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THE METAL–AMMONIA REDUCTION OF AROMATIC COMPOUNDS

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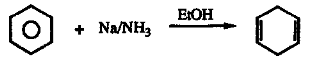
CONTENTS

1. INTRODUCTION

The reduction of aromatic rings by solutions of alkali metals in liquid ammonia was discovered by Wooster and Godfrey[1] who reacted toluene with sodium in ammonia followed by the addition of water. They reported a "highly unsaturated liquid product" which was not further identified. However, the real development of this reaction was to follow by A. J. Birch[2] and so the reaction has come to bear his name although in some cases it is simply called metal–ammonia reduction, especially where "classical" Birch conditions are not employed.[3] For example, Wilds and Nelson[4] found an advantage in adding alcohol last, as opposed to having it present when the metal is added, and it was subsequently learned that alcohols should be avoided altogether with polynuclear compounds (see below). This reaction is illustrated in its most simple case with the conversion of benzene to 1,4-cyclohexadiene by sodium metal in ammonia followed by the addition of excess ethanol.[3e]



Birch initially suggested the intermediacy of dianions in these reductions,[3a] but he and others later realized that the radical anion ($ArH^{\cdot -}$) could itself be protonated, especially in the presence of

$$\begin{tikzcd}
ArH + e^- \arrow[r, shift left] & ArH^{\cdot -} \arrow[l, shift left] \arrow[r, shift left, "e^-"] \arrow[d, "H^+"] & ArH^{=} \arrow[l, shift left] \arrow[d, "H^+"] & \\
& ArH_2\cdot \arrow[r, "e^-"] & ArH_2^- \arrow[r, "H^+"] & ArH_3
\end{tikzcd}$$

alcohols.[5,6] This produces the radical, $ArH_2\cdot$, which is expected to quickly take up another electron producing the same monoanion which would result from a dianion mechanism. This will be discussed in more detail below.

2. REACTIVITY

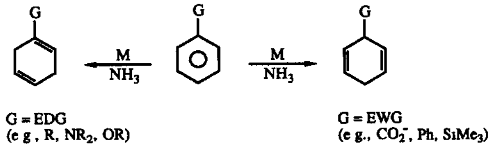
2.1. *Aromatic substrates*

Krapcho and Bothner-By investigated the kinetics of the metal–ammonia–alcohol reductions of benzene and substituted benzenes,[7] and determined the following rate expression:

$$-d(ArH)/dt = k(ArH)(M)(ROH).$$

As one might expect from this rate expression, reactions were faster with the more acidic alcohols. However, yields were better with less acidic proton sources (t-BuOH > EtOH > H_2O > NH_4Cl) as a result of the competitive reaction with the metal itself.

Relative rates as well as regiochemistry (see below) are affected by the nature of substituent groups which may serve to stabilize or destabilize the radical anion or, in the case of bulky groups, to inhibit solvation. Hence electron donors (EDG) tend to deactivate the ring (with the exception of anisole)[7] and direct reduction to produce 2-substituted-1,4-dihydroaromatics whereas electron withdrawing groups (EWG) have the opposite effect resulting in 1-substituted-1,4-dihydro products.



The energetics of the actual electron addition process have been considered in several ways.[6,8] In the gas phase this is simply the electron affinity (EA)

$$ArH + e^- \rightleftharpoons ArH^{\cdot -} \quad \Delta H^\circ = -EA.$$

where $-EA$ represents the energy liberated by the addition of an electron to an aromatic, ArH. In solution, however, solvation must be taken into account and the free energy change reflected by the half-wave potential of a reversible one-electron addition is given by:

$$\Delta G^\circ = (G^\circ_{ArH})_{gas} - (G^\circ_{ArH^{\cdot -}})_{gas} + (G^\circ_{electron})_{Hg} + (\Delta G^\circ)_{solvation}$$

where $(G^\circ_{ArH})_{gas} - (G^\circ_{ArH^{\cdot -}})_{gas}$ is equal to the electron affinity.

According to molecular orbital (MO) theory, EA is also related to the energy of the lowest

Table 1. Electron Affinities, Half-Wave Potentials and Calculated LUMO Energies of Selected Hydrocarbons

Molecule	EA_{gas} (eV)[a]	EA_{soln} (eV)[b]	$-E_{1/2}$ (V)[c]	$-m_{n+1}$[d]
Naphthalene	0.152	0.148	1.98	0.6180
Triphenylene	0.284	0.285	1.97	0.6840
Phenanthrene	0.308	0.307	1.94	0.6052
Anthracene	0.552	0.556	1.46	0.4142
Pyrene	0.579	0.591	1.61	0.4450
1,2-Benzanthracene	0.686	0.630	1.53	0.4523

[a] Taken from reference 12. [b] R S. Becker and E. Chen, *J Chem Phys.*, 45, 2403 (1966)
[c] Taken from reference 8a. [d] Where $\alpha + m_{n+1}\beta$ is the energy of the LUMO.[8a]

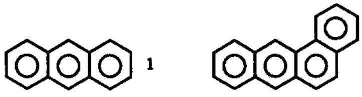
vacant molecular orbital,[6,8] and EA's calculated in this way correlate well with polarographic half-wave reduction potentials. Hence, observed electron

$$EA = \beta m_{n+1} + \alpha$$

affinities, half-wave potentials and calculated LUMO energies all bear a relationship to relative reactivities and some representative values are provided in Table 1.

