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Nucleophilic Addition to Singlet Diradicals: Heterosymmetric Diradicals

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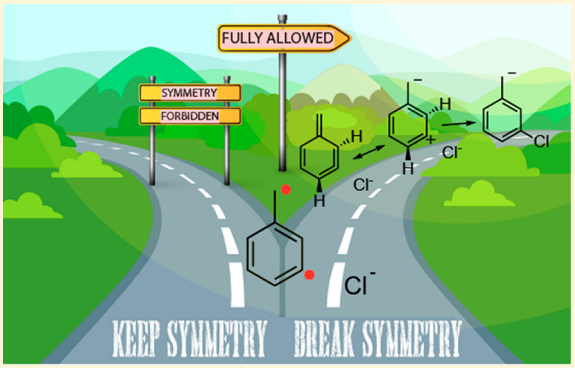
Supporting Information

ABSTRACT: In the preceding paper, we examined the addition of nucleophiles to homosymmetric diradicals and showed that the reaction occurs with no symmetry restrictions or other electronic impediments. In this work, we examine the addition of nucleophiles to heterosymmetric diradicals, by using the addition of chloride to *m*-dehydrotoluene as a case study. Using CASPT2 and density functional theory calculations, we show that the addition of chloride to *m*-dehydrotoluene is predicted to be barrierless at the asymptotic limit if C_s symmetry is broken, and the reaction is allowed to proceed through a nonplanar geometry. A nonplanar cyclic allene acts as the transitioning structure between open-shell and closed-shell species for the addition of chloride, with a continuous and smooth changing of the wave function by the evolution of orbital and configuration interaction coefficients, such that there is no abrupt switch from diradical to closed-shell species along the reaction coordinate. The overall conclusion from our analysis is that both homosymmetric and heterosymmetric diradicals can undergo reaction with closed-shell reagents without a barrier, and one cannot rule out the direct addition of nucleophiles to diradicals when considering the reaction mechanism.



INTRODUCTION

In the preceding paper, we provided a first-principles, theoretical description of the addition nucleophiles to *homosymmetric diradicals*, those diradicals where the nonbonding atomic orbitals are related by an element of symmetry.[1] The theoretical model presented explains how the wave function transitions from the open-shell diradical to the closed-shell phenyl anion upon addition of the nucleophile. By using multiconfiguration and spin-flip calculations, we were able to show that the change from diradical to closed-shell occurs continuously, with no obvious transition between the electronic structures, and that the addition of chloride occurs without an activation barrier. This approach accounts for the observed reactivity of diradicals such as *meta*-[2,3] and *para*-benzyne,[4] which have been found to undergo addition reactions with nucleophiles.

Whereas the addition of a nucleophile to a homosymmetric diradical is relatively straightforward, nucleophilic addition to a "heterosymmetric" diradical is more complicated. In the Salem and Rowland formulation,[1] a heterosymmetric diradical is a diradical in which the nonbonding atomic or molecular orbitals, φ_1 and φ_2, have different symmetry and therefore cannot mix. In these diradicals, the ground-state electronic structures of the triplet and singlet are the open-shell states, $\phi_1^1\phi_1^1$, and the closed-shell wave functions, such as $\lambda\phi_1^2 - \sqrt{1-\lambda^2}\,\phi_2^2$, are higher in energy than the open-shell state. However, the closed-shell state is preferred for the product after addition of the nucleophile. Therefore, the previous analysis describing the transformation of the wave function by variation of the coefficients in the MCSCF wave function does not apply to heterosymmetric diradicals because there needs to be a fundamental change in the nature of the wave function.

Nonetheless, nucleophilic addition to heterosymmetric $\sigma\pi$ diradicals has been proposed. For example, Myers and co-workers[5,6] found that α,3-dehydrotoluene formed in the cyclization of (*Z*)-hepta-1,2,4-trien-6-yne reacts with methanol by both hydrogen atom abstraction and nucleophilic addition and proposed the reaction pathways shown in Scheme 1.

