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ORIENTATION IN METAL AMMONIA REDUCTIONS

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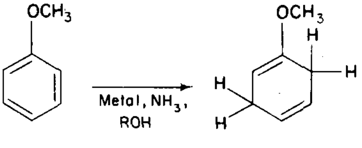
Abstract—The unique orientation effects observed in the alkali metal-ammonia reactions of aromatic compounds are considered from a molecular orbital viewpoint. The Birch rule governing the reduction of substituted aromatics, the peculiar effect of substituents on the ease of hydrogenolysis of benzyl alcohols, the similar effect in the dealkylation and dearylation of alkyl aryl ethers and aryl ethers, the course of dealkoxylation of alkyl aryl ethers, are all found to be reasonably accommodated by molecular orbital theory.

AMONG the reactions of organic chemistry the metal ammonia reduction[1,2,5] has taken its place as one of considerable synthetic utility. From a mechanistic viewpoint this reaction, together with variants, presents many interesting and intriguing features. It is the purpose of the present paper to report the applicability of molecular orbital theory in explaining certain aspects of the metal ammonia reduction which have hitherto been enigmatic. Of special interest are the orientation effects observed: (a) in the formation of dihydrobenzenes from substituted aromatics,[2] (b) in the hydrogenolysis of substituted benzyl alcohols,[3] and (c) in the dealkylation and dearylation of alkyl aryl ethers and aryl ethers.[4]

In the case of reduction of substituted aromatics to yield 1,4-dihydrobenzenes there has been noted[2] a strong driving force favoring formation of the 1,4-dihydrobenzene having the maximum number of alkoxyl or alkyl groups on the residual double bonds and having the minimum of these groups on the 1,4-carbon atoms reduced, with alkoxyl groups having a more pronounced effect than alkyl groups. This constitutes the Birch rule[2] defining the reaction course. Thus,[2,3a] reduction of anisole affords 2,5-dihydroanisole as the predominant product:



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[1] The alkali metal–ammonia–alcohol reduction of aromatics to dihydrobenzenes was first reported by Wooster [C. B. Wooster and K. L. Godfrey, *J. Amer. Chem. Soc.* **59**, 596 (1937); C. B. Wooster, U.S. Pat. (Du Pont) No. 2182242 (1938), *Chem. Zentr.* **I**, 3987 (1940)]. Correct structures were first assigned by Birch and co-workers, who have elegantly investigated the generality and nature of the reaction.

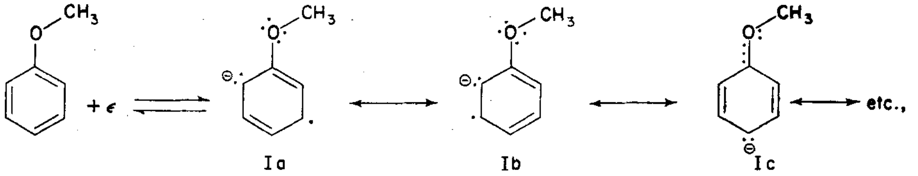
[2a] A. J. Birch, *J. Chem. Soc.* 430 (1944); [b] *Ibid.* 593 (1946); [c] *Ibid.* 102 (1947); [d] *Quart. Rev.* 69 (1950); [e] A. J. Birch and H. Smith, *J. Chem. Soc.* 17 (1958); [f] A. J. Birch and D. Nasipuri, *Tetrahedron* **6**, 150 (1959).

[3a] A. J. Birch, *J. Chem. Soc.* 809 (1945); [b] A. J. Birch and S. Mukherji, *Ibid.* 2531 (1949); [c] refs. 2*d* and 2*e*.