In principle, this correlation should be valid whether radical anions or dianions are invoked since the same molecular orbital is involved.[6] However, consider the results with anthracene (**1**) and 1,2-benzanthracene (**2**) which suggest that anthracene may be slightly faster in reduction to the radical anion, but 1,2-benzanthracene forms the dianion more easily.[10] At any rate, if protonation of the intermediate comes from a weak acid like ammonia (see below), or even *t*-butyl alcohol, the dianion is expected to be important. For example, Szwarc *et al.*[11] studied the protonation of the anthracene radical anion in dimethoxyethane. When methanol, ethanol, isopropanol and water were used as protonating agents, the reaction was 1st order in radical anion. However, with *t*-butanol the expression became:

Half-Wave Reduction Potentials



1 **2**

	1	2
1st Wave	1915 mV	1960 mV
2nd Wave	2655 Mv	2615 mV

$$-d[ArH^{\cdot-}, Na^+]/dt = k_1[ArH^{\cdot-}, Na^+] + k_{11}[ArH^{\cdot-}, Na^+]^2$$

where $[ArH^{\cdot-}, Na^+]^2$ represents dianion protonation via the process

$$2ArH^{\cdot-}, Na^+ \rightleftharpoons ArH^{=} + ArH.$$

Thus in the reduction of polynuclear compounds we expect that dianion concentration will be the determining factor whether or not it parallels ease of radical anion formation.

A similar conclusion was reached by Paddon-Row *et al.*[12] who could not obtain satisfactory results in obtaining a linear relationship between reaction rates ($\ln k_0$) and the LUMO energies for several substrates. This was true whether these values were derived from Hückel or *ab initio* calculations. However, they pointed out that the observed rates (k_0) are dependent on both the equilibrium constant and the protonation rate,

$$k_0 = Kk_H$$

Table 2. Reaction of Alkali Metals with *t*-Butanol[a]

Metal	Iron (ppm)	Reaction Time (min.)
Li	0	253
Li	0.5	144
Li	1.0	72
Li	10.0	16
Na	0	255
Na	0.5	5
Na	1.0	4
K	0	68
K	0.5	2.5

[a] H L. Dryden Jr., G M. Webber, R R. Burtner and J A Cella, *J Org Chem*, 26, 3237 (1961).

and that k_H is dependent on many factors such as proton source, counter ion, solvent, etc. Similar conclusions were drawn by Birch *et al.*[13]

2.2. *Metals*

The heats of sublimation and ionization potentials decrease in the series $Li > Na > K > Rb > Cs$ and so reducing power should increase in this series.[11b] However the heats of solvation of the cations become important and, in fact, the reduction potentials in ammonia (−50°C) are: Li, −2.99; Na, −2.59; K, −2.73 V.[4] Krapcho and Bothner-By[7] found lithium to be most reactive (62.5) and potassium the least reactive (0.23) relative to sodium (1.0) in the reduction of benzene. However, the latter two values may be a bit low.[7b]

In addition, to being the most reactive, lithium also has the highest solubility in ammonia and is the least sensitive to impurities. The presence of trace amounts of iron (which could come from a steel cylinder of ammonia) catalyzes the reaction of alkali metals with ammonia

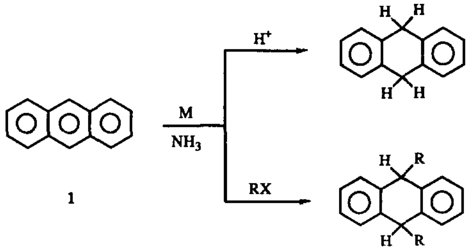
$$M+NH_3 \rightarrow M^+NH_2^- + 1/2H_2$$

and also accelerates the destruction of metal by alcohols. As shown in Table 2, this is a more serious problem with sodium or potassium than with lithium. The most serious problem with lithium would appear to be its reaction with nitrogen gas which makes alternative inert atmospheres desirable. Nonetheless, sodium can be quite satisfactory especially with polynuclear aromatics where the reductions are fast and therefore less sensitive to these other processes. In fact, sodium is often the metal of choice in cases where the lithium salts of the final monoanions may be protonated by ammonia leading to overreduction. This will be discussed in greater detail below.

3. NATURE OF THE INTERMEDIATES

Neither the original Birch conditions nor the Wilds–Nelson modification produce especially good results with polynuclear compounds, since the products of these reactions are generally themselves reducible under the reaction conditions, and the first real success in this area came from the Harvey group in 1969.[62] It turns out that a good understanding of the intermediates involved is critical to the selection of appropriate reaction conditions.

The earlier suggestions that dianions might be involved, coupled with the observation that the addition of alkyl halides to metal–ammonia solutions of anthracene leads to dialkylated products, prompted Harvey[3e] to suggest the intermediacy of $\mathbf{1}^=$ as a "stable" species in ammonia (where



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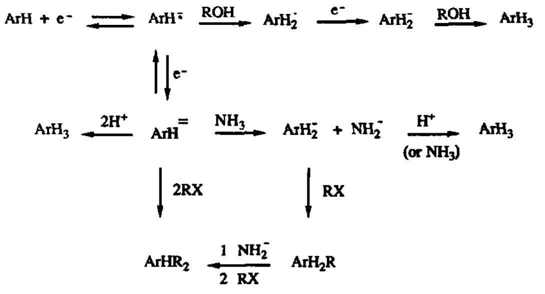
stable means resistant to protonation by ammonia). However, in a later study[14] with the reduction and reductive alkylation of biphenyl, Harvey's group suggested that dialkyl products may arise from monoanion alkylation followed by amide ion deprotonation and a second alkylation. We subsequently[15] investigated the behavior of naphthalene and anthracene, and suggested that this secondary amide reaction might well be the dialkylation route for most two, three and possibly four ring polynuclear aromatics.

