

A Mechanistic Analysis of the Birch Reduction

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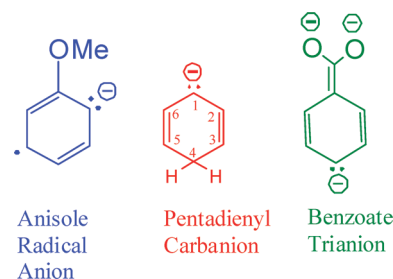
CONSPECTUS

The Birch Reduction is one of the main reactions of organic chemistry. The reaction involves the reaction of dissolving metals in ammonia with aromatic compounds to produce 1,4-cyclohexadienes. Discovered by Arthur Birch in 1944, the reaction occupies 300 pages in *Organic Reactions* to describe its synthetic versatility. Thus, it is remarkable that the reaction mechanism has been so very controversial and only relatively recently has been firmly established. Perhaps this is not that surprising, since the reaction also has many unusual and esoteric mechanistic facets. Here, I provide a description of how I have applied ever-evolving levels of quantum mechanics and a novel experimental test to understand details of the mechanism and the origins of the selectivities observed in the Birch reduction.

The reaction involves an initial radical anion resulting from introduction of an electron from the blue liquid ammonia solution of free electrons formed by the dissolution of Li or related metals. This radical anion is protonated by an alcohol and then further reduced to a carbanion. Finally, the carbanion is protonated using a second proton to afford a nonconjugated cyclohexadiene. The regiochemistry depends on substituents present. With 18 resonance structures in the case of anisole radical anion, prediction of the initial protonation site would seem difficult. Nevertheless, computational methods from Hückel theory through modern density functional calculations do correctly predict the site of protonation. An esoteric test established this mechanism experimentally. The nature of the carbanion also is of mechanistic interest, and the preponderance of the resonance structure shown was revealed from Hückel calculations involving variable bond orders. For the trianion from benzoic acid, parallel questions about structure are apparent, and have been answered. Some mechanistic questions are answered experimentally and some by modern computations.

Recently, our mechanistic understanding has led to a variety of synthetic applications. For example, the preparation of alkyl aromatics from benzoic acids makes use of the intermediates formed in these reactions.

This Account provides an overview of both experimental techniques and theoretical methodology used to provide detailed mechanistic understanding of the Birch Reduction.



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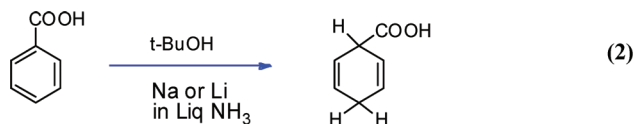
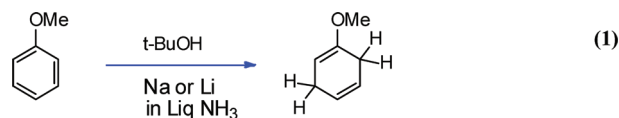
Introduction

The Birch Reduction is one of the basic reactions of synthetic organic chemistry. Its complex mechanism is the theme of this Account. While the mechanism has been controversial over the past decades, evidence has gradually accumulated that delineates the correct mechanism. The Birch Reduction has a mechanism that is particularly intriguing and has a number of unusual facets. This Account describes the several possible mechanisms and the details we elaborated leading to the final mechanistic picture.¹

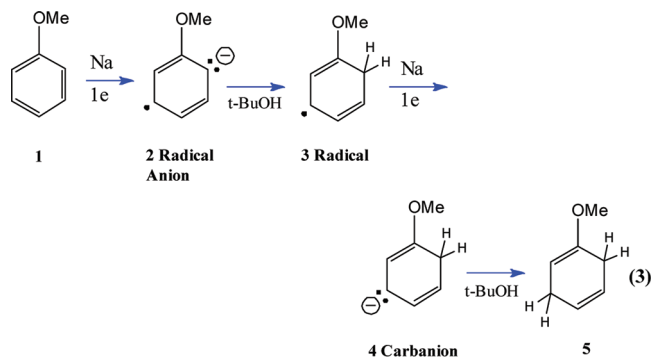
The Basics

The reaction was discovered by Arthur Birch in 1944.² The reaction of monocyclic benzenoids affords

