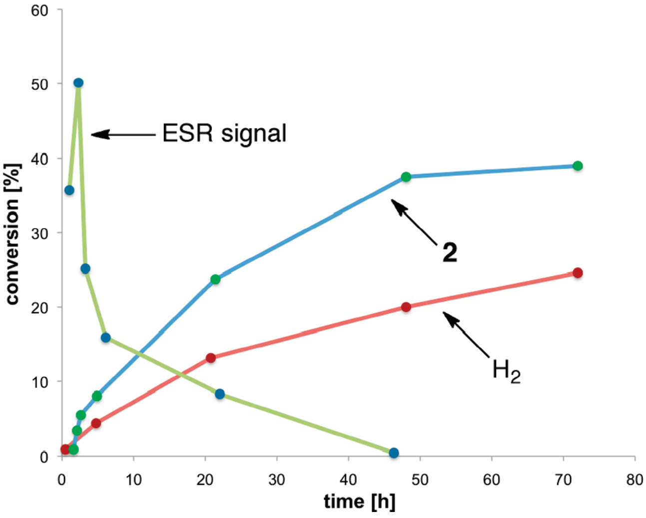

FIGURE 2. Change in ESR signal intensity (relative units) and yields of perylene (**2**) and H_2 over time in the cyclodehydrogenation of 1,1′-binaphthyl (**1**) by potassium metal at room temperature.[7b]

turned a wine-red color, which Solodovnikov et al. attributed to the dianion of 1,1′-binaphthyl ($\mathbf{1}^{2-}$); however, the ESR spectrum of the 1,1′-binaphthyl radical anion ($\mathbf{1}^{\bullet-}$) could also still be recorded at this stage. After 1 d, the solution became purple, which the authors attributed to the dianion of perylene ($\mathbf{2}^{2-}$); by this time, the ESR signal had dropped to 10% of its maximum amplitude. A UV−vis absorption spectrum of the purple solution matched that reported in the literature for the dianion of perylene ($\mathbf{2}^{2-}$).[13] Heating the wine-red solution from 20 to 100 °C caused it to turn purple and caused the ESR spectrum to change from that of the 1,1′-binaphthyl radical anion ($\mathbf{1}^{\bullet-}$) to that of the perylene radical anion ($\mathbf{2}^{\bullet-}$). Exposing purple solutions of the perylene dianion ($\mathbf{2}^{2-}$) to oxygen caused the color to change first to blue (perylene radical anion, $\mathbf{2}^{\bullet-}$) and then to yellow (neutral perylene, **2**). It seems safe to conclude that electron transfer reactions among the species present in the solution at various stages allow interconversions between the radical anion and dianion of 1,1′-binaphthyl ($\mathbf{1}^{\bullet-} + e^- \leftrightarrows \mathbf{1}^{2-}$) and likewise between the radical anion and dianion of perylene ($\mathbf{2}^{\bullet-} + e^- \leftrightarrows \mathbf{2}^{2-}$).

In 1992, a careful NMR study of the closely related cyclization shown in Figure 3 was reported by Ayalon and Rabinovitz.[14] In this case, [5]helicene (**3**) was reduced independently with sodium metal and with lithium metal in THF-d_8 at −33 °C over periods of several days to give the dianion of benzo[*ghi*]perylene ($\mathbf{5}^{2-}$). Exposure of the final reaction mixture to oxygen gave the neutral hydrocarbon, benzo[*ghi*]perylene (**5**). By continuous NMR monitoring, the growth and disappearance of even-electron species could be observed; no ESR or UV−vis absorption spectra were reported. As the first paramagnetic species formed ($\mathbf{3}^{\bullet-}$), the NMR signals for **3** disappeared. Then, over time, the NMR signals for $\mathbf{4}^{2-}$ grew in; no signals were ever seen for the dianion of the open [5]helicene ($\mathbf{3}^{2-}$). After prolonged exposure of the solution to the alkali metal, the NMR spectrum of the dihydrobenzo[*ghi*]perylene dianion ($\mathbf{4}^{2-}$) was slowly replaced by that of the benzo[*ghi*]perylene dianion ($\mathbf{5}^{2-}$). This rearomatization step, in which two hydrogen atoms are lost, could be accelerated by warming the reaction mixture to 25−30 °C.