They attributed the nucleophilic addition product to reactivity of a zwitterionic structure, **1z**, that contributes to the overall diradical electronic structure, whereas the hydrogen abstraction product was presumed to be formed from the covalent diradical structure, **1d**. Similar reactivity has been observed for α,3-dehydrotoluene formed photochemically from a chlorobenzylsilane prescursor.[7] More recently, Winter and co-workers[8] found phenyloxenium ion, an open-shell singlet, σ,π diradical, reacts as an electrophile with selected nucleophiles (Scheme 2) instead of undergoing the radical reactivity expected for an analogous triplet diradical.

In this paper, we consider the reaction of nucleophilic addition to a σ,π diradical. Our approach is similar to that in

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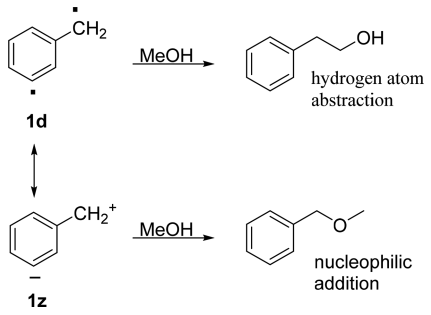
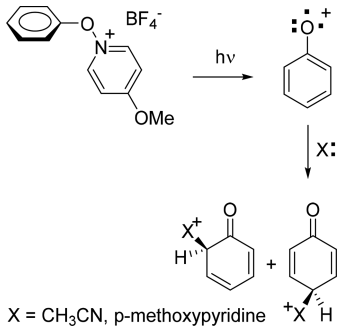
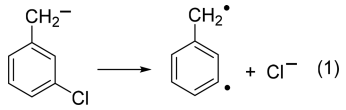
Scheme 1



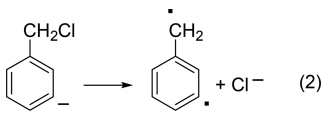
Scheme 2



the previous paper,[9] and we consider the dissociation of 3-chlorobenzyl anion (eq 1) to form α,3-dehydrotoluene, an



open-shell singlet diradical with a singlet−triplet splitting of approximately 2 kcal/mol.[10]This reaction has been studied experimentally by Squires and co-workers,[10,11] who used the measured dissociation energy to determine the enthalpy of formation of the diradical. However, an important assumption required in order to make this measurement is that the dissociation occurs without a barrier in excess of the dissociation limit. Similarly, the α,3-dehydrotoluene could be formed by elimination of the 3-chloromethylphenyl anion (eq 2).



A qualitative correlation diagram for the dissociation of 3-chlorobenzyl anion, restricted to C_s geometry, is shown in Figure 1. The π^2 electronic structure preferred for the benzylic anion correlates with the highest energy electronic state of the diradical.[11] In contrast, the $^1\sigma\pi$ ground state of the diradical correlates to an excited state in the benzylic anion, such that formation of the diradical from the anion requires a symmetry-forbidden surface crossing. In the original study, Squires and co-workers argued that the formally symmetry-forbidden transition from the closed-shell electronic structure of the benzyl anion to the diradical can occur through nonplanar dissociation trajectories,[11] which results in σ,π-mixing. This hypothesis is consistent with the analysis of Michl and co-workers, who examined the effects of a point-charge

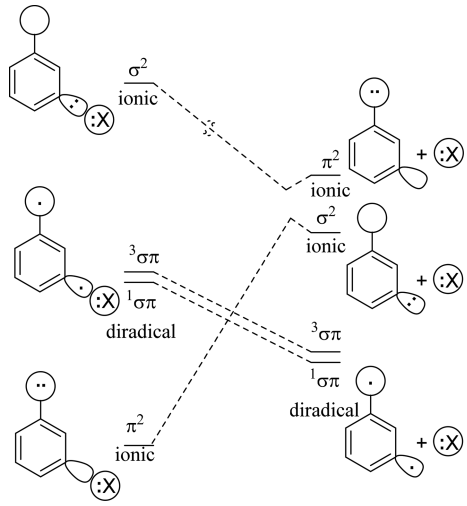


Figure 1. Symmetry correlation diagram for the reaction of a nucleophile with a heterosymmetric α,3-dehydrotoluene diradical. The transition between the closed-shell states occurs via an avoided crossing.

perturbation on relative singlet-state energies in ethylene as a function of geometry, showing a continuous transition from the (planar) closed-shell to (twisted) open-shell electronic structure.