1,4-dihydrocyclohexadienes. Experimentally, the reaction is run in liquid ammonia with an alkali metal and an added alcohol. Two representative examples are the reaction of anisole (note eq 1) and that of benzoic acid (eq 2). Wilds and Nelson have reported that lithium leads to better yields than sodium.³



In 1944, Birch² described the reaction and suggested a mechanism involving initial formation of the radical-anion by electron introduction from the blue free-electron solution in the liquid ammonia. Note eq 3 which depicts initial ortho protonation (vide infra) while Birch had suggested meta.



The empirical rule Birch suggested was that for electron donor substituents such as methoxy or methyl the dihydro aromatic is formed with the maximum number of substituents on the residual double bonds. With electron withdrawing groups, the rule is reversed.

For my mechanistic discussion, I need to note that the reaction is third-order overall: first-order in the reactant, first-order in electrons, and first-order in the alcohol.⁴ This then leads to the conclusion that the rate-limiting step is protonation of the radical-anion **2** to afford radical **3**. Thus, one reactant molecule, one electron, and one alcohol molecule are required to reach the transition state.

Free Electrons in Liquid Ammonia. The blue solutions from alkali metals dissolved in liquid ammonia are said to contain free electrons. In reality there are three species: actual free but solvated electrons, a metal anion or alkali (e.g., Na^{\ominus}), and an electrone consisting of a complexed alkali metal cation with a trapped electron (e.g., $[\text{Na}(\text{NH}_3)_6]^{\oplus}\text{e}^-$).⁵ The electrone and the alkali anion both contribute to the blue color. With atoms other than sodium, the blue color seen in Pyrex glassware is due to exchange with the sodium silicate of the glass.

The Reaction Regioselectivity with Electron Donors. Equation 1 depicts the Birch Reduction of anisole as it occurs, but consideration of eq 3 leads one to wonder why this regiochemistry is preferred. Thus, para and ipso protonation must not be occurring. Mechanisms involving initial ortho and meta protonations lead to the same observed final product; note Figure 1. Thus, the choice of ortho versus meta would seem to be more philosophical than practical. However, if somehow the protonation of the radical-anion were with deuterium and the subsequent carbanion protonation were with protium, perhaps orchestrated by Maxwell's

Demon, we would anticipate two possible products of the same basic carbon structure, one resulting from initial ortho protonation and the other from initial meta protonation. The idea of deuterium and then protium protonation may seem esoteric, but my later discussion will consider it. For now, we revert to just protium being involved.

Birch had suggested Mechanism Meta as the one involved.² However, in 1961, I made use of Hückel computations of the anisole radical-anion⁶ and found that the site of highest electron density was ortho to the methoxy. I then suggested that Mechanism Ortho was energetically preferred.⁶

Birch had noted that there was no experimental evidence for the ortho versus meta regioselectivity, and he continued in successive publications to consider that the first protonation was meta in spite of my theoretical prediction. This clearly was a challenge.

Over the decades, the question was controversial. In 1969, Burnham reported a study using UHF computations.⁷ He employed a model for the transition state and also considered the energies of the alternative protonated radical-anions. He concluded that protonation is unlikely to occur predominately ortho and suggested a preference for meta protonation. Subsequently, Radom, in a study coauthored with Birch, reported computations employing the RHF/STO-3G and UHF/STO-3G methods.⁸ In this study, molecular electrostatic potentials (MEPs) were used. Radom and Birch concluded that there was a slight ortho preference but with mixtures expected.

Curiously, in subsequent publications, Birch continued to argue for only meta protonation in spite of his work with Radom.