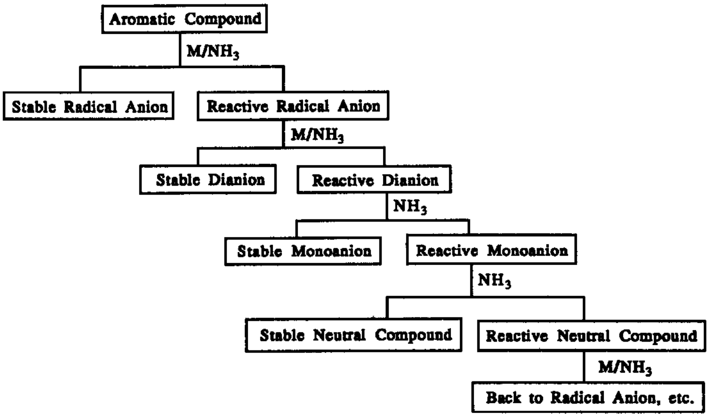
We can now provide a description (Scheme 1) that includes all of the possible pathways. The upper path illustrates the classical Birch reduction which uses alcohol to shift the initial (and often unfavorable) equilibrium. This is the case for benzene and many of its derivatives (except for highly activated compounds like benzoate, etc.), and the addition of alcohol is required for reduction to take place at all. With more active substrates, like polynuclear compounds, the radical anion $ArH^{\overline{\cdot}}$ may accept a second electron providing the dianion $ArH^{=}$. In contrast to the radical anion which is only weakly basic, the dianion is quite basic[16] and most two, three and four ring polynuclear dianions will be protonated by ammonia ($pK_a \sim 34$) to produce a monoanion. Larger systems or especially stabilized dianions (e.g. aromatic—see below) may persist in ammonia in which case the addition of alkyl halides produces dialkylation. However, dialkylation (and even trialkylation, etc.) can also arise via monoanions since the initial alkylation produces a neutral, dihydro product with acidic hydrogens (diphenylmethane has a pK_a of 33.5). Hence the number of alkyl groups incorporated during reductive alkylation is not a good indicator of the intermediate involved.

A more pictorial description is provided by Scheme 2, which also includes an additional possibility; protonation of the monoanion by ammonia. This is the expected course when dianion protonation by ammonia produces a monoanion which is only singly benzylic (or allylic). In such cases these anions are too basic (limited delocalization) to persist in ammonia (e.g. phenanthrene—see below). Of course monoanion protonation produces a neutral molecule and if it represents a reducible system, the cycle begins again.

We demonstrated the absence of dianions with sodium–ammonia solutions of anthracene in the following way.[15] If the dianion were present, then it must be in equilibrium with its corresponding



Scheme 1.



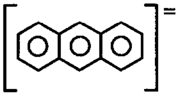
Scheme 2.

radical anion (Eq. 1) which, in turn, must be in equilibrium with the neutral aromatic, ArH.[11b] We prepared a sodium–ammonia solution of anthracene and quenched an aliquot portion with NH_4Cl

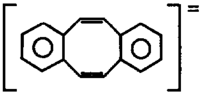
$$\mathrm{ArH} \underset{-M}{\overset{+M}{\rightleftharpoons}} \mathrm{ArH}^{\overline{\cdot}} \underset{-M}{\overset{+M}{\rightleftharpoons}} \mathrm{ArH}^{=} \qquad (1)$$

$$\mathrm{M} + \mathrm{NH_3} + \mathrm{Fe} \longrightarrow \mathrm{MNH_2} + 1/2\,\mathrm{H_2} \qquad (2)$$

producing 9,10-dihydroanthracene; this demonstrated that metal addition had taken place. Next we added iron ($FeCl_3$) which removes the metal by serving as a catalyst for its reaction with ammonia (Eq. 2). If the dianion had been present, the removal of the metal would have shifted the equilibria back to the left and final quenching of the reaction (NH_4Cl) would have produced anthracene. Instead we obtained only 9,10-dihydroanthracene. The validity of this approach was demonstrated by repeating the experiment with a system expected to be stable in ammonia. Dibenzocyclooctatetraene (**3**) was chosen since its dianion is aromatic, and, in fact, in this case the fully unsaturated **3** was recovered.



$\mathbf{1}^{=}$ Protonated by NH_3



$\mathbf{3}^{=}$ Persistent in NH_3

We also reasoned that if only monoanions were present, more rapid alkylation/quenching might trap them and reduce dialkylation. To this end, we carried out a number of experiments with naphthalene and anthracene where the substrate/metal/ammonia–THF solutions were inverse quenched into a large excess of alkyl halide in ether. This can be done simply as illustrated in Fig. 1. After the reaction is run for the desired period, a glass tube is attached leading to the alkyl

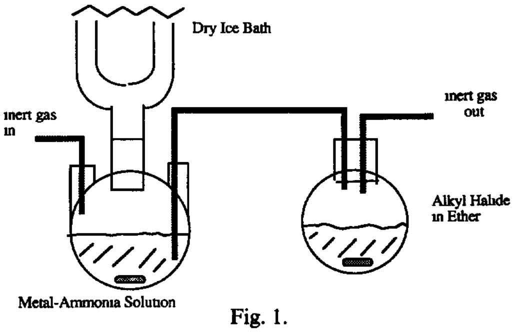


Fig. 1.