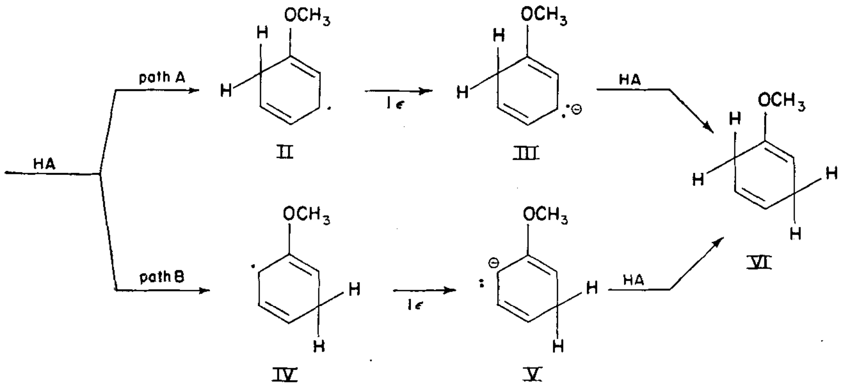
[4a] P. A. Sartoretto and F. J. Sowa, *J. Amer. Chem. Soc.* **59**, 603 (1937); [b] A. L. Kranzfelder, J. J. Verbanc and F. J. Sowa, *Ibid.* **59**, 1488 (1937); [c] F. C. Weber and F. J. Sowa, *Ibid.* **60**, 94 (1938); [d] K. Freudenberg, F. Klinck, E. Flickinger and A. Sobek, *Ber. Dtsch. Chem. Ges.* **72**, 226 (1939); [e] ref. 2*c*; [f] A. J. Birch, *J. Chem. Soc.* 2106 (1949); [g] K. E. Hamlin and F. E. Fischer, *J. Amer. Chem. Soc.* **75**, 5119 (1953); [h] A. J. Birch, *Aust. J. Chem.* **7**, 256 (1954); refs. 2*a*, 2*d* and 2*e*.

[5] A. W. Wilds and N. A. Nelson, *J. Amer. Chem. Soc.* **75**, 5360 (1953).

In order to ferret out the driving force controlling orientation, one must first know the gross mechanistic details. Fortunately, there seems to be some agreement in the literature that the alkali metal–ammonia–alcohol reduction of aromatic compounds involves reversible electron introduction to the π-system followed by a rate limiting protonation of the resulting radical anion, resulting from one electron introduction, or dianion, resulting from two electron introduction;[2d,f,6a,7,8] for simple alkoxyl and alkylbenzenes it appears that it is the anion radical which is involved.[8] Accordingly, the reduction of anisole may be formulated in the following manner:



Anion radical I; 18 contributing structures plus 3 structures having a three electron bond (i.e., one-half of one antibond)



As has been noted both by Birch[2f] and Bothner-By[6], the 2,5-dihydro structure of the product (e.g. VI) requires that the radical anion intermediate (I) be protonated either *ortho* to the methoxyl group, as in path A, or instead meta to the methoxyl function, as in path B. In either event the anion (III or V) derived from introduction of a second electron must subsequently be protonated *para* to the site of the initial protopic attack in order to account for the observed product, VI. Thus selectivity is manifested in both protonation steps of the metal–ammonia reduction. The driving forces responsible for this selectivity are of considerable interest and will now be examined.

An understanding of the selectivity of protonation of an anion radical as I is not readily derived from qualitative valence bond reasoning. Eighteen low energy resonance structures (e.g. Ia and Ib) may be written for I; in these the negative

[6a] A. P. Krapcho and A. A. Bothner-By, *J. Amer. Chem. Soc.* **81**, 3658 (1959); *cf.* also [b] J. F. Eastman, C. Keenan and H. Secor, *Ibid.* **81**, 6523 (1959); [c] A. Krapcho and A. Bothner-By, *Ibid.* **82**, 751 (1960).

[7] For another view of the mechanism *cf.* W. Hückel and G. Graner, *Chem. Ber.* **90**, 2017 (1957); W. Hückel and I. Nabik, *Ibid.* **89**, 2115 (1951); W. Hückel, B. Graf and D. Munkner, *Liebigs Ann.* **614**, 47 (1958).

[8] Evidence has been presented by Krapcho and Bothner-By (ref. 6) that it is the anion radical which is protonated in the reduction of benzene and alkylbenzenes. Similarly, Birch and coworkers (ref. 2*e*) have concluded that it is the anion radical which is generally protonated in the rate limiting step.

charge appears equally on all ring carbon atoms. Additionally, three structures such as Ic are possible in which the odd electron interacts with the methoxyl group with formation of a three electron π-bond;[9] in these structures the electron appears at the *ortho* and *para* positions. No convincing support is seen for prediction of an *ortho* and/or *meta* charge accumulation to account for a selective attack at these positions.[10]

TABLE 1. π-ELECTRON DISTRIBUTION OF RADICAL ANIONS

Methoxybenzene and position	Total density*	Odd electron density	Highest pair density
Monomethoxy			
substituted carbon	0·9722	0·0000	0·2381
ortho	1·2784	0·2500	0·3613
meta	1·2488	0·2500	0·2946
para	1·0214	0·0000	0·2591
ortho-Dimethoxy			
substituted carbon	1·0897	0·0915	0·3018
ortho–meta	1·3519	0·3242	0·3341
meta–para	1·0985	0·0791	0·2273
meta-Dimethoxy			
substituted carbon	1·0503	0·0792	0.2290
ortho–ortho	1·3591	0·3021	0·3021
ortho–para	1·1402	0·0911	0·3370
meta–meta	1·3459	0·3481	0.3481
para-Dimethoxy			
substituted carbon	0·9924	0·0000	0·2211
ortho–meta	1·2764	0·2500	0·3253

* Resulting from distribution of 9 π-electrons in the monomethoxy and 11 π-electrons in the dimethoxy cases.