Then in 1990 and 1993 I devised an experimental test, with Wang, of the regioselectivity of the radical-anion protonation.^{9,10} This has been alluded to earlier in this discussion as, in the extreme, persuading Maxwell's Demon to perform the radical anion protonation with deuterium and then the later final anion protonation with protium. This thought led us to initiate our 1990–1994 research. While the extreme Maxwell's Demon experiment was not accomplished, an approximation to that was performed.

Thus, we ran the Birch reduction of anisole with *tert*-butyl alcohol deuterated to a small extent; note eq 4. Knowing that radical anions are considerably less basic than the corresponding carbanions,¹¹ and thus that the protonation will be less exothermic and more selective, one can anticipate that the radical-ion protonation will accumulate much less deuterium.

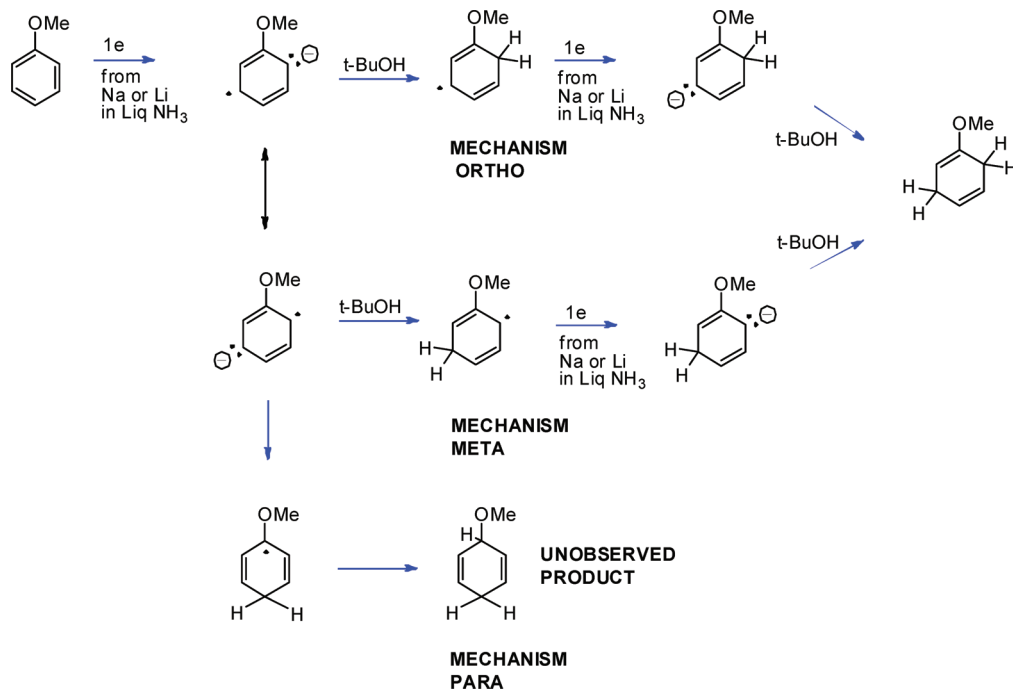
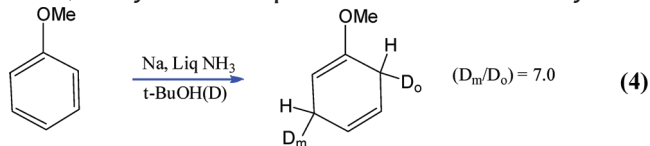


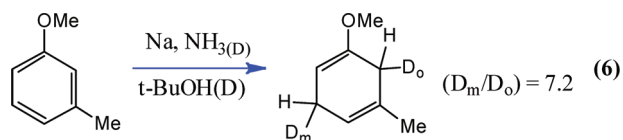
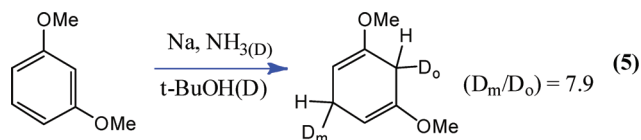
FIGURE 1. Mechanisms and regioselectivity.