We now consider the reaction in light of our previous study on the addition of chloride to *p*-benzyne. The conclusion of that work is that the approaching nucleophile polarizes the diradical, introducing of zwitterionic character into the wave function,[1] which allows for the addition of the nucleophile. This approach works for homosymmetric diradicals, where open- and closed-shell configurations can mix because of symmetry. However, for a polarized heterosymmetric diradical, if the perturbation does not break the element of symmetry that separates the nonbonding orbitals, then the electronic states remain either purely closed-shell (ionic) or purely open-shell (covalent).[1] In this respect, the nucleophilic addition to heterosymmetric diradicals is more similar to the reaction of nucleophiles to radicals.[12−15] Thus, in order to get the closed-shell and open-shell configurations to mix, it is necessary to break the symmetry of the system.[16−22] For the reaction of α,3-dehydrotoluene with a nucleophile, that involves nonplanarity.

In this work, we have examined the dissociation of 3-chlorobenzyl anion (or, conversely, the addition of chloride to the 3-position in α,3-dehydrotoluene) by considering planar and nonplanar reaction pathways. As expected, the closed-shell and open-shell states are distinct at planar geometries, but they mix when the system is allowed to adopt nonplanar geometries. By considering the relative weights of closed-shell and open-shell configurations in the wave function, it is shown that there is a continuous transition from a closed-shell to open-shell wave function when proceeding through a nonplanar geometry, similar to what was found for nucleophilic addition to *p*-benzyne. The reaction is also similar to that with *p*-benzyne in that the addition occurs without an energy barrier.

■ COMPUTATIONAL METHODS

In this work, we have calculated the energy for dissociation of 3-chlorobenzyl anion to α,3-dehydrotoluene by using the state-averaged (SA)-CASSCF approach, as we did for formation of *p*-benzyne.[9] A relaxed scan of the C−Cl coordinate of the *m*-chlorobenzyl anion was conducted using a CASPT2//CASSCF procedure. Specifically, a relaxed potential energy surface scan of the C−Cl coordinate was

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conducted for both the $^1A'$ state and $^1A''$ state of the *m*-chlorobenzyl anion, restricted to C_s symmetry, at the SA-CASSCF(14,12)/aug-cc-pVTZ level using the MOLCAS 8.2 software package.[23] CASPT2-(14,12)/aug-cc-pVTZ single points were conducted at the CASSCF geometries to capture dynamical correlation. The active space included all the benzene π electrons and π orbitals, the lone pair anion electrons and orbitals, as well as the σ and σ^* C−Cl electrons. Four additional electrons and three a′ σ orbitals were added to the active space for a total of 14 electrons in 12 orbitals (4 a′ and 8 a″). For the nonplanar geometries, the geometry optimization was conducted using the SA-CASSCF(12,10)/cc-pVDZ level of theory, giving a 1:1 weighting to the two lowest energy roots. Single-point energies were conducted at these geometries at the CASPT2(14,12)/aug-cc-pVTZ level of theory using the SA-CASSCF reference. Analysis of diradical character was carried out by comparing weights of the closed-shell and open-shell configurations in the SA-MCSCF wave function, as described in the previous paper.[9]

UB3LYP. As in the study of the reaction of *p*-benzyne, the potential energy surfaces were also calculated by using an unrestricted singlet calculation, at the B3LYP/6-31+G* level of theory to get the "half-and-half" state. This approach is better suited for heterosymmetric diradicals, such as the dehydrotoluenes, because the open-shell singlet and triplet states are very similar in geometry and in energy.[11] Therefore, errors due to geometry differences and spin-contamination are minimal. The resulting value of $\langle S^2 \rangle$ is very close to 1 for the half-and-half state, consistent with the singlet being a pure diradical.