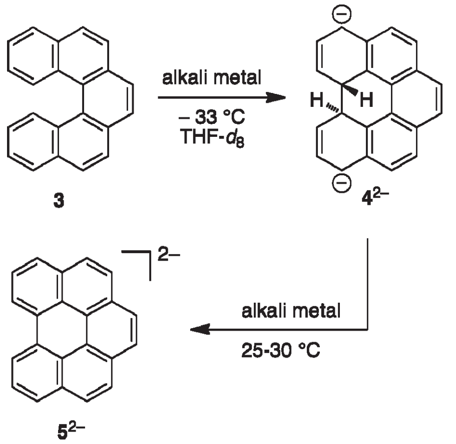

FIGURE 3. Anionic cyclodehydrogenation of [5]helicene (**3**) by alkali metals.[14]

Two important additional conclusions can be drawn from this report: (i) the two C−H bonds remain intact until after the C−C bond has been formed and two electrons have been added, and (ii) rearomatization by rupture of the two C−H bonds is slower than the initial cyclization (at least in this loaded case) but occurs under an inert atmosphere, before the solution is exposed to oxygen. Against this background, we now add our observations.

Results and Discussion

From the outset, we reasoned that this reaction should be conducted at elevated temperatures so that it could be pushed to completion in less than a day. We began by screening a few solvents, using both sodium metal and potassium metal. Owing to the high reactivity of alkali metals, only ethers, hydrocarbons, and tertiary amine solvents were examined. Thus, we heated 1,1′-binaphthyl (**1**) overnight in various solvents with excess metal and compared the yields of perylene (**2**) formed under the different conditions. Potassium metal in THF at 80 °C in a pressure vessel proved far superior to all of the other combinations examined (73% yield),[15] so we settled on potassium and THF as the metal and solvent for further studies. An operating temperature above the melting point of potassium metal (63 °C) in a pressure vessel with constant stirring ensures a large area of clean metal surface throughout the course of the reaction, and this undoubtedly contributes to the success of these conditions. On a small scale, the anionic products were oxidized to the neutral hydrocarbons by exposure to oxygen in the workup, but elemental iodine was used as the oxidizing agent for larger scale reactions.

With this basic protocol in hand, the optimization was then turned toward determining the minimum number of equivalents of potassium metal required to effect complete conversion. An excess of potassium metal (5 equiv)[16] was

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[13] Balk, P.; Hoijtink, G. J.; Schreurs, J. W. H. *Recl. Trav. Chim. Pays-Bas Belg.* **1957**, *76*, 813.

[14] Ayalon, A.; Rabinovitz, M. *Tetrahedron Lett.* **1992**, *33*, 2395.

[15] Other conditions examined (metal, solvent, temperature) all gave yields of 10% or less: (a) potassium, 1,2-dimethoxyethane, 80 °C; (b) potassium, diglyme, 80 °C; (c) potassium, toluene, 80 °C; (d) sodium, THF, 66 °C; (e) sodium, diglyme, 162 °C; (f) sodium, tetramethylethylenediamine (TMEDA), 120 °C; (g) sodium, toluene, 110 °C.

[16] The maximum amount of potassium that could be consumed in this reaction should be 4 equiv, even if all of the H_2 were reduced to KH.[17]

TABLE 1. Screening of Different Equivalents of Potassium Used to Cyclize 1,1′-Binaphthyl (1) to Perylene (2) at 85 °C in Tetrahydrofuran in a Pressure Vessel

equiv of potassium	time (d)	conversion (%)[a]
5.0	2	quant
3.0	2	quant
3.0	1	90−quant[b,d]
2.5	7	quant[b]
2.5	1	0−78[d]
2.2	7	quant
2.2	4	64−70[c,d]
2.0	3	58
1.8	5	58
1.8	4	48
1.0	6	28−40[d]
0.5	12	5
0.5	7	0

[a]Conversion based on NMR integration. [b]Quantitative yield isolated. [c]70% yield isolated. [d]Ranges resulting from multiple runs.

chosen as the starting point, and the stoichiometry was progressively adjusted. With 5 equiv of potassium metal in a pressure vessel at 85 °C in THF for 2 d, the cyclodehydrogenation of 1,1′-binaphthyl (**1**) to perylene (**2**) is remarkably clean and essentially quantitative; no starting material remains, and no other significant products are detected by NMR analysis of the crude material obtained after workup. Table 1 summarizes the results from lower amounts of potassium at various reaction times, all in THF at 85 °C in a pressure vessel.