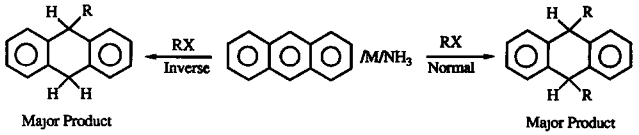
Table 3. Reductive Alkylation of Anthracene and Naphthalene[a]

Substrate	Metal	Temp °C	RX[b]	Quench[c]	—% Composition— ArH_2R	$ArHR_2$
Naphthalene	Na	-78	MeBr	Normal	20	80
Naphthalene	Na	-78	MeBr	Inverse	90	—
Naphthalene	Na	-78	EtBr	Normal	25	75
Naphthalene	Na	-78	EtBr	Inverse	90	9
Anthracene	Na	-78	MeBr	Normal	15	80
Anthracene	Na	-78	MeBr	Inverse	88	12
Anthracene	Na	-33	MeI	Normal	14	64
Anthracene	Na	-33	MeI	Inverse	95	5
Anthracene	Li	-78	MeI	Normal	58	42
Anthracene	Li	-78	MeI	Inverse	97	3
Anthracene	Li	-33	EtBr	Normal	40	60
Anthracene	Li	-33	EtBr	Inverse	97	3
Anthracene	Na	-33	EtBr	Normal	—	80
Anthracene	Na	-33	EtBr	Inverse	82	18

[a]Run in NH_3/THF (2:1) for 10-15 min [b]In the case of inverse quench with MeBr, the alkyl halide was condensed as a liquid into excess ether. [c]Inverse quench means that the reaction mixture was pumped under inert gas into excess RX in ether.

halide solution (the tube is not attached earlier due to the possible reaction of NH_3 vapor with RX). Lowering the tube beneath the surface of the ammonia solution pumps it across due to the pressure of the inert gas. (**Caution**: this may need to be done slowly especially if alkyl halide ether solution is not cooled to dry ice temperatures).

The results in Table 3 are dramatic! Whereas normal quenching produces substantial amounts of dialkylation, the inverse procedure affords the monoalkylated product, often in yields of 90–97%. An obvious question, of course, is whether or not the dialkylation (0–18%) during inverse quenching arises from small amounts of dianions. It was demonstrated that the amide deprotonation/alkylation could take place even under inverse quench procedures by adding $NaNH_2$ to the reaction mixture prior to quenching. Hence dianion need not be present to explain the small amounts of dialkylation. It is also interesting to note a decrease in dialkylation when lithium is used. This is presumably due to the lower solubility of $LiNH_2$ making it less effective in the subsequent deprotonation reaction as compared to $NaNH_2$.

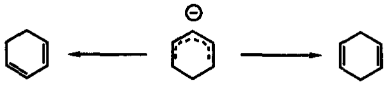


The irreversible protonation of dianions in ammonia was later demonstrated spectroscopically by Müllen *et al.*[17] For example, they found that anthracene gave an ESR spectrum characteristic of the radical anion upon initial contact with alkali metal in ammonia–THF, but that it disappeared with further metal contact. This latter solution gave a carbon NMR spectrum consistent with the monoanion and not the dianion. Furthermore hν irradiation of this latter solution did not regenerate an ESR spectrum as would be expected if dianions were present. Hence this study is quite consistent with the previous work described above.

4. REGIOCHEMISTRY

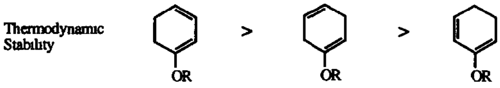
4.1. 1,3- *vs* 1,4-*Products*

The regiochemistry of this reaction has been of continuing interest to researchers. It is considered to be a classic example of kinetic vs thermodynamic control since the non-conjugated product **5** is favored over the conjugated one, **4**. Interestingly, Doering *et al.*[18] considered **4** to be "devoid of conjugated" in view of the rather small difference between the heats of hydrogenation for **4** (−53.64±0.29 kcal/mol) and **5** (−53.90±0.33 kcal/mol). However, base catalyzed equilibration



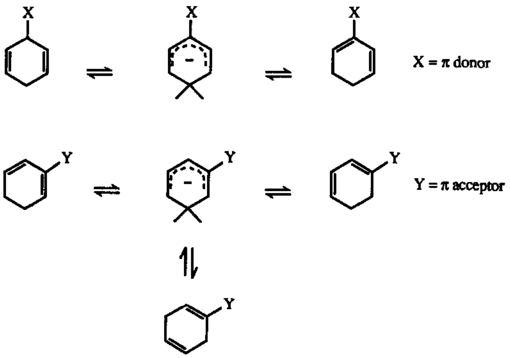
4 **5**

between **4** and **5** was demonstrated by Bates *et al.*[19] with the conjugated isomer favored by −0.41 kcal/mol (110°C). In any event, generalization is not possible since the alkoxy derivatives **6–8** show the perhaps unexpected order of thermodynamic stability with the nonconjugated isomer **7** midway between **6** and **8**.[20]

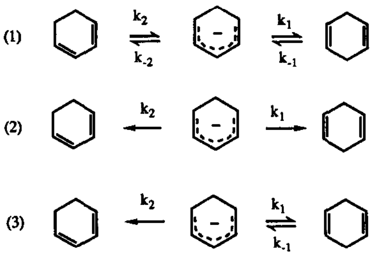


6 **7** **8**

Birch *et al.*[21] considered the effect of substituents on the relative energies of both the 1,3- and 1,4-isomers. Their STO-3G calculations invariably predict the 1-substituted-1,3-cyclohexadienes to be the most stable (CH_3, CN, NO_2, F, OH, NH_2) in agreement with the above illustration. They also provided a scheme for the interconversion of substituted cyclohexadienes and a somewhat simplified version is presented as Scheme 3. These authors suggest that these calculations may be used to predict Birch reduction products formed under equilibrium conditions. In fact, most metal–ammonia reductions do not involve such an equilibrium (shown as Eq. 1 in Scheme 4), but rather



Scheme 3.



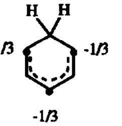
Scheme 4.

proceed via irreversible protonation to provide the nonconjugated product with a small amount (~1%) of the conjugated isomer (Eq. 2). That is, the products are related to the ratio k_1/k_2. However, let us consider the requirements for the establishment of the system described by Eq. 1. Protonation of radical anions by alcohols (i.e., benzenes) yields alkoxides and protonation of dianions by ammonia (i.e. polynuclears) gives amide. Since the latter is the far stronger base, we will focus on it.