RESULTS AND DISCUSSION

The relative energies for the dissociation of 3-chlorobenzyl anion to form the singlet α,3-dehydrotoluene diradical, calculated at the CASPT2 level, are shown in Figure 2. There are

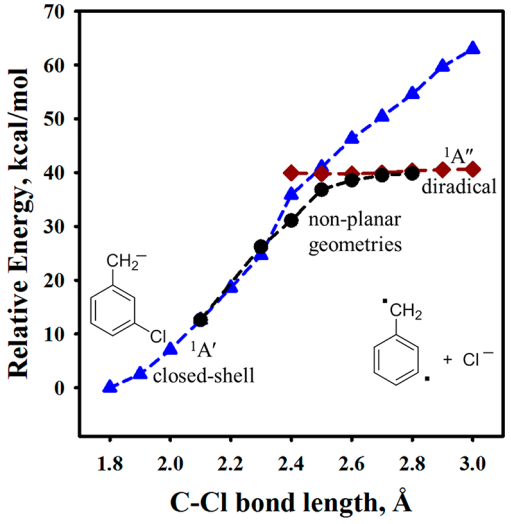

Figure 2. Potential energy plots for the dissociation of 3-chlorobenzyl anion, calculated at the CASPT2(14,12)/aug-cc-pVTZ level of theory. The blue triangles and red diamonds are the energies of the planar $^1A'$ (closed-shell) and $^1A''$ (diradical) states, respectively. The black circles are the energies for nonplanar geometries.

three curves shown in the figure. The blue diamonds show the energies of the planar, closed-shell state, π^2 state. At short bond distances, this is the ground state of the system, corresponding to the chlorobenzyl anion. At a long C−Cl distance, the energy of the π^2 state increases significantly, and the lowest energy state is the singlet diradical, $\sigma\pi$ state, shown as red diamonds in Figure 2.

Although the energy of the $\sigma\pi$ state is essentially constant over the bond lengths considered, there is, in fact, a shallow minimum near 2.6 Å, which likely results from electrostatic interaction between the halide and diradical. Below 2.3 Å, there is a dramatic change in the energy for the corresponding root in the MCSCF calculation, which results from variational collapse,[24] where the wave function consists of a benzylic radical with the extra electron in a highly diffuse orbital in the augmented basis set. This state is not a reliable electronic state,[24] and its presence likely indicates that this electronic state undergoes autodetachment at these geometries. The energy of the system at the adiabatic dissociation limit, ≈40 kcal/mol, is slightly higher than the reported experimental value of 34.2 ± 2.8 kcal/mol.[11]

As shown in Figure 2, the transition from diradical to closed-shell occurs via nonplanar geometries. At a short C−Cl distance, the structure is basically planar, and the energy is the same as that of the planar, closed-shell $^1A'$ state. At 2.7 Å and above, the energy of the nonplanar system is essentially the same as that for the planar diradical. Again, this is not surprising considering the geometry, which consists of a nearly planar α,3-dehydrotoluene ring, with the chloride only about 5° out of planarity.

Near the crossing point, however, the nonplanarity of the system is more pronounced. An image of the calculated geometry with a C−Cl distance of 2.4 Å is shown at the top of Figure 3.

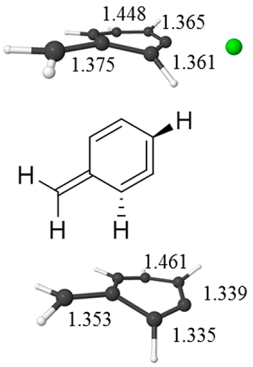

Figure 3. Nonplanar geometry calculated for 3-chlorobenzyl anion (top), with a C−Cl bond distance of 2.4 Å, with a comparison to the allenic structure, optimized at the B3LYP/6-311+G** level of theory (bottom). Lengths of representative bonds, in Å, are provided for comparison.

The largest distortion is found for the ring itself, where carbons are in the range of 8−10° out of planarity, and the hydrogens at positions 2 and 4 make a dihedral angle of about 65°. Considering the dihedral bond angles and the bond lengths, the geometry of the dehydrotoluene at this point resembles that of the allenic structure.

A simple calculated geometry of the allenic structure of α,3-dehydrotoluene (RB3LYP/6-311+G**) is also shown in Figure 3 for comparison, which shows that the geometry distortions in the dissociating benzyl anion are similar to those in the allenic structure, just not to the same extent. In the allene, the ring distorts to more like 10−20° out of planarity, and the allenic hydrogens make a dihedral angle close to 90°. Thus, the mixing of the two states occurs through a relatively minor geometry distortion near the crossing of the two surfaces, where the states are degenerate. Mixing is maximized when states are nearly degenerate, and so only small geometrical perturbations may be needed.[25,26] In itself, the distorted geometry of the dehydrotoluene is higher in energy than the