In contrast, LCAO molecular orbital calculations are capable of yielding a prediction of electron distribution in radical anions such as I. Furthermore, examination of the predictions for a series of methoxybenzene radical anions reveals an interesting and consistent pattern of electron distributions. The results of these calculations are indicated in Chart I and Table 1. The details of the calculations are outlined in the section on Calculations.

Inspection of these results reveals that for mono and dimethoxybenzenes the electron density of the radical anion is greatest at positions *ortho* to methoxyl groups with the electron density increasing with an increasing number of such methoxyl groups. Ring carbon atoms *meta* to methoxyl groups are found to be less electron rich while positions *para* to methoxyl groups are seen to have a strikingly lower

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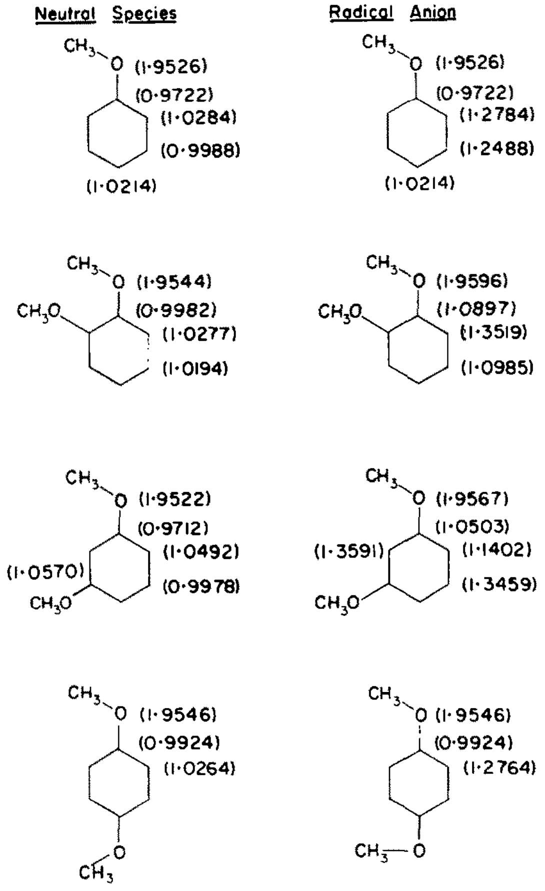
[9] Stabilization of an odd electron species by interaction of the odd electron with an alkoxyl group is a general phenomenon. As has been noted by M. J. S. Dewar, *The Electronic Theory of Organic Chemistry* p. 243. Oxford University Press (1949), the interaction is similar to the stabilization of a carbonium ion by alkoxyl except that in the odd electron case there is one extra electron which must go into an antibonding π-orbital with loss of some of the energy gained in formation of a two electron bonding π-orbital. The overall π-bond may be termed a three electron bond.

[10] Qualitative arguments in favor of a *meta* buildup of charge (ref. 2*f*) or "free charge" (ref. 2*e*) have been advanced. It was suggested that the position of greatest (free) electron density will be the *meta* position as a result of opposition to accumulation of charge *ortho* and *para* due to the substituent.

electron density. Ring carbon atoms bearing a methoxyl group also have a dramatically lower electron density. In order to give some idea of the significance of the differences in electron densities, the electron densities of the neutral aromatic species are included in Chart I; it is seen that the *ortho* carbon of anisole is 0·03 electron more rich than the *meta* carbon atom. This compares with (e.g.) an enhanced electron density of 0·31 for the *ortho* position of the radical anion of anisole, 0·28 for *meta* and 0·05 for *para* compared to the methoxyl substituted carbon of this species. Thus the differences in electron densities in the anisole radical anion are relatively large.