The anisole reduction was run at $-78\text{ }^{\circ}\text{C}$ with sodium in liquid ammonia and *tert*-butyl alcohol containing ca. 2% deuterium. The ratio of *m*- to *o*-deuterium content in the 2,5-dihydroanisole product was determined by deuterium



ium NMR analysis utilizing the Pr(fod) shift reagent to separate methylene absorption peaks.

The experimental result, as depicted in eq 4, was that most of the deuterium (7:1) appeared in the meta position, signifying that the selective radical-anion protonation occurred at the ortho site with hydrogen. That the anisole mechanism was general was established by parallel examples we carried out with 1,3-dimethoxybenzene and with 3-methoxytoluene as shown in eqs 5 and 6.



We ran several different checks. One was the independent generation of the final carbanions in the same deuterated

solution with the finding that the extent of deuteration was a major part of the deuteration in the Birch reductions themselves. It also was established that the dihydroaromatic products were not exchanging deuterium under the Birch reduction conditions. Finally, the kinetics of the reactions was established as third order in agreement with the known order for benzene.

Regioselectivity with Electron Withdrawing Groups.

Figure 2 gives the regioselectivity in the reaction of benzoic acid. It seen that there is 1,4-protonation with a two-electron reduction. The mechanistic aspects are considered later in connection with computations. The same regioselectivity is observed for benzamides and related compounds.

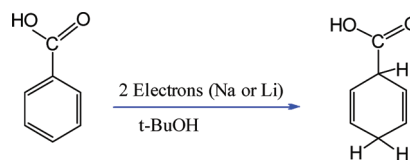


FIGURE 2. Regioselectivity in the reduction of benzoic acid.

The Second Step of the Birch Reduction. Having considered the initial radical-anion protonation step, we were left with the question of why the final step, that of the cyclohexadienyl carbanion, invariably affords the unconjugated product by protonating in the center of the delocalized system. There was an answer to this question in my 1961 publication.⁶ This considered the preferred site of

protonation of the parent 1,4-pentadienyl carbanion.⁶ See also my book on organic quantum mechanics.¹²

I noted that while ordinary Hückel computations are naïve in giving charges of conjugated anionic systems, the bond orders obtained are more realistic. Thus, the charges obtained for a pentadienyl anion are equal at atoms 1 and 3 (and 5) but the bond order 1–2 is greater than that of bond 2–3. With this in mind, a second computation, where the resonance integrals were taken as proportional to the bond orders, led to an increase in the charge at atom 3. In a third iteration, the charges and bond orders have close to converged. This is discussed in the following section on computations.

Earlier, I had noted that this selective protonation in the center of pentadienyl systems is a general phenomenon for conjugated linear anions.^{13,14} For example, the enolate of cholesten-4-one protonates kinetically to afford cholest-5-en-3-one,^{13,14} a result from protonation of the dienolate system alpha to the carbonyl at C-3.

Computational Aspects

The Radical Anion Protonation. In 1961, using simple Hückel computations, I had obtained the radical anion electron densities shown in Figure 3.⁶ In 1993, I obtained the densities using Gaussian 1992 ROHF/6-31G* (Figure 4).¹⁵ It is of some interest to compare the results which qualitatively parallel the HMO results and are within 5%. Thus, we are reminded that SCF computations start with a Hückel beginning and add electron–electron interactions.¹² Inspection of the densities makes clear that a methoxy or methyl substituent leads to the highest electron density at the ortho position. The meta position has less electron density, and the para has the lowest density. Thus, our computational results are in accord with the

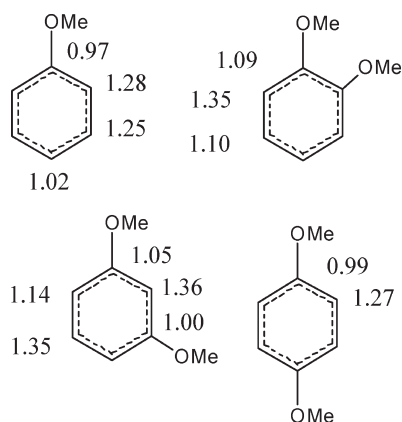


FIGURE 3. 1961 radical anion electron densities.⁶

regioselectivity of the Birch Reduction assuming that protonation occurs at the site of highest electron density.