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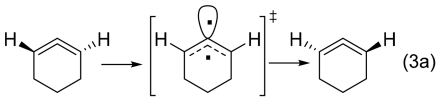
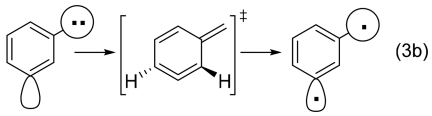
J. Org. Chem. 2018, 83, 12397−12403

planar state, and so the nonplanar distortion does cause the energy of the system to increase. However, that energy increase is offset by the bonding interaction that occurs with the approaching nucleophile that would not be possible for the planar diradical. Because of the bonding that occurs, the energy of the system in the transition region is lower than that at the dissociation asymptote.

The similarity between the geometries in Figure 3 provides a convenient physical picture for understanding the dissociation of the 3-chlorobenzyl anion to the α,3-dehydrotoluene, with the transition from closed-shell anion to open-shell diradical occurring through a cyclic allene geometry. In this respect, the transition in electronic states is similar to that observed for, inter alia, the racemization of 1,2-cyclohexadiene,[27] which is a nonplanar, cyclic allene that racemizes through the planar, open-shell diradical intermediate (eq 3a).[28−30] For the dehydrotoluene, the two planar electronic states can be viewed as interconverting through the nonplanar cyclic allene geometry (eq 3b).





When going through the nonplanar geometry, the transition from closed-shell occurs continuously. The extent of diradical character in the SA-MCSCF wave function through the transition is shown in Figure 4. Diradical character starts to be introduced near 2.2 Å, and the transition is essentially complete by 2.6 Å.

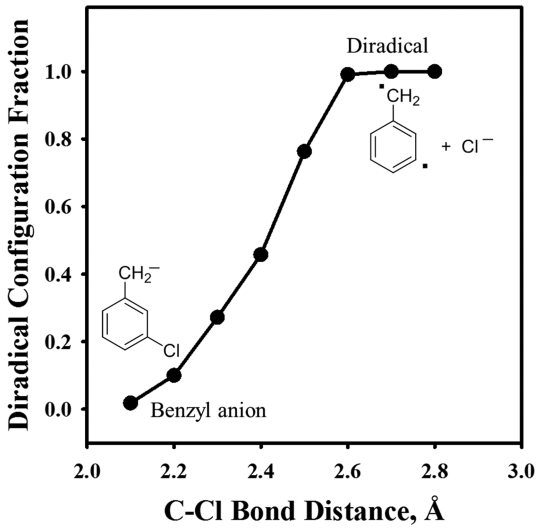


Figure 4. Diradical character in the dissociation of 3-chlorobenzyl anion to α,3-dehydrotoluene, obtained from the configuration weights calculated at the SA-CASSCF(14,12)/aug-cc-pVTZ level of theory.

The most significant conclusion from the plot in Figure 4, however, is that there is no single point during the dissociation, where it can be said the system switches from closed-shell to diradical.

More extensive curves can be obtained by using the UB3LYP approach, and the results are shown in Figure 5. Again, the planar closed-shell (blue, short dashes) and open-shell (red, long dashes) states are distinct, with an energy crossing near 2.5 Å, similar to where it is found in with the CASSCF calculations. Mixing of the states through the nonplanar geometry occurs over the range of 2.3−2.6 Å, also consistent with the CASSCF results.

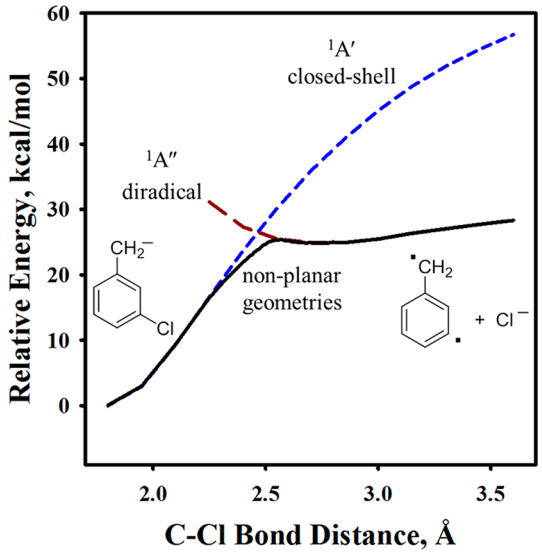


Figure 5. Potential energy curves for the dissociation of 3-chlorobenzyl anion at planar and nonplanar geometries, calculated at the UB3LYP/6-31+G* level of theory.