We find that the conversion of **1** to **2** is still quantitative with 3 equiv of potassium after 2 d in THF at 85 °C. Shortening the reaction time to 1 d with 3 equiv of potassium still gives quantitative conversion most of the time, but small amounts of unconverted starting material were detected in some experiments run under these conditions. With lesser amounts of potassium (2.5 and 2.2 equiv), the conversion of **1** to **2** can still be pushed to completion after 7 d in THF at 85 °C in a pressure vessel, but the reaction is definitely slower than with 3 equiv of potassium under the same conditions.

Although fewer than 3 equiv of potassium may be impractical for this reaction, it is noteworthy that even 0.5 equiv of potassium metal is enough to produce small amounts (5%) of **2** from **1** at 85 °C in THF over a period of 12 d.

Finally, the temperature dependence of the reaction was investigated, all with 3 equiv of potassium metal in THF in a pressure vessel (Table 2). A temperature of 95 °C was found to be the most reliable for ensuring 100% conversion of **1** to **2** in 1 d, but the NMR spectrum of the crude product was not as clean as that from the 85 °C reactions. Like Solodovnikov et al., we see the cyclodehydrogenation occurring only relatively slowly at room temperature. The conditions we recommend as optimum for converting **1** to **2** are 3.0−3.5 equiv of potassium metal in THF in a pressure vessel at 85 °C for 12 h (see Experimental Section).

The mechanism by which 1,1′-binaphthyl (**1**) is converted into the dianion of perylene ($\mathbf{2}^{2-}$) by potassium metal requires two single-electron reductions, one C−C bond-forming step, two C−H bond-breaking steps, and a H−H bond-forming step. In principle, the two C−H bond-breaking steps and the H−H bond-forming step could all be concerted, but they may not be; the order of the steps has never been determined.

TABLE 2. Screening of Different Temperatures for Cyclization of 1,1′-Binaphthyl (1) Using 3 equiv of Potassium in Tetrahydrofuran

time (d)	temp (°C)	conversion (%)[a]
1	95[b]	quant
1	85[b]	90−quant
1	70[b]	45
1	55[b]	34
3	25	15
1	25	8

[a]Conversion based on NMR integration. [b]Reactions run in a pressure vessel.

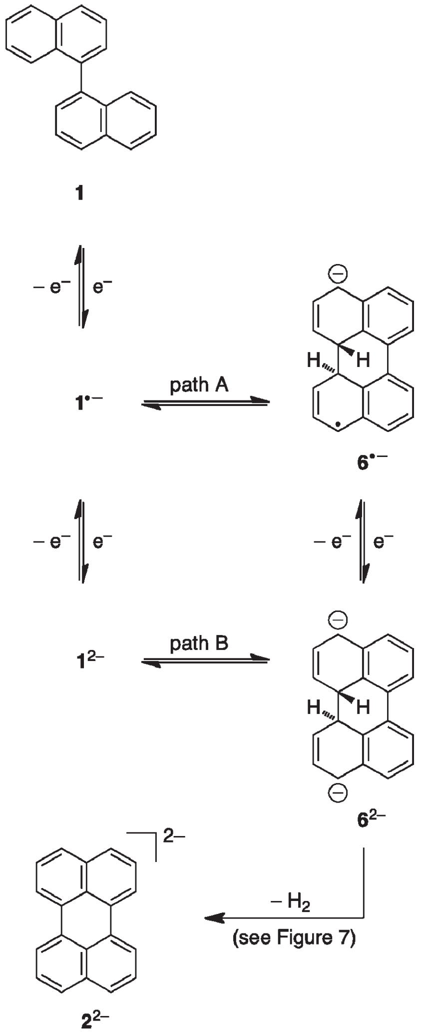

FIGURE 4. First steps in the mechanism of the anionic cyclodehydrogenation of 1,1′-binaphthyl (**1**) to perylene (**2**) by alkali metals.

