

# Oxidative Electrocyclization of Diradicaloids: C–C Bonds for Free or How to Use Biradical Character for $\pi$ -Extension

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**ABSTRACT:** Herein, we show that biradical character and appropriate distribution of spin density can be used for synthetic purposes. We demonstrate the rational domino annulation that includes dehydrative  $\pi$ -extension (DPEX) as the initiation step and subsequent oxidative electrocyclizations (EC) promoted by favorable localization of the unpaired electrons enabling up to four C–C bonds formed during the reaction. Contradicting to the Woodward–Hoffmann rules, the reaction proceeds at room temperature, whereas termination occurs when biradical character vanishes.

**C** ynthesis of polycyclic aromatic compounds has become One of the most relevant branches in modern materials science.<sup>1,2</sup> The possibility to manage the physical properties through the size, shape, and edge topology<sup>3</sup> allows the design of materials for a wide variety of optoelectronic applications.<sup>4–11</sup> C–C bond formation techniques serve as the main tools in the bottom-up construction of the desired materials with atomical precision. It is, therefore, crucial to develop new synthetic tools and to broaden the scope of the existing methods such as annulative  $\pi$ -extension (APEX),<sup>12,13</sup> Scholl reaction, alkyne annulation,<sup>14,15</sup> aryne trimerizations,<sup>16</sup> palla-dium-catalyzed reactions,<sup>17,18</sup> etc. To achieve this goal, it is vital to understand how different substrates behave upon exposure to different reaction conditions. However, it can be not as trivial as it seems. Among vivid examples demonstrating this fact is the Scholl reaction, which has been known for over 100 years, and despite comprehensive studies by Müllen et al.<sup>19</sup> this transformation continues to reveal new examples of intricate transformations.<sup>20–22</sup>

Recently, we have contributed to the field by developing the dehydrative  $\pi$ -extension (DPEX) reaction.<sup>6,23</sup> Ambient conditions and the simplicity of the protocol provide rapid access toward polycyclic aromatic hydrocarbons (PAHs) and nanographenes with zigzag edges and high biradical character. The latter leads to low chemical stability, as open-shell systems tend to undergo uncontrollable oligomerization in solution.<sup>24,25</sup> It is, indeed, a complicated task to gain control over the reactivity of such species.<sup>26,27</sup>

However, as we envision, if the radicals are localized in the "right" places, this tendency can be used to promote intramolecular processes. Among them is  $6\pi$ -electrocyclization,

a subclass of pericyclic reactions that play an important role in both synthetic and theoretical chemistry.<sup>28–30</sup> According to Woodward–Hoffmann rules, this reaction can proceed through photochemical or thermal activation.<sup>31</sup> The second often requires extremely high temperatures, particularly in the case of unactivated hexatrienes.<sup>32</sup> Unlike them, open-shell structures play by different rules. They undergo thermal electrocyclization at ambient temperatures. This is connected with low HOMO–LUMO gaps resulting in the partial occupation of HOMO and LUMO in the ground state.

This transformation represents a challenge for chemists due to the overall complexity of pristine biradicals' synthesis and poor control over degradation pathways that unstable diradicaloids undergo. Several recent reports have studied the mechanistic aspects of  $6\pi$ -electrocyclization of phenalenylbased diradicaloids.<sup>33–37</sup> Despite valuable insights, the mechanism of the reaction remains not fully understood.<sup>38</sup> While these works have been foreshadowing new synthetic methods to be developed, to the best of our knowledge there are no direct synthetic applications that emerged from the area.

Herein, we demonstrate such a synthetic application exploiting DPEX and the Clar model for effective cascade reactions. Thus, the DPEX reaction can generate biradical moieties suitable for the "forbidden"  $6\pi$ -electrocyclization.

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Meanwhile, the precursor design can be rationalized by using the Clar model, which can predict the favored position of the radicals and explain the outcome of the reaction. This reasoning is also supported by the fractional occupation number weighted electron density (FOD) analysis and DFTcalculated energy barriers. From a synthetic standpoint, this domino reaction gives rapid access to violanthrenes and  $\pi$ extended 5-helicenes unavailable via alternative methods.

The concept of the domino annulation is shown in Figure 1. The intermediate obtained after DPEX can be represented via



Figure 1. Concept of the report illustrated by the example of violanthrene (1) synthesis.

three isomeric structures (1-*trans*, D1, and 1-*cis*). D1 has several resonance forms, the most stable of which are depicted in Figure 1. As it will be shown later, the efficiency of intramolecular electrocyclization at room temperature correlates with the stability of the resonance form having radical centers localized on carbon atoms directly participating in the new bond formation. The respective resonance forms are indicated as the Most Contributing Resonance Structure (MCRS).