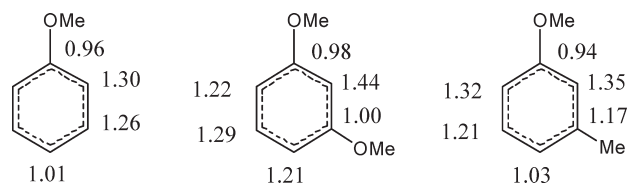


FIGURE 4. 1993 ROHF/6-31G* radical anion electron densities.¹⁰

Figure 5 gives some electron densities from using the first singly occupied molecular orbital of the radical anion.¹⁰ Such frontier densities have been considered^{8b} as a predictor of protonation sites. It is quickly seen that these densities do not parallel those of the complete radical anions. Hence, using frontier densities would indeed lead to the erroneous prediction of a preferred meta protonation.

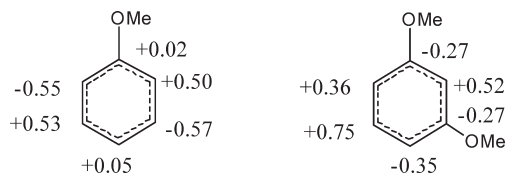


FIGURE 5. 1993 frontier MO coefficients.

Thus far, I have considered electron densities as controlling the regioselectivity of protonation. A second factor is the energy of the protonated radical anion formed in the rate-limiting step. Note Figure 6. It is seen that the radical produced by protonation ortho to methoxy or ortho to methyl leads to the energetically preferred species. Protonation meta leads to a higher energy radical. It thus seems that ortho protonation is favored by the energy of the radical being formed. Nevertheless, that para substitution favors the

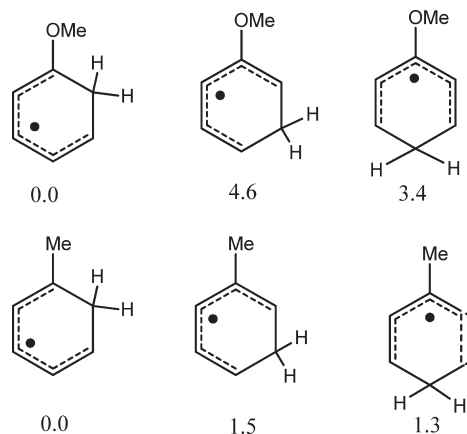


FIGURE 6. Relative energies of the protonated radical anions. Note that the energies (kcal/mol) are relative to the ortho-protonated species. The energies are from B3LYP/6-3C*.^{16a}

energy more than meta in the anisole case, and this suggests that the effect is not a major one.

A further treatment, this by the Delta Density Analysis,^{16b,17} is of interest. In this, the increase in density at each site resulting from addition of one electron to anisole is considered. Note Table 1 where the protonation of the anisole radical anion is considered: ipso, ortho, meta, and para.^{16b} It is seen that the maximum density enhancement on electron introduction is ortho.