An important feature observed in the potential energy curves in Figures 2 and 5 is that *addition of the nucleophile to the diradical occurs without a net energy barrier!* Although there is a shallow minimum evident in the UB3LYP calculation, the energy at the top of the barrier to form the benzyl anion is lower than the energy of the asymptote. To an extent, the lack of overall barrier can be attributed to the weak attractive forces between the ion and neutral diradical, creating an energy minimum for the electrostatic complex. Therefore, even if the transition occurs on the repulsive part of the ^{1}A″ surface, the energy is still below that of the asymptote, as shown in Figure 5. A barrier could result if the crossing were to occur much later in the addition, where the repulsive region is more steeply rising, but that is not predicted for the present situation. However, it may be the case in the addition of a neutral nucleophile, such as methanol, especially in solution.

Addition to the Benzylic Position. Although this calculation focuses on the addition of chloride to form the benzyl anion, it can also apply to addition of the nucleophile to the benzylic position. This is significant because the nucleophilic addition of methanol to α,3-dehydrotoluene occurs exclusively at the benzylic position.[5−7,31] Myers and co-workers originally attributed the formation of nucleophilic addition products to the polar diradical, which is a combination of **1d** and **1z**. Subsequently, Carpenter and co-workers carried out extensive studies[31,32] to determine the mechanism of the reaction between α,3-dehydrotoluene and methanol and the origins of the selectivity between apparent radical reactivity and nucleophilic addition. On the basis of detailed experimental and computational analyses, they proposed a nonadiabatic process involving direct formation of the zwitterionic structure, **1z**, as a separate

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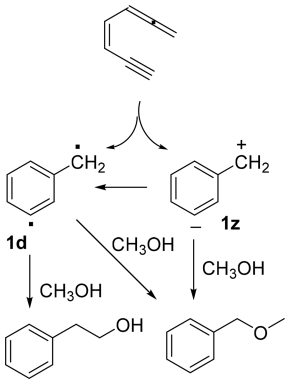
state upon cyclization of the eneyneallene precursor. An important argument for the existence of the nonadiabatic pathway was that the direct addition of methanol to the diradical could not occur. The mechanism for the potential pathway (mechanism E from Cremeens, Hughes, and Carpenter), shown in Scheme 3, involves cyclization of the eneyneallene to

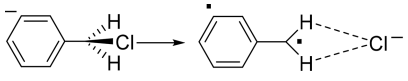
Scheme 3



form either **1d** or **1z**, which can react with methanol to form the benzyl ether. Cremeens, Hughes, and Carpenter[32] ruled out this mechanism on the basis of their observation that CH_3OH does not transfer the hydroxyl hydrogen atom to phenyl radical, with the implication that formation of the benzyl ether from the diradical, **1d**, would proceed by a stepwise process involving hydrogen atom transfer followed by coupling of the benzyl and methoxy radicals. The stepwise mechanism is similar to that for the formation of phenethyl alcohol, where the initial step is CH hydrogen abstraction.

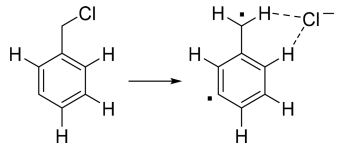
Fagnoni and co-workers[7] reconsidered the question of whether OH hydrogen atom transfer is possible for the diradical. They found that the computed barriers for CH or OH hydrogen atom transfer are sufficiently similar (16.12 vs 17.65 kcal/mol) for OH abstraction to compete with CH abstraction in the reaction. This prediction is qualitatively consistent with independently reported branching ratios for the reaction of phenyl radical with methanol,[33,34] which have found that OH abstraction does occur.

However, this work shows that it does not matter whether that OH hydrogen abstraction can occur or not because addition of the nucleophile to the diradical can occur directly provided it proceeds through a nonplanar geometry. In fact, addition at the benzylic position of (planar) α,3-dehydrotoluene can only occur through a nonplanar process, such that there are no symmetry restrictions on the nucleophilic addition of methanol, for example, and therefore, the addition does not require the existence of the zwitterionic electronic state.[5−7,31,32] To investigate this process computationally, we have calculated the potential energy surface for the dissociation of the 3-chloromethylphenyl anion (eq 4) by using unrestricted B3LYP calculations.