CHART I

LCAO MO Pi Electron Distribution of some Methoxybenzenes*



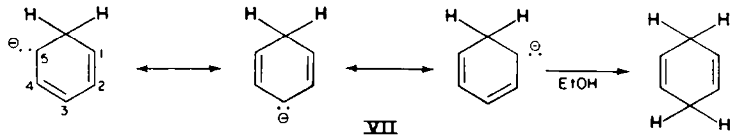
* The indicated electron distributions are for the total of all Pi electrons. Net charge obtained by subtracting one.

Having found interesting and consistent differences in electron densities at different carbon atoms of radical anions, one is faced with the question whether these may validly be used in interpreting relative rates of protonation of a given species.

One might well question whether instead of relating selectivity of protonation to electron densities he should not consider π-localization energies. It does appear, however, that for protonation of ordinary mesomeric anions the bonding electron pair is not greatly localized in the transition state and that as a result localization energies do not give predictions in the proper direction. Thus protonation of mesomeric anions is often observed to exhibit a kinetic preference for the less stable of tautomeric products (*vide infra*), a result not according with an interpretation based on localization energy; minimum electron localization is incurred when the mesomeric anion proceeds to the most conjugated product. Formation of the less stable tautomer is, however, understood on the basis of protonation of the most electron rich position in a transition state in which the pair is still heavily delocalized. An *a priori* judgment whether the transition state for protonation of radical anions involves as little carbon hydrogen bonding would be difficult, and it appears best to use the adequacy of the electron density approach in dealing with radical anion protonation as criterion of the validity of the assumed transition state.

One notes that for each of the mono and disubstituted methoxybenzene radical anions in Chart I protonation at the position of greatest electron density affords a radical capable of proceeding further to the 1,4-dihydrobenzene predicted by the Birch rule. Since the positions of lowest electron density of the radical anion are those which are substituted by a methoxyl group or *para* to a methoxyl group, in no case will a proton attack a carbon atom either bearing a methoxyl group or *para* to a methoxyl group. For example, *ortho* protonation of the radical anion (I) from anisole affords radical II which may proceed onward to 2,5-dihydroanisole (VI) via path A.[11]

Having considered the course of the first protonation step, one must next scrutinize the second and product forming protonation in which a mesomeric anion as III affords a dihydrobenzene in order to ascertain the reason for a preferential formation of the unconjugated product. Thus while *a priori*, any of carbon atoms 1, 3 or 5 of such a carbanion might be protonated, it is in general the central position which is attacked, as has been noted by Birch.[2d] In the simpler case of the metal ammonia reduction of benzene, the final step involves the protonation of mesomeric anion VII. Since 1,4-dihydrobenzene is actually the major product,[6a,12] it is seen again that of carbon atoms 1, 3 and 5 it is the central atom 3 which is preferentially protonated.



This result, however, receives no theoretical rationale in terms of the charge distribution of the pentadienyl anion as given by the simple LCAO molecular orbital theory,

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[11] Inspection of Table 1 also shows that protonation at the site having the highest density of the high energy electron pair will lead to observed product. A similar observation is made with respect to the odd electron density. Furthermore, addition of the odd electron densities to the total π-electron densities for a given radical anion, as obtained from Table 1, affords the total π-electron distribution for the corresponding dianions. Since in general the prediction based on electron density distribution of the dianion is found to agree with that based on the radical anion, in special cases where the dianion is the species reduced, the same product will be anticipated.

[12] W. Hückel and U. Wörffel, *Chem. Ber.* **88**, 338 (1955).

for the negative charge is predicted[13] to be equally distributed among carbon atoms 1, 3 and 5. The inability of electron density predicted by the simple model to account for the observed protonation has already been noted by Hammond.[14] However, the LCAO MO theory assumes equal overlap between atoms 1 and 2, 2 and 3, etc. Simple qualitative resonance considerations lead to the expectation that bonds 1–2 and 4–5 should be shorter and involve greater overlap than bonds 2–3 and 3–4; this is because in two of the three resonance structures written for VII bond 1–2 and 4–5 are double while in only one of the three structures are bonds 2–3 and 3–4 double. The simple LCAO MO theory, while naive in giving electron densities, is in agreement with these resonance arguments and predicts (*cf.* Table 2, first approximation) a higher π-bond order 1–2 and 4–5 than 2–3 and 3–4. Furthermore, when unequal overlap is taken into account, the ratio of electron densities on atoms 1 and 3 of VII is given by