The equilibrium conditions described by Eq. 1 require that both k_{-1} and k_{-2} have meaningful values, and these deprotonation reactions have been examined independently.[22] 1,4-Cyclohexadiene reacts with amide ion at −50°C to produce the anion, independent of counterion (K, Na, Li). However even after 3 h, the conjugated isomer did not react with $LiNH_2$ at all, and only slightly (< 15%) with $NaNH_2$. Reaction with KNH_2 was faster, but at −60°C even this reaction was found to be sluggish (~35°C).[22] Therefore we suggest that the occasional formation of conjugated products is not necessarily the result of thermodynamics, but rather reflects the kinetic scheme shown in Eq. 3. That is, as long as the conjugated isomer is formed in some amount, however small, it is formed irreversibly and hence will build up under conditions where the nonconjugated isomer is formed reversibly. This process is not expected for benzene or its unactivated derivatives since alkoxide, not amide, will be the strongest base present (alcohol cosolvents are necessary for reduction), and neither of the cyclohexadiene isomers will be deprotonated by alkoxide in ammonia at −33°C (or lower).[23]

4.2. *Protonation sites*

Product outcome is a result of the sites of protonation in (a) the initial radical anion or dianion, and (b) the final monoanion. With benzene itself, of course, only the latter process is important to regiochemistry, and it has been assumed that this protonation will occur at the position of highest electron density.[24] However simple Hückel MO theory predicts equal charge densities at the 1- and 3-positions (**9**) which suggests that the conjugated isomer (**4**) should be the major product in a 2 : 1 ratio (statistically corrected). However, more sophisticated treatments such as the Pople method do indicate higher charge density at the 3-position.[25] The correct product is also predicted by the "principle of least motion"[25] which considers average bond orders for the three canonical forms (**11**). Hence protonation at the 3-position would produce the least change in nuclear position.



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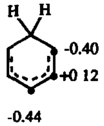

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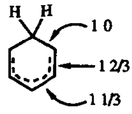

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Currently, calculated charge densities and/or HOMO coefficients for the radical anion or dianion (initial protonation) and the resultant monoanion (final protonation) have become useful in predicting product outcome.[6,8,26] This method, however, is most successful for alternant polynuclear hydrocarbons and may fail in other instances.

With benzenes, for example, Birch *et al.*[27] prefer the use of molecular electrostatic potentials (MEP). These electrostatic maps do a good job in describing the long to intermediate range interactions between the proton and the anionic species. As these authors point out, however, complications may arise at shorter distances due to polarization, charge-transfer, etc. The method of Paddon-Row *et al.*[12] may also be especially useful for benzenes. They consider the stabilization resulting from the interaction of the singly occupied MO of the anion radical (SOMO) with the OH σ^* MO of the alcohol.

A number of aromatic hydrocarbons are shown in Fig. 2 for which Dewar *et al.*[8a] have calculated the positions of initial (circle) and final (square) protonations based on SCF MO theory. Most of these predictions for which experimental results exist turn out to be correct although there are

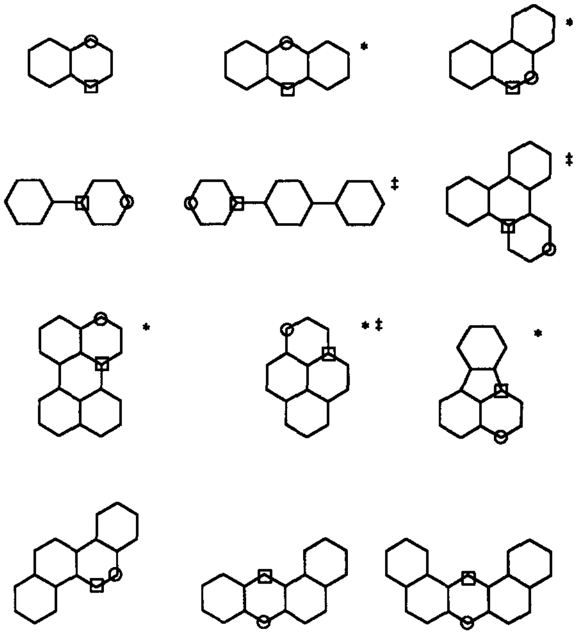
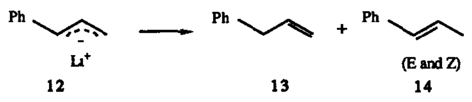


Fig. 2. Calculated reduction of aromatic molecules: circles denote initial and square final protonation sites. After ref. 8*a* which provides calculations for over 70 hydrocarbons. The asterisk indicates similar results calculated recently by a slightly different method (ref. 17), and the dagger means some disagreement with experimental results (see text below).

exceptions (see below). The position of initial protonation for those structures marked with an asterisk were more recently calculated by Müllen *et al.*[17] using the difference in π-electron energy between the dianion and the monoanion as the criterion for protonation. This method produced comparable results, at least where similar compounds were studied.

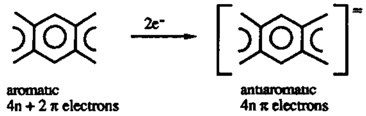
It must be emphasized that all of the methods discussed herein (as well as some others like ^{13}C-NMR chemical shifts) are based on the premise that protonation will take place at the position of highest electron density. This may not be true! We have suggested[28] previously that protonation of dianions may be influenced by the stability of the resultant monoanion as originally proposed by Barton *et al.*[29] (a proposal which does not appear to enjoy much current popularity). Certainly this and other effects such as solvation, counterion, etc. may play an important role. A recent, striking example is provided by 1-phenylpropenyllithium (**12**).[30] Protonation of **12** in TMEDA by phenylacetylene gives **13**/**14** = 8 : 92, whereas acetic acid under the same conditions gives 42 : 58. Clearly simple charge density (which predict **14**) does not provide an adequate explanation here.