One can safely assume that the first step is a single-electron reduction of **1** to produce the radical anion $\mathbf{1}^{\bullet-}$. This odd-electron intermediate might then close spontaneously to the dihydroperylene anion radical ($\mathbf{6}^{\bullet-}$), or it might live long enough to accept a second electron and get reduced to the dianion of 1,1′-binaphthyl ($\mathbf{1}^{2-}$). Cyclization of $\mathbf{1}^{2-}$ would give the dianion of dihydroperylene ($\mathbf{6}^{2-}$), whereas the same intermediate could be formed alternatively by single-electron reduction of $\mathbf{6}^{\bullet-}$ (Figure 4).

Whether the C−C bond forming step occurs at the anion radical stage (path A) or at the dianion stage (path B) is uncertain. Attempts to answer this question by molecular

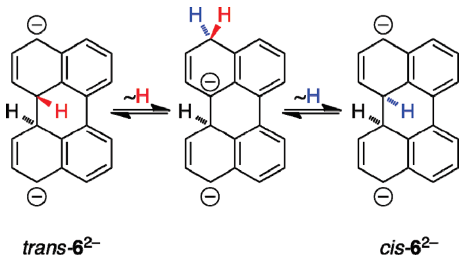

FIGURE 5. A plausible mechanism for the *trans*-to-*cis* isomerization of $\mathbf{6}^{2-}$ by two symmetry-allowed suprafacial [1,4]-shifts of hydrogen.

orbital calculations would likely be futile, because the partially solvated counterions in such species are bound to play a significant role that is difficult to model. Fortunately, from a broad perspective, the order of the steps for the second electron addition and the cyclization is relatively inconsequential. The fact that this reaction can be driven to 100% conversion does indicate, however, that the dianion of 1,1′-binaphthyl ($\mathbf{1}^{2-}$, presumed by Solodovnikov to be the red-wine colored species) cannot be a mechanistic dead end; if $\mathbf{1}^{2-}$ is unable to cyclize by path B, then it must be able to return to the radical anion $\mathbf{1}^{\bullet-}$ by donating one of its electrons to another species in solution and cyclize by path A. All of the electron transfer steps and the cyclization steps in Figure 4 should be reversible, and the intermediates in this manifold are removed irreversibly only after C−H bonds begin to be broken as $\mathbf{6}^{2-}$ goes to $\mathbf{2}^{2-}$.

The mechanism by which the cyclized dianion $\mathbf{6}^{2-}$ loses the two hydrogen atoms is more obscure. How and when is the new H−H bond formed? The direct observation of H_2 by Solodovnikov et al. proves that the two hydrogen atoms are lost as H_2 and not as 2 KH, but there is no evidence that the two hydrogen atoms in the observed H_2 both originated from the same molecule. Ayalon and Rabinovitz established that the hydrogen atoms on the newly joined carbon atoms are oriented *trans* with respect to one another;[14] thus, a concerted loss of H_2 from dianion $\mathbf{6}^{2-}$ appears geometrically impossible.

Figure 5 outlines a plausible pathway for the isomerization of *trans*-$\mathbf{6}^{2-}$ to *cis*-$\mathbf{6}^{2-}$ by two symmetry-allowed suprafacial [1,4]-shifts of hydrogen over the allylic anion moiety. A ${}_{\sigma}2_{s} + {}_{\sigma}2_{s}$ pericyclic loss of H_2 from *cis*-$\mathbf{6}^{2-}$ is symmetry-forbidden in the ground state, however, because the HOMO of the perylene dianion is symmetric with respect to the plane between the two carbon atoms from which the hydrogens are lost (Figure 6).

We propose a radical chain mechanism involving free hydrogen atoms (H$^{\bullet}$) to account for conversion of the cyclized dianion $\mathbf{6}^{2-}$ to H_2 and the perylene dianion ($\mathbf{2}^{2-}$). Figure 7 depicts the two steps of our proposed propagation cycle. Thus, abstraction of a hydrogen atom from $\mathbf{6}^{2-}$ by a free hydrogen atom (H$^{\bullet}$) would result in the formation of a very strong H−H bond (104 kcal/mol) and the rearomatization of one of the benzene rings at the expense of a very weak C−H bond (tertiary and conjugated with a very electron-rich π-system). This step should be strongly exothermic. Subsequent rearomatization of the other benzene ring by homolysis of the second (now even weaker) C−H bond would deliver the final product ($\mathbf{2}^{2-}$) and release a new hydrogen atom (H$^{\bullet}$) to carry on the next cycle.