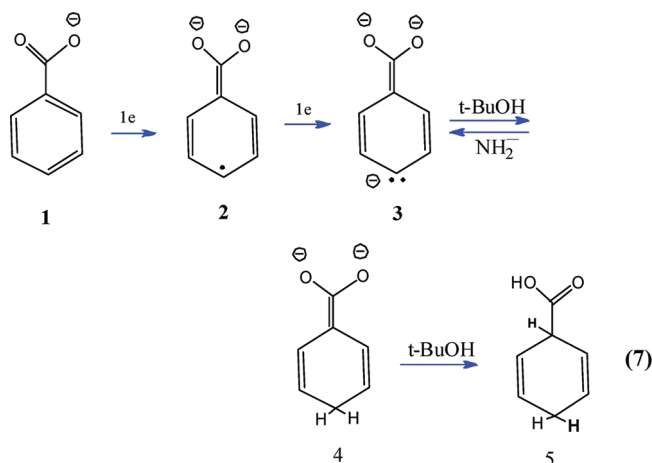
TABLE 1. Delta Density Analysis of Electron Introduction to Anisole^{16b}

site	delta density ^a	total charge	pi density
ipso	37	0.35	0.99
ortho	285	-0.47	1.32
meta	109	-0.29	1.10
para	52	-0.28	1.10
ortho'	342	-0.44	1.32
meta'	131	-0.41	1.21

^aElectron density scaled by 1000.

The Birch Reduction with Electron-Withdrawing Groups.

The mechanism in the case of an electron withdrawing group, such as benzoate, is shown in eq 7 where *tert*-butyl alcohol is employed as the proton source.

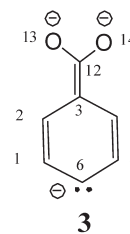


When the Birch reduction is run with *tert*-butyl alcohol, the protonated benzoate dianion **4** is found to be present as established by S_N2 alkylation with alkyl halides at the ipso position. With excess sodium and without *tert*-butyl alcohol, anion **3** is present and a second alkylation, this at the para position, occurs. My B3LYP/6-31G* computations^{16b} on carbanion **3** reveal that the site of highest electron density in the ring is para to the original carboxyl and greater than ipso and thus in accord with the para protonation (note Table 2).

The Final Step of the Birch Reduction. As noted in the introductory material, invariably the final Birch Reduction products have 1,4-cyclohexadienyl structures. Thus, the cyclohexadienyl carbanion must protonate in the center to

TABLE 2. Summary of Natural Population Analysis of the Dibenzoate Dianion^a

Atom	Charge
C 1	-0.34
C 2	-0.27
C 3	-0.40
C 4	-0.27
C 5	-0.34
C 6	-0.73
C 12	0.70
O 13	-0.93
O 14	-0.93



^aTotal Charge including H's not in the Table is -3.00.

afford the unconjugated diene system. Of course, had protonation taken place at the end of the pentadienyl anionic system, the conjugated 1,4-diene resulting would have been reduced further to a cyclohexene.

The proclivity for the basic pentadienyl carbanions, present in the cyclohexadienyl systems, to protonate in the center is not understood with the most simple Hückel computation, since the charges at atoms 1, 3, and 5 are equal as noted qualitatively earlier. I have noted that the naiveté in densities is not found in the bond orders obtained. Table 3⁶ gives some quantitative detail. Thus, a reiterative computation¹⁸ having the form of eq 8 where P is the bond order of the previous iteration and Beta represents the off-diagonal element in the new Hückel computation iteration; A and B are positive constants. It is seen from Table 3 that both the bond orders and charges quickly converge with the charge on the central atom 3 becoming the largest.

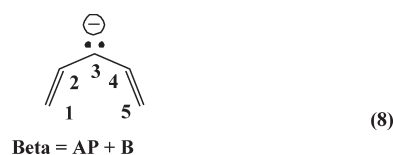


TABLE 3. Three Hückel Iterations Using Resonance Integrals Paralleling Bond Orders^{a,b}

approximation	charge atom 1	charge atom 3	bond order 1-2	bond order 2-3
one	1.333	1.333	0.788	0.578
two	1.317	1.365	0.802	0.564
three	1.316	1.368	0.802	0.562

^aThe central atom is 3, and atoms 1 and 5 are terminal. Note the charge on atom 5 is the same as that on atom 1 by virtue of symmetry. ^bCharges on 2 and 4 are unity.