$$\frac{Q_1}{Q_2} = \frac{q_1 - 1}{q_3 - 1} = \frac{S_{23}^2}{S_{12}^2}$$

where Q_1 and Q_3 are the net charges, q_1 and q_3 are the total electron densities and S_{12} and S_{23} are the overlap integrals for π-bonds 1–2 and 2–3, respectively.[15] Therefore, since $S_{12} > S_{23}$, the electron density at carbon three is higher than at carbon one, rationalizing the preferential attack of a positive species at the central carbon atom of the pentadienyl carbanion system.[16] By successive approximation, using the bond orders from each approximation to give the overlap and exchange integrals for the next iteration, there are obtained the results given in Table 2. It is seen that the electron density at the central carbon atom does build up to a constant value higher than that at the end atoms. It is suggested that this bond order effect is heavily responsible for the ubiquitous phenomenon of central protonation of mesomeric anions.

TABLE 2. CHARGE DENSITIES CALCULATED FOR THE PENTADIENYL CARBANION BY SUCCESSIVE LCAO MO APPROXIMATION WITH CHANGING BOND ORDERS

Approximation	$q_1 = q_5$	$q_2 = q_4$	q_3	p_{12}	p_{23}
First	1·333	1·000	1·333	0·788	0·578
Second	1·317	1·000	1·365	0·802	0·564
Third	1·316	1·000	1·368	0·802	0·562

Similar calculations for the 1-methoxypentadienyl carbanion moiety (VIII) and for the 2-methoxypentadienyl carbanion system (IX), using the bond orders obtained from the unsubstituted case as an approximation, indicate a similar accumulation of charge at the central carbon atom. Thus both the central protonation of mesomeric anion intermediates of the metal ammonia reduction of aromatic and the course of

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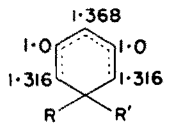
[13] This prediction is most easily arrived at by the method of non-bonding molecular orbitals as described by J. Longuet-Higgins, *J. Chem. Phys.* **18**, 265 (1950); *Proc. Chem. Soc.* 157 (1957); M. J. S. Dewar, *J. Amer. Chem. Soc.* **74**, 3341, 3345 (1952).

[14] G. S. Hammond, *J. Amer. Chem. Soc.* **77**, 334 (1955).

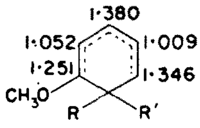
[15] This derives from solution of the secular equation with or without neglect of overlap, making the assumption that the resonance integral is proportional to the overlap integral.

[16] The first suggestion that the proton donor most rapidly attacks the site of highest electron density appears to have been made by A. J. Birch [ref. 2*d* and *Disc. Faraday Soc.* **2**, 250 (1947)] and by M. J. S. Dewar [*Ibid.* **2**, 261 (1947)].

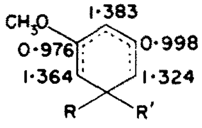
the initial protonation of the radical anion intermediates are explicable on a molecular orbital basis.



VII

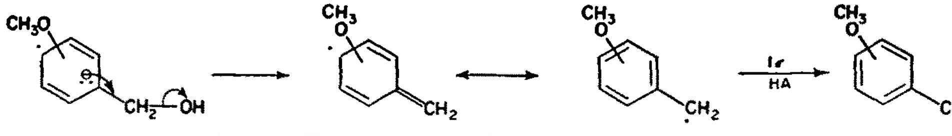


VIII



IX

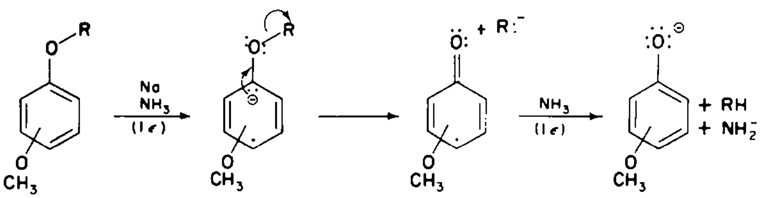
Further applicability of the molecular orbital considerations is found in understanding some unusual orientation effects described in the literature for hydrogenolytic and ether cleavage reactions occurring in metal ammonia reactions. Most readily understood is the unique pattern of hydrogenolysis of substituted benzyl alcohols on treatment with metals in liquid ammonia. It has been reported by Birch and coworkers[3] that this reaction is inhibited by strong electron donors para to the benzylic grouping; reduction of the aromatic ring predominates in such cases. Ortho and meta electron donors were reported to hydrogenolyze smoothly. The hydrogenolysis process is reasonably pictured as involving expulsion of hydroxide anion from the initially formed aromatic radical anion; such explusion would proceed best when the ring position bearing the carbinol moiety is most electron rich. Since ring atoms *para* to an electron donor are relatively electron poor compared to the *meta* and *ortho* positions (*cf.* Table 1) one would anticipate hydroxide expulsion *para* to methoxyl to be difficult compared to the *meta* and *ortho* orientations.