At first, we did not entertain any mechanisms involving free hydrogen atoms (H$^{\bullet}$), because we assumed that such a reactive species would simply abstract an α-hydrogen from THF. On further consideration, however, we realized that even the great abundance of THF is probably not enough to overcome the far greater hydrogen donor ability expected for $\mathbf{6}^{2-}$. Furthermore, the THF α-radical, if formed, could likewise abstract a hydrogen atom from $\mathbf{6}^{2-}$ and thereby carry on the chain reaction. As with all radical chain reactions, chain termination would result only from infrequent radical−radical encounters.

Initiation of this chain reaction requires a source of either free hydrogen atoms (H$^{\bullet}$) or the other chain-carrying intermediate ($\mathbf{7}^{\bullet 2-}$). One source of these initiators could be the thermal homolysis of one of the very weak C−H bonds in $\mathbf{6}^{2-}$, a process that would actually give both $\mathbf{7}^{\bullet 2-}$ and a free hydrogen atom (H$^{\bullet}$), thereby initiating two independent chain reactions simultaneously.

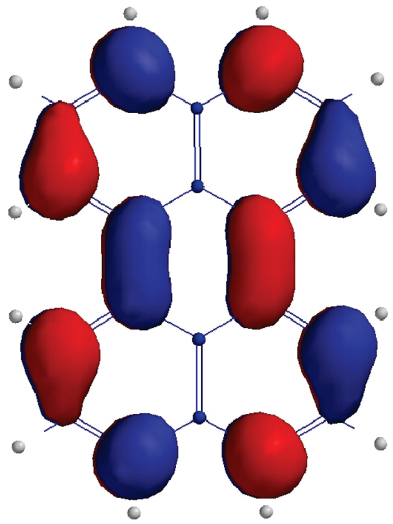

FIGURE 6. Highest occupied molecular orbital (HOMO, B3LYP/6-31G*) of perylene dianion ($\mathbf{2}^{2-}$).

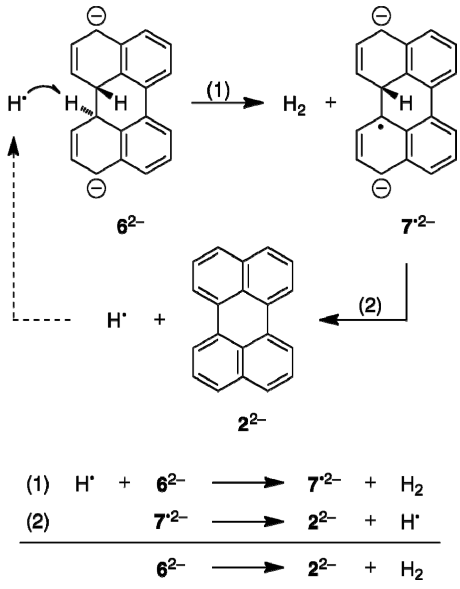

FIGURE 7. Two-step propagation cycle in the proposed radical chain mechanism for conversion of the dihydroperylene dianion ($\mathbf{6}^{2-}$) to the perylene dianion ($\mathbf{2}^{2-}$) and H_2.

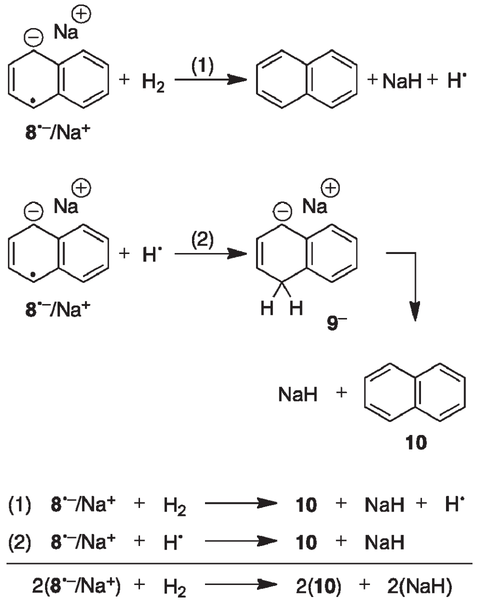

FIGURE 8. Published mechanism for the reduction of H_2 to NaH by sodium naphthalenide.[17]