5. STRUCTURE OF THE INTERMEDIATES

5.1. *Dianions*

It might be expected that the addition of a pair of electrons into the antibonding orbitals of six-membered rings would produce especially unstable structures since an aromatic ring is being converted into an antiaromatic[31] π system. Indeed Stevenson *et al.*[32] have suggested a value of 96.4

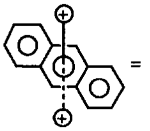


kcal/mol for the heat of formation of the benzene dianion $[(\text{Na}^+)_2]$. Moreover, the Rabinovitz group[33] has observed paratropic behavior in the NMR spectra of these dianions, and such ring currents are taken as evidence of antiaromatic character. Hence the report by Streitwieser *et al.* concerning the second acidity constant of 9,10-dihydroanthracene (DHA), is truly remarkable.[34,35] Deprotonation of DHA by cesium cyclohexylamide in cyclohexylamine provided a normal acidity constant ($\text{p}K^1_{\text{CsCHA}} = 30.3$). However, the second acidity constant was determined to be only 3.8 pK units higher! In fact, the monoanion is almost as acidic as diphenylmethane ($\text{p}K_{\text{CsCHA}} = 33.4$) which

is, of course, a neutral compound and does not lead to an antiaromatic system.

These authors suggest two reasons for the unexpected stability of the DHA dianion: delocalization and ion triplets. They point out that the antiaromatic character does not seriously offset the net stabilization provided by the delocalized, 16-electron π system. Furthermore, Streitwieser, has proposed ion triplets for this and other dianions.[35] A simple point charge model for such a dication salt of a dicarbanion is shown in Fig. 3. In fact a crystal structure of dilithioanthracene(TMEDA)$_2$ has been determined[36] and the lithiums were found on opposite sides of the ring plane with one over the central ring and the other under an end ring. Streitwieser pointed out that simple coulombic considerations would lead to a structure with the lithiums symmetrically arranged above and below the plane (i.e. as in Fig. 3). He suggested that such a structure may actually be present in solution, and the X-ray structure may be the result of crystal packing or Madelung forces.

More recently,[37] MNDO calculations were carried out for the naphthalene, anthracene and phenanthrene dianions. When the anthracene dianion was calculated using point positive charges, the minimum energy structure (**15**) corresponded exactly to that suggested by Streitwieser.[35]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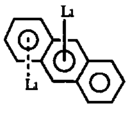

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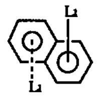

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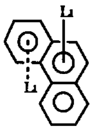


18

However, when lithium atoms were included, the low energy geometry more closely reproduced the X-ray structure[36] (**16**). Hence it was argued that **16** is inherently more stable and is likely to be the preferred arrangement in solution. Similar structures were found for naphthalene (**17**) and

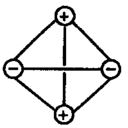
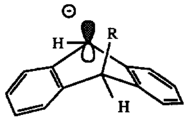


Fig. 3. Coulombic interactions for a point charge model of a dianion (after reference 35).

phenanthrene (**18**). In all cases a variety of arrangements were tested (i.e., Li atoms on the same side, one or both on edges, etc.) and the unsymmetrical over and under structures were always best, usually by several kilocalories. Phenanthrene, however, did show a second structure close in energy to **18** with the Li atoms over and under the outside rings (1.3 kcal/mol higher).

5.2. *Monoanions*

Structures for the monoanions require additional consideration since the site of unsaturation generated by dianion protonation means that coplanarity of the carbocyclic ring system may no longer be assumed.[38] In fact the 9,10-dihydroanthracene (DHA) monoanion was long regarded as a boat-shaped molecule with sp^3 hybridization at the anionic center.[39] However, in the light of proton[40] and carbon[41] NMR data, the structure would appear to be best viewed as sp^2 hybridized

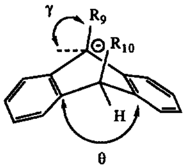


R = H, t-Bu

with substituents (e.g. *t*-Bu) causing some degree of puckering in the central ring. However, even with *t*-Bu the "*para*" carbons show a substantial upfield shift which must be attributed to extensive delocalization (which of course, falls off with ring puckering since the benzene rings lose their coplanarity).

More recently, the geometries of DHA anions were calculated by MNDO where γ in Fig. 4 refers to the deviation of R_9 from trigonal coplanarity, and θ refers to folding about the central ring (planar = 180°). The results suggest a substantial flattening of the central ring in each case with generally a smaller perturbation resulting from the position of the R groups (Table 4).

Thus anions of the 1,4-dihydro type are expected to have a strong tendency towards planarity (especially dihydrobenzenes and dihydronaphthalenes) except where substantial non-bonded interactions may develop through substitution patterns. Such a case may arise with a large polycyclic



9-anion, R_9 = alkyl, R_{10} = H
10-anion, R_9 = H, R_{10} = alkyl

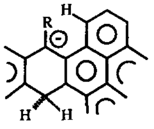
Fig. 4. DHA monoanion geometry.