(4)

As shown in Figures 2 and 5, the potential energy surfaces calculated at the UB3LYP/6-31+G* level of theory are very similar to those obtained by using the more rigorous CASPT2 approach. For this calculation, the chloride was held in a fixed dihedral angle with respect to the ring of about 90°, near the angle in the optimized geometry of the phenyl anion. In a fully relaxed calculation in which the chloride is allowed to move freely in space, the calculated process does not involve direct dissociation, but instead, as the C−Cl distance approaches 3 Å, where the system is essentially pure diradical, the chloride prefers a coplanar geometry as an ion molecule complex, as shown in eq 3.



(5)

The calculated potential energy curve for the dissociation of the 3-chloromethylphenyl anion is shown in Figure 6. There is

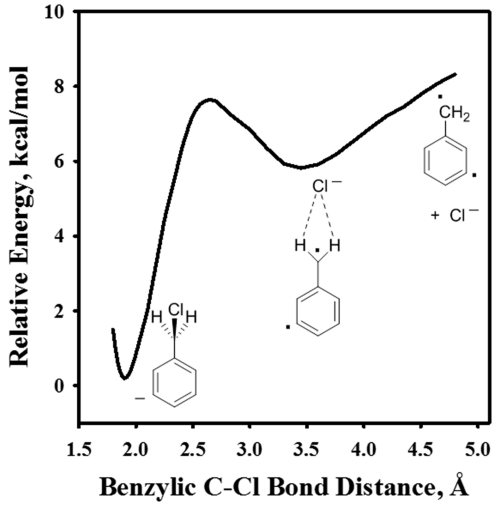


Figure 6. Potential energy surface for the dissociation of 3-chloromethylphenyl anion, calculated at the UB3LYP/6-31+G* level of theory. The chlorine dihedral angle with the ring was fixed to be 90° in the calculation.

a shallow energy corresponding well to an ion-neutral complex at the C−Cl distance of about 3.5 Å, corresponding to a H−Cl distance of about 3 Å. Although the potential energy curve in Figure 6 is not the lowest energy surface for the approach of the nucleophile, it still shows that nucleophilic addition can occur without an activation barrier. The expected value for $\langle S^2 \rangle$ in the unrestricted calculation (see Supporting Information) shows that the transition from the closed-shell anion to the diradical occurs continuously over the range of 2.3−3.0 Å in this calculation. Unlike the reaction at the ring position described in the previous section, the diradical does not adopt a cyclic allene geometry during the addition at the benzylic position, due to the nonplanar trajectory of the chloride addition. Ultimately, there are no restrictions, orbital or energetic, on the addition of a nucleophile to the benzylic position of α,3-dehydrotoluene, which means the direct formation of the benzyl methyl ether shown in Scheme 3 cannot be ruled out.

Although this work shows that there are no restrictions on the addition of the nucleophilic addition to the diradical, the more compelling challenge in the interpretation of the nucleophilic addition of methanol to α,3-dehydrotoluene is the preference for the addition at the α-position as opposed to the

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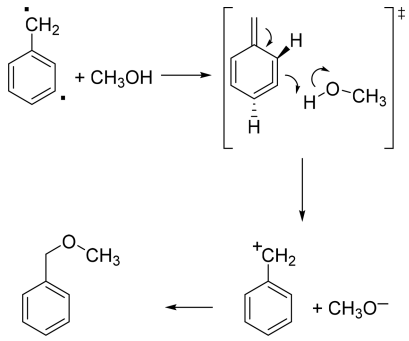
J. Org. Chem. 2018, 83, 12397−12403

energetically favored ring position. At the B3LYP/6-31+G* level of theory, addition of chloride to the ring is energetically preferred by nearly 20 kcal/mol over addition at the benzylic position, which can be attributed to delocalization of the charge in the benzylic anion. Therefore, considering that addition to neither position has an activation barrier, either product should be formed in the reaction, and addition to the ring should be thermodynamically preferred. This is consistent with what is observed in the gas phase, where a 3-chloromethylphenyl anion has been found to rearrange to a 3-chlorobenzyl anion.[35]

It is even more difficult for methanol addition. Fagnoni and co-workers[7] have used CASSCF theory to calculate the potential energy surface for addition of methanol to the benzylic position of α,3-dehydrotoluene and have found the addition is predicted to be energetically unfavorable, even when including a solvent model. It was found that with hydrogen bonding assistance, it is possible to stabilize the methanol adduct such that it is stable, but this type of cooperative effect should also allow for addition to the ring position and therefore does not account for the selectivity difference in product formation.