We have initiated our studies with three simplest model intermediates (obtained from P1, P1a, and P2) containing two interconnected benzophenalenyls, i.e., the smallest fragments which can be constructed via the DPEX reaction. This choice is also justified by similarities to the previously studied phenalenyl fragments.<sup>34,35</sup>

The syntheses of the symmetric precursors P1 and P1a were performed in two steps including mono-Suzuki reaction and subsequent dimerization via Miyaura conditions in the presence of strong base.<sup>39</sup> The asymmetric P2 was obtained via a three-step procedure (see the Supporting Information (SI)). The diradicaloids were generated under conditions of DPEX reaction. For simplicity, only MCRSs of the respective diradicaloids (RS1, RS1a, and RS2) are shown in Figure 2. In the case of P1 and P2, the initiation step was followed by in situ electrocyclization and oxidation yielding violanthrene (1) and isoviolanthrene (2) as main products, respectively. Noteworthy, no traces of 1 were found in the case of P1a (inseparable mixture of different products was formed).

This outcome can be explained via simple qualitative reasoning.<sup>40</sup> To achieve higher efficiency, it is desirable to



**Figure 2.** Domino reaction including DPEX as the initiation step and subsequent oxidative electrocyclization of diradicaloids. Reaction conditions: SnCl<sub>2</sub>/*i*-PrOH, H<sub>2</sub>SO<sub>4</sub>, DCM, room temperature, overnight.

have unpaired electrons localized on the corresponding carbon atoms (Figure 2).

Despite several possible resonance forms, it is the form containing the biggest number of Clar's sextets (CS) that mainly contributes to the preferred positions of radicals. Thus, it can be seen from Figure 2 that the more sextets that are involved in the MCRS, the better the yields that are achieved. Therefore, P2 represents the best precursor in this series as it has four sextets in the MCRS. However, even in this case, the unpaired electrons are significantly delocalized (Figure 1). To address the issue, we have designed the precursor P3 that gives diradicaloid RS3 in which spin density is concentrated on the "correct" carbon atoms. Therefore, the yield of the domino reaction increases to 76%. An intriguing aspect of this transformation is that it terminates at the  $\pi$ -extended 5-helicene 3 due to the formation of the closed-shell system.

To investigate whether the approach can be extrapolated to induce longer domino reactions we have prepared precursor P4 which gives diradicaloid 4a (Figure 3). Oxidative electrocyclization of 4a leads to diradicaloid 4b, which finally transforms into tetrabenzobisanthrene (TBBA, 4). Thus, this cascade enables the transformation of the linear oligophenylene P4 into  $\pi$ -extended helicene TBBA in 60% yield, which corresponds to 88% per C–C bond.

Although it has been recently shown that bulky substituents can prevent TBBA from the cyclization under Scholl conditions,<sup>41</sup> pristine molecules bearing a *fjord*-region cannot be obtained via this reaction. Contrary to hexabenzocoronene,<sup>42</sup> the distortion in **4** caused by the helical moiety enhances solubility and allows not only measurement of the



Figure 3. Synthesis and characterization of TBBA: (a) Domino reaction including DPEX and two subsequent oxidative electrocyclizations. (b) UV-vis spectrum of TBBA in toluene. (c) DFT-calculated structure of TBBA. (d) Comparison of DFT-calculated and recorded (300 MHz,  $C_2D_2Cl_4$ ) <sup>1</sup>H NMR spectrum of TBBA. The calculated spectrum was scaled by a factor of 0.88. The assignment of signals is based on DFT.

UV-vis spectrum but also recording of the <sup>1</sup>H NMR spectrum (Figure 3).

To support our qualitative model, we have performed DFT calculations investigating the electronic structures and the transformations of the diradicaloids RS1a, RS1, RS2, and RS3 (computation details can be found in the SI). The distributions of the biradical density obtained from the FOD analysis (Table 1) are in perfect agreement with the prediction based on the Clar model (Figure 2). The applicability of the FOD analysis and its comparison with other alternative methods have been discussed previously.<sup>23,43</sup> Based on the data for RS1, RS1a, and RS2, a strong correlation between N FOD, biradical character  $y_{1}^{44}$  the reaction barrier, and the length of the forming C–C bond in transition states can be noticed. This observation can be interpreted as follows: a higher biradical character (measured as y or N FOD) induces an earlier TS and therefore a lower barrier. Although this trend fits for RS1, RS1a, and RS2, the larger systems (RS3, 4a, 4b) are significantly more complex, e.g., chemically irrelevant lengths of the C-C contacts in the corresponding TSs were found. Recent work of Juriček et al.<sup>36</sup> demonstrates that even CASSCF treatment of such diradicaloid reactions does not provide barriers quantitatively comparable with the experimental results. Thus, despite all the efforts applied to the investigation of the electronic structures and qualitative agreement with the experimentally obtained yields, the presented results should be taken as a semiquantitative evaluation.

In summary, we present how DPEX together with a simple empirical model provides rapid access to intricate PAHs. While DPEX enables the effective generation of diradicaloid intermediates, the Clar model allows the rational design of the domino reaction enabling up to four C–C bonds formed in one step.

Table 1. Plots of the FOD Density ( $\sigma = 0.01 \text{ e/bohr}^3$ ) of Diradicaloids, Their Biradical Characters, Barriers of Electrocyclization, and Length of C–C Bonds in Transition States



## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01717.

Details of the synthetic procedures, DFT calculations, copies of NMR, mass, UV-vis, and HPLC chromatograms (PDF)

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