Table 4. MNDO Calculated Geometries for 9-R- and 10-R-9,10-Dihydroanthracene Monoanions[a]

	angles in degrees[b]				
	9-anion		10-anion		Patent Hydrocarbon
R_9 or R_{10}[b]	θ	γ	θ	γ	θ
H	180	0	180	0	159
Me	161	1	165	4	153
Et	169	1	164	4	152
t-Bu	154	2	149	7	137
Ph	180	0	169	2	158

[a]From reference 42 [b]See Figure 4 for explanation

system (e.g. **19**). On the other hand, "1,2-dihydro" type products may also be produced (the actual numbering system is 9,10-dihydro in the phenanthrene case; **20**), and the parent 1,3-cyclohexadiene ring is not inherently planar as is 1,4-cyclohexadiene.[43] Hence **20** presumably undergoes a rapid ring inversion when unsubstituted (i.e. $R_9 = R_{10} = H$),[44] but may adopt a preferred conformation to allow for the known pseudoaxial preference of groups at R_{10} (as shown).[45] Moreover, the hybridization at C9 is not known; sp^3 hybridization was suggested to account for reduction stereochemistry[44] (when $R_9 = R_{10}$ = alkyl, the protonation of **20** gives *cis* products), but the sp^2 model (as illustrated) would work as well. It is expected, of course, that the nature of substitution either at C9/C10 or on the aromatic rings will greatly affect geometry, and also, perhaps, hybridization.



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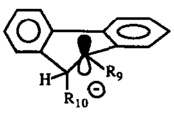


20

5.3. *Ion pairs and aggregates*

Finally, some attention should be given to questions concerning aggregation and ion pairing. Nothing is known about the possible presence of dianion or monoanion aggregates in ammonia. However, aggregation is expected to diminish at low concentrations and with highly delocalized anions,[46] and this description fits most metal–ammonia reductions. Moreover even if present, the aggregates are expected to be less reactive[47] and so their properties will be unimportant to the eventual outcome of the reactions.

Streitwieser,[35] has suggested contact ion pairs for the dianion triplets and this would appear to be quite reasonable in view of the dinegative charge. The monoanions are likely to vary from contact ion pairs to solvent separated ion pairs with the latter favored by systems with more extensive delocalization.

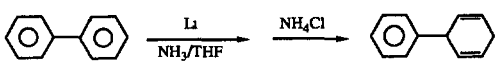
The nature of ion pairing for THF solutions of the DHA monoanion has been investigated by NMR and UV spectroscopy,[48] and it would appear to exist as a mixture of contact and solvent separated ion pairs. However, ammonia is a more powerful solvent and taken with the fact that DHA–Li and DHA–Na show very similar carbon NMR shifts in NH_3/THF,[17] we favor solvent separated ion pairs.

6. THE REDUCTION OF SELECTED AROMATICS

Thus far, this report has tried to provide insight into the fundamental nature of the metal–ammonia reduction of aromatic compounds. A number of examples follow, but no attempt is made to provide a comprehensive survey due in part, to the vast number of compounds that have been reduced by this method. Moreover, these examples will be limited to multi- and polynuclear aromatics and the reader is referred to the recent, thorough review by Hook and Mander[3h] for applications to a wide variety of benzene derivatives. In addition, this report will not include reduction in other solvents such as HMPA, glyme, THF, etc. or amines.

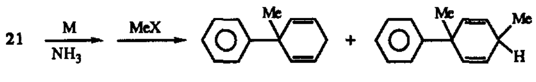
6.1. *Biphenyl and the terphenyls*

The reduction product of biphenyl (**21**) had been a matter of controversy[3e] until 1968 when the isolation and identification of **22** was reported. This reaction is best accomplished with Li over Na



21 **22**

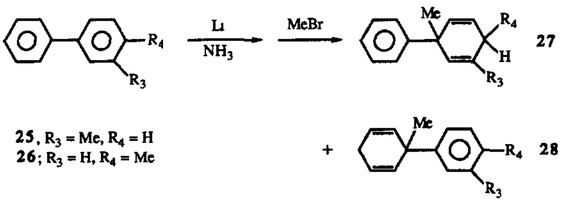
and requires rapid quench and quick isolation.[3e] Most dihydrobenzenes are relatively sensitive compounds and tend to rearomatize (among other things). This is especially true for oils like **22**. Reductive methylation can also be accomplished with **21** providing both mono- and dimethylated



23 **24**

products (**23** and **24**) with the ratio of **23** : **24** being quite sensitive to the metal and other experimental conditions.[49]

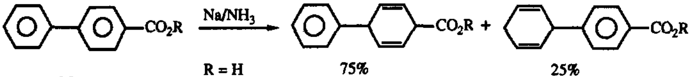
The reductive methylation of 3- and 4-methylbiphenyl[50] is especially interesting since a methyl substituent is generally considered as deactivating in this reaction and so exclusive reduction in the non-methylated ring might be expected. This is not the case, however, since **25** produces 80% reduction in the methylated ring (**27**; R_3 = Me, R_4 = H) and **26** shows only slight regioselectivity



25, R_3 = Me, R_4 = H
26; R_3 = H, R_4 = Me

(**27**:**28** = 45/55; R_3 = H, R_4 = Me). This, of course, raises a question about the stabilizing vs destabilizing effect of methyl substituents on anions,[50,51] and it appears that methyl may well be stabilizing when it is positioned on a carbon which bears little negative charge but is highly olefinic.[50]

The carboxylate group is generally regarded as one of the strongest activating groups[3,7] but surprisingly, biphenyl-4-carboxylic acid (**29**) reduced to give a mixture of products.[51] However,



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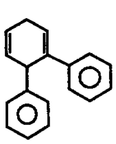
R = H	75%	25%
R = t-Bu	100%	0%

complete regioselectivity can be achieved by use of the *t*-butyl ester; aromatic carboxylic esters can be reduced in the ring efficiently without competition from ester reduction/dimerization if 1.5 eq of a proton donor (e.g. H_2O) is included.[53]

o-Terphenyl and *m*-terphenyl each reduce in the central ring to produce **30** and **31**. On the other hand, *p*-terphenyl gives a mixture of two dihydro products, **32** and **33**, and the ratio is quite sensitive