A similar treatment of the 1-methoxy- and 2-methoxypentadienyl carbanions affords similar results.⁶ Note Figure 7. In each case, the central carbon has the highest electron density and central protonation is expected and observed.

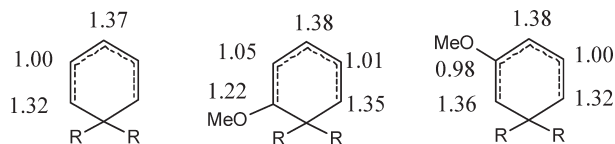
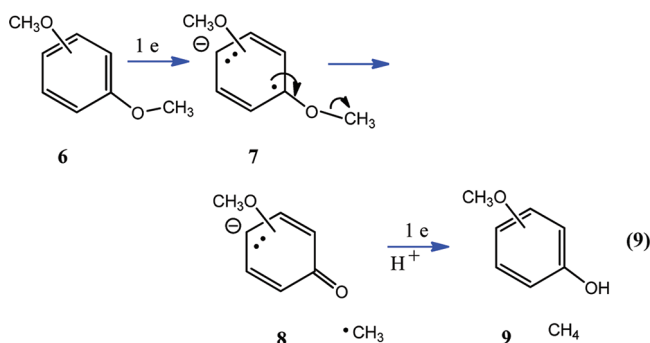


FIGURE 7. π -Densities of methoxy substituted carbanions compared with simple cyclohexadienyl (1961).

The Importance of Theory in Understanding of Regioselectivity with Electron Donors. Since both ortho and meta mechanisms eventually lead to the same final Birch reduction product, it might be wondered if the ortho versus meta considerations are worthwhile completely aside from esoteric mechanistic understanding.

The first obvious point is that the radical anion densities clearly reveal why para protonation does not occur. Beyond that, there are known reactions where the ortho versus meta prediction is relevant. Thus, it is known that dimethoxybenzenes undergo O–C fission as indicated in eq 9.^{19,20}



The facility of this ether cleavage is governed by substituents as: *o*-methoxyl > *m*-methoxyl > hydrogen > *o*-methyl > *m*-methyl > *p*-methyl > *p*-methoxyl.¹⁹ Hence, the ortho–meta pattern found in the ordinary Birch Reduction is repeated here.

One might think that the usual control is involved. However, the alkyl fission reaction is a minor side reaction, and one does not anticipate, or find, a high electron density at a methoxy-bearing carbon. Nevertheless, an odd-electron density is possible and suggested by the activation energies for methyl loss. It appears that provision of the odd-electron occurs only on considerable bond stretching.

Thus, Table 4 illustrates the variation of activation energy of ortho, meta, and para species with oxygen–methyl stretching and methyl expulsion^{16b} as obtained from UB3LYP-QST2/6-31G*. It is seen that the highest transition state barrier by far is for the para isomer while the

ortho regioisomer has the lowest activation energy. Thus, the experimental pattern is paralleled in my computations.

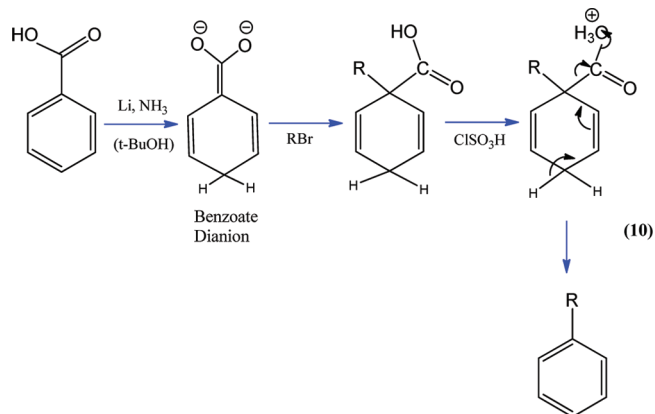
TABLE 4. Relative Energies: Reactant, Transition State, and Activation Energy for Radical Anions^a

O-Me stretching species	ortho	meta	para
DiMeoBenzene RA 7 ^b	0.00	17.5	16.3
MeoBenzylRATS 8 ^c	2.0	25.1	27.8
Δ TS ^d	2.0	07.7	11.5

^aEnergies in kcal/mol relative to the ortho-radical anion. ^bReactant radical anion. ^cTransition state from QST2. ^dActivation energy for anionic fission.