The same substituent effect is observed in the dealkylation of alkyl aryl ethers and the dearylation of aryl ethers occurring in competition with reduction when these ethers are treated with alkali metals in liquid ammonia. Birch has reported that the cleavage of a group from an aryl ether oxygen atom occurs most readily when the aryl group bears an *ortho* electron donor as methoxyl or methyl, somewhat less readily with a *meta* electron donor present and is inhibited with a *para* donor as methoxyl. Thus in the demethylation of anisole derivatives, the *ortho* methoxyl derivative gave 89 per cent of demethylation product, the *meta* isomer afforded 71 per cent, and *para* isomer gave only 3 per cent.[2d] Similarly, the reaction of 3,4-dimethoxy-2′-phenylethylamine has been reported by Hamlin and Fischer[4g] to afford 85 per cent of 3-hydroxy-4-methoxyphenylethylamine on treatment with sodium in liquid ammonia; thus the methoxyl group meta to the alkyl side chain loses its methyl group in preference to that *para* to the alkyl side chain. A number of similar examples have been described.[4] The effect of substituent groups seems to be in accord with the reactivity sequence expected for a radical anion intermediate, and one may picture the reaction as involving expulsion of a carbanion[17] from the anion radical;

[17] The mechanistic details of the reaction are not completely unambiguous. Not only is it possible that the species losing the methyl group is actually the dianion, but also the evidence on the question whether a methyl radical or a methyl carbanion is lost is incomplete. In a study of the ease of cleavage of different groups (ref. 2*a*) benzyl was found to be lost readily, a result explicable on either a radial or anionic basis. Isopropyl and n-propyl were found to be similar, a result hard to understand on either basis. Methyl was lost more readily than propyl suggesting loss as a carbanion. In any event the various mechanistic variations would be subject to similar substituent group effects.

in view of the low electron density *para* to a methoxyl group, the difficulty in dealkylation occurring here is understandable. With *meta* and *ortho* methoxyl groups the dealkylation would be expected to become more facile.[18]



In summary, it may be noted that species having an extreme number of valence bond structures and not readily amenable to simple qualitative resonance considerations are most readily treated from a molecular orbital viewpoint.

CALCULATIONS

The calculations on the methoxybenzenes were carried out by the simple LCAO MO method with neglect of overlap. The carbon–oxygen exchange integral was taken as $0{\cdot}6\beta_{C-C}$ and the oxygen Coulomb integral as $\alpha_C + 1{\cdot}5\beta_{C-C}$. The secular determinants were factored by use of group theory and the residual determinants were solved where necessary using a 1604 computer and the Jacobi method for diagonalization; earlier calculations were carried out on an IBM 650 computer.[19]

In the case of the pentadienyl species, the bond orders obtained in the usual fashion were related to the overlap integrals for the next approximation using the method of Mulliken[20] where $S = 0{\cdot}080p + 0{\cdot}115$; here p is the total bond order for a given bond. $\beta(P) = \beta_0 S/0{\cdot}25$.

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[18] There are a number of reports of the failure of a 3,4-methylenedioxyalkylbenzene to undergo the dealkylation reaction; rather loss of the 3-oxygen occurs with formation of a 4-hydroxyalkylbenzene. This is unusual, since the very similar 3,4-dimethoxyalkyl benzenes do lose the methyl group from 3-methoxyl group. This difference is reasonable if one considers the geometry of the carbon–oxygen bond of the methylenedioxy group which would have to be cleaved; this bond is perpendicular to the aromatic ring *p*-orbitals and a smooth increase in overlap accompanying bond breaking is impossible.

[19] Assistance with the computing by Vernon Sandel, John Munch and Duane Meeter is gratefully acknowledged. Also, acknowledgment to the donors of the Petroleum Research Fund of the American Chemical Society is gratefully made.

[20] N. Muller and R. S. Mulliken, *J. Amer. Chem. Soc.* **80**, 3489 (1958); N. Muller, L. W. Pickett and R. S. Mulliken, *Ibid.* **80**, 4770 (1953). In the present work no adjustment of the Coulomb parameters were made; such further refinement would undoubtedly have improved the quantitative, although not qualitative, significance.