Once the first H_2 is formed, more free hydrogen atoms ($H^\bullet$) will be generated in this reaction mixture from a background reaction that must also be mentioned. For many decades, it has been known that the radical anions of aromatic hydrocarbons can slowly reduce H_2 (e.g., sodium naphthaleninde + $^1/_2H_2 \rightarrow$ naphthalene + NaH).[17] The mechanism for this reaction has been studied, and the intermediacy of anion $\mathbf{9}^-$ has been verified experimentally (Figure 8).[17] Presumably, many of the anionic species present in the cyclization of **1** to $\mathbf{2}^{2-}$ are also capable of reducing H_2, and that background reaction could provide another source of free hydrogen atoms ($H^\bullet$) to initiate the radical chain reaction we have proposed.

The operation of this background reaction can also explain why the yield of H_2 reported by Solodovnikov et al. never equaled the yield of perylene; as perylene and H_2 were being formed in their experiments, the amount of H_2 was concurrently being depleted by reduction to KH throughout the course of the reaction. The fact that the H_2 level rises continuously during this reaction (Figure 2), however, indicates that the reduction of H_2 is slow compared to the rate of cyclization and rearomatization. It is intriguing to note that H_2 is serving as an oxidizing agent in this transformation.

If the reduction of H_2 were fast compared to the rate of cyclization and rearomatization, then H_2 would not accumulate, and the overall stoichiometry for the cyclodehydrogenation would be

$$4K + \mathbf{1} \rightarrow \mathbf{2}^{2-}/2K^+ + 2KH$$

We have found that 2.2 equiv of potassium metal is sufficient to drive the formation of perylene to completion (Table 1), and this would not be possible if a 4:1 stoichiometry were required.

How does our mechanistic proposal account for the observation by Solodovnikov et al. that the yield of perylene after 3 d at room temperature drops from 39% to only 10% if the potassium is removed from the reaction mixture by filtration after the first hour? According to Solodovnikov's ESR spectrum, the concentration of the initial radical anion ($\mathbf{1}^{\bullet-}$, although possibly already closed, $\mathbf{6}^{\bullet-}$) had reached its maximum when the potassium was removed. Before any C−H bonds could be broken, however, the radical anion would need to have been converted to $\mathbf{6}^{2-}$ by acquiring a second electron. In the absence of potassium metal, generation of dianions $\mathbf{1}^{2-}$ and $\mathbf{6}^{2-}$ could be accomplished by disproportionation of either $\mathbf{1}^{\bullet-}$ or $\mathbf{6}^{\bullet-}$, and the loss of H_2 would then produce perylene dianion ($\mathbf{2}^{2-}$). Conversely, if the solution were still in contact with potassium metal, all of the starting material would automatically be reduced to the closed dianion ($\mathbf{6}^{2-}$) by the potassium, thereby accelerating perylene production, which would then not be dependent on disproportionation reactions of radical anions to generate the pivotal intermediate $\mathbf{6}^{2-}$.

Similar arguments can account for our observation that 1,1′-binaphthyl (**1**) can be cyclized to perylene (**2**) even with as little as 0.5 equiv of potassium metal, albeit only in low conversion at elevated temperatures over many days (Table 1).

One final comment is in order concerning the hydrogen-abstracting ability of the anionic species involved in this reaction. When the reactions are run in dry THF under a nitrogen atmosphere and are then quenched with either dry oxygen or iodine, we obtain essentially no Birch reduction products. On the other hand, in reaction mixtures that come into contact with an adventitious proton source prior to completion of the oxidation, we see varying amounts of 3,4-dihydro-1,1′-binaphthyl (**11**),[18] unless the starting material has been converted entirely to perylene dianion ($\mathbf{2}^{2-}$). Mass spectral analysis of the **11** obtained from a reduction of 1,1′-binaphthyl (**1**) run in THF-d_8 showed no evidence for any deuterium in the **11**, so none of the organic intermediates involved are capable of abstracting hydrogens, either as protons or as hydrogen atoms, from THF.