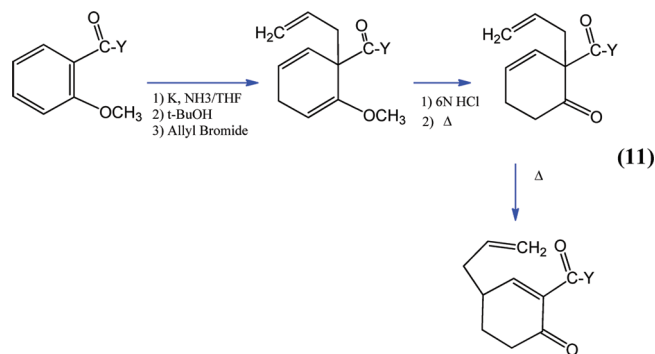
Continuing Importance and Interest in the Birch Reduction. The past decade has seen the Birch Reduction utilized as a reliable synthetic tool. Since the 1992 *Organic Reactions*²¹ chapter which outlines much of the early synthetic efforts, there has been a continuing stream of applications. While the theme of this Account is mechanistic, nevertheless there are several recent items which are worth mentioning as applications of the principles considered.

One such example is the method described by Linker et al.²² permitting the replacement of a carboxyl group by alkyl substituents. The mechanism is outlined in eq 10, and we are reminded of eq 7 in which dianions derived from carboxylic acids result from para protonation. The example shown in eq 10 is for benzoic acid itself, but the method is operative with alkyl benzoic acids. Without the presence of an alcoholic proton donor, it is possible to doubly alkylate, ipso and para.



Still another variation of the Birch reduction is the Birch–Cope combination as depicted in eq 11. This reaction has been carried out with a variety of acid derivatives and with ring substituents.²³ Implicit in the sequence is the use of hydrolysis of intermediate enol ethers to

permit alkylation of the resulting beta-dicarbonyl moiety; this is followed by subsequent Cope rearrangement.



Conclusion

It is quite clear that the Birch Reduction not only has proven itself to be a useful and reliable organic reactions but also it has shown itself to be especially intricate, yet mechanistically understandable. This understanding has resulted from the combined use of devised experiment and planned computation.

Supporting Information. Computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

BIOGRAPHICAL INFORMATION

Howard E. Zimmerman is a native of Connecticut. During World War II, he served in the U.S. Armored Corps in Europe as a tank gunner and a final rank of technical sergeant. He obtained his B.S. at Yale in 1950 and his Ph.D. in 1953. After an NRC postdoc with R. B. Woodward at Harvard, he started as an Assistant Professor at Northwestern University. He moved in 1960 to the University of Wisconsin where he is now A. C. Cope and Hilldale Professor of Chemistry.

He has received the James Flack Norris Award in Physical Organic Chemistry of the American Chemical Society, the American Institute of Chemistry Pioneering Award, the Halpern Award of the Northeastern ACS Section, Election to the National Academy of Sciences in 1980, and the 2006 Porter Medal.

He is well-known for the Zimmerman–Traxler aldol transition state, the Möbius–Hückel concept, the Di- π -Methane rearrangement, the introduction of excited state structures for photoreactivity, the roles of excited state energy barriers and conical intersections on photoreactivity, and the synthesis and chemistry of semibullvalene and barrelene. Eighty-seven of his research students have become professors.

FOOTNOTES

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