How then can we account for the formation of the benzyl methyl ether? Although OH hydrogen atom abstraction followed by radical coupling could explain it, this work suggests an alternate possibility, with the first step involving *proton transfer* to form the benzyl cation, followed by capture of the nucleophile. Just as this work has shown that it is possible to add a nucleophile to the diradical provided the reaction occurs through a nonplanar process, so too could an electrophile add without restriction through a nonplanar geometry (Scheme 4).

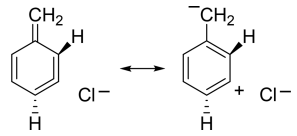
Scheme 4



Although protonation of the cyclic allene structure has been mentioned as an option,[31] it has not been seriously considered because the cyclic allene is not a stable state of the system. However, electrophilic addition to the diradical has been shown to be energetically very favorable,[36] and therefore, if the diradical can be protonated directly through a nonplanar trajectory, then it could account for selective formation of the ether. Computational studies of electrophilic addition to diradicals are currently in progress.

CONCLUSIONS

Nucleophilic addition to singlet, heterosymmetric diradicals is formally symmetry-forbidden, with the diradicals having rigorously open-shell electronic structures, such as σπ, whereas the product is closed-shell. As such, it may be surprising that nucleophilic addition to heterosymmetric diradicals has been observed. In this work, we have shown that nucleophilic addition is allowed for nonsymmetric pathways that allow the orbitals to mix. Ultimately, when reacting through a nonplanar pathway, the system reduces to a Salem and Rowland *nonsymmetric* diradical, with a wave function similar to that described in the preceding paper for the addition of chloride to *p*-benzyne. In the nonsymmetric system, the nucleophile adds through polarization of the wave function in the presence of the nucleophile (eq 6).Calculations show that α,3-dehydrotoluene does indeed adopt a cyclic-allene-like structure during nucleophilic addition. By following the nonplanar pathway, the addition of chloride to the ring position is predicted to occur without a barrier, and with continuous transition from an open-shell diradical to a closed-shell benzyl anion.



(6)

Similar considerations apply to nucleophilic addition to the benzylic position of α,3-dehydrotoluene, which can only occur through nonplanar pathways. However, although there are no symmetry restrictions on the addition of the nucleophile to the benzylic position and there is no barrier for the reaction, it is not as energetically favorable as addition to the ring. Consequently, exclusive formation of the benzyl ether is not consistent with what is predicted for nucleophilic addition. Alternatively, we propose that a previously suggested but unexplored pathway involving protonation may be responsible because, just as nucleophilic addition can occur via nonplanar geometries, so too can electrophilic addition, including protonation. Studies of electrophilic addition to the dehydrotoluene are in progress.

The main conclusion of this work and the study described in the preceding paper is that, when considering the interplay of electronic structure and geometry, there are no impediments for the addition of nucleophiles to diradicals or the transition from diradical to closed-shell electronic structures. In retrospect, this should not be surprising because diradicals addressed in this work are commonly generated by cyclization of closed-shell precursors.[37,38] Barriers for reactions may arise from other sources (e.g., geometric distortion, charge separation, repulsion, etc.), but there are no orbital symmetry impediments along symmetry breaking pathways, and so such reactions can be barrierless. Therefore, when considering the reactions of diradicals, including those generated thermally or even photochemically, all types of Lewis acid/base-type reactivity cannot be ruled out and needs be considered.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b01414.

Geometries, energies, and wave function information obtained from SA-MCSCF calculations, including CI coefficients for nonplanar structures; UB3LYP geometries and energies for addition of chloride to the benzylic position (PDF)

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Notes

The authors declare no competing financial interest.

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