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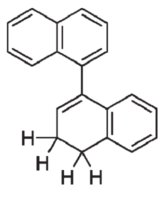

Conclusions

Oxidative cyclization of 1,1′-binaphthyl (**1**) to perylene (**2**) can be achieved in essentially quantitative yield by heating **1** with three or more equivalents of potassium metal in THF at 85 °C in a pressure vessel overnight. The reaction can be driven to completion at the same temperature with as little as 2.2 equiv of potassium, but it then requires much longer times (4−7 days). The use of sodium or potassium in various other solvents proved inferior. An overall reaction mechanism is proposed that accounts for all of the experimental observations reported by Solodovnikov et al., by Ayalon and Rabinovitz, and from this study. The *trans*-dihydroperylene

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[17] Bank, S.; Lois, T. A.; Prislopski, M. C. *J. Am. Chem. Soc.* **1969**, *91*, 5407 and references therein.

[18] Dal Zotto, C.; Wehbe, J.; Virieux, D.; Campagne, J.-M. *Synlett* **2008**, 2033.

dianion (**6^{2-}**) is believed to be the pivotal intermediate from which H_2 is lost. A radical chain reaction involving free hydrogen atoms ($H^•$) in the two-step propagation cycle is proposed to account for the formation of H_2 from **6^{2-}**. Anionic cyclodehydrogenations of the sort investigated here are complementary to those performed under strongly acidic/oxidizing conditions, photochemically, or thermally (flash vacuum pyrolysis). It is our hope that a better understanding of anionic cyclodehydrogenations such as this one will encourage their wider use in organic synthesis.

Experimental Section

General. The tetrahydrofuran (THF) used in this reaction was dispensed from a Glass Contour solvent purification system. ^1H NMR spectra were recorded in $CDCl_3$ on a 500 MHz instrument. **CAUTION:** Glass encased magnetic stirbars should be used for all reactions involving potassium metal; potassium reacts with standard Teflon-coated stirbars to produce KF and highly reactive carbon as a finely divided black powder that, in one instance, upon exposure to oxygen, resulted in a vigorous explosion.

Perylene (2) from Binaphthyl (1) by the Action of Potassium Metal. To a flame-dried and nitrogen-flushed 350-mL pressure vessel equipped with a glass-encased magnetic stirbar[19] was added dry tetrahydrofuran (THF, 250 mL) and 1,1′-binaphthyl (**1**) (221 mg, 0.87 mmol). The solvent was degassed for 15 min while a freshly cut piece of potassium metal[20] (108 mg, 2.77 mmol) was rinsed with hexanes and THF and then added to the reaction mixture. The vessel was sealed and heated in an oil bath to 85 °C; the mixture turned dark purple within 2 h. After 12 h at 85 °C, the reaction mixture was allowed to cool to room temperature, and the solution was removed from the remaining potassium by vacuum cannulation into a flame-dried flask under a nitrogen atmosphere. The pressure vessel was washed with some dry THF, and the solution again was removed by vacuum cannulation. The dark purple to blue solution was quenched by adding a solution of iodine (560 mg, 4.41 mmol) in ~6 mL of dry THF over a period of 15 min, which caused the solution to turn yellow and then dark red. To the solution was then added slowly ethanol (5 mL) followed by sodium thiosulfate (10% in water, ~50 mL) until the color no longer changed (typically a yellow solution). The reaction was then exposed to air, and the organic solvents were removed on a rotary evaporator. To the remaining aqueous solution containing precipitates was added dichloromethane (DCM, 100 mL), and the aqueous layer was extracted 3 times. The combined organic layers were washed with brine and dried over $MgSO_4$, and the solvent was removed on a rotary evaporator. The residue was adsorbed onto silica, and the mixture was subjected to flash column chromatography (SiO_2, 1:15 DCM/hexanes) yielding 219 mg (quantitative) of **2** as a yellow solid. The ^1H NMR spectrum matched that obtained from authentic perylene, with no more than traces of impurities (< 5%). To the residues in the pressure vessel was added THF (50 mL), and any remaining potassium was slowly quenched by the slow addition of EtOH and then water.

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(19) Note the CAUTION in the General Section.

(20) Not cleanly cutting all sides of the potassium piece generally leads to a significant drop in yield.