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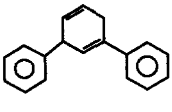

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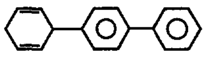

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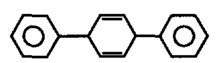


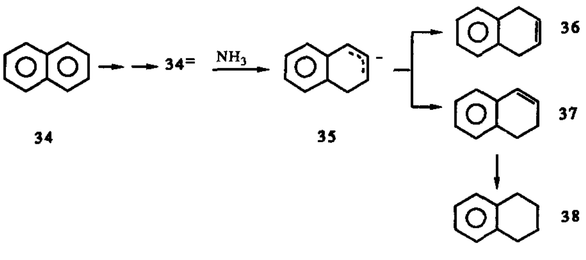
33

to conditions.[54] When H_2O is used instead of NH_4Cl as a quench, the inner ring product is repressed. On the other hand inner ring reduction is increased in the order Ca < K < Na < Li. Ion pair association, coupled with a relatively stable dianion which is only slowly protonated by ammonia was suggested as an explanation for this unusual behavior.[54]

6.2. *Naphthalenes*

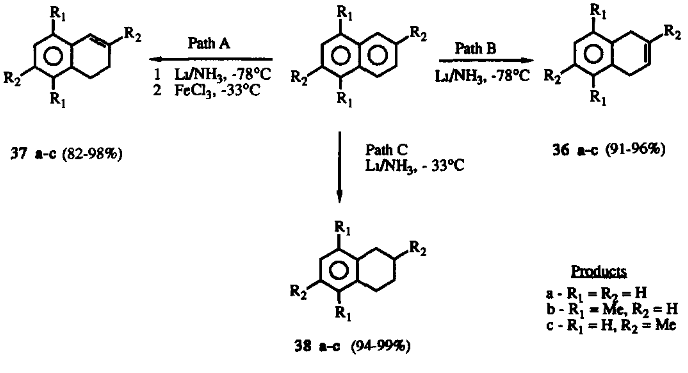
A great number of naphthalenes have been reduced by metal–ammonia solutions as summarized in the review by Harvey.[3e,55] More recent studies, however, have provided considerable mechanistic insight.[15,22]

The reduction of naphthalene itself (**34**) is highly dependent on the conditions.[15] The use of Na at −78°C with a rapid NH_4Cl quench produces the best results providing 96–97% **36**, 1–2% **37** and 2% **38**. With Li at −78°C, or Na at −33°C, the yield of **36** drops to *ca* 80% with a corresponding increase in **38**. We believe that with Li, or Na at increased temperatures, the monoanion **35** is itself slowly protonated by ammonia to give **36** and **37** in a *ca* 98 : 2 ratio. However, **36** is formed reversibly under these conditions and **37** is formed irreversibly (this has been demonstrated separately).[22] Of course **37** is quickly reduced in the presence of metal–ammonia solutions and shows up as **38**.



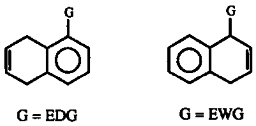
This understanding of the mechanism has allowed the development of a synthetic scheme[22] for the selective synthesis of 1,4-dihydro, 1,2-dihydro or 1,2,3,4-tetrahydro products (Scheme 5). In path A, a normal reduction is carried out with careful temperature control at −78°C. Under these conditions (< 30 min), the monoanion **35** persists. $FeCl_3$ is then added to destroy active metal and convert it to $LiNH_2$, and the temperature is allowed to rise to −33°C whereupon **35** is protonated by ammonia to **36**. Under these new conditions (i.e. in the presence of $LiNH_2$), **36** is isomerized to **37** which is not reduced since the metal has been removed. Path B represents the "normal" reduction which works well even with Li if relatively short reaction periods (20–30 min) are used together with good temperature control and rapid quench. Finally, path C combines the use of excess metal with higher temperatures and the slowly (but irreversibly) formed **37** is eventually reduced (reaction times of 2 1/2 h were required for the methylated derivatives).

The effect of α-substituents on the reduction of naphthalene derivatives is generally straight forward. Electron donating groups (EDG) result in reduction in the unsubstituted ring while electron

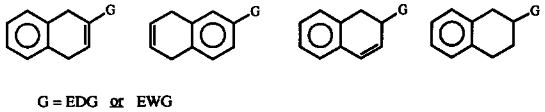


Scheme 5.

α - Substituents

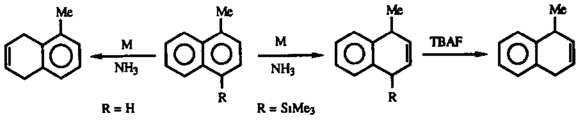


β - Substituents



withdrawing groups (EWG) promote reduction in the same ring. On the other hand β-substituents are not so well behaved and sometimes the EDG/EWG approach fails to predict which ring will be reduced. Often mixtures are obtained which sometimes include substantial amounts of tetrahydro products. The latter arise, no-doubt, due to the formation of 1,2-dihydro products which are readily reduced further.[3]

An attempt has been made to control regiochemistry in this reaction through the use of a trimethylsilyl substituent.[56] Hence 1-methylnaphthalene (**38**, R = H) reduces in the non-methylated ring as expected, but the addition of a trimethylsilyl group (**38**, R = $SiMe_3$) forces reduction in the same ring. Subsequent removal of the silicon with tetrabutylammonium fluoride (TBAF) results in a "Misoriented Birch Reduction." Similarly 2-methylnaphthalene (**39** = R = H) provides a mixture of dihydro products but the addition of a trimethylsilyl group (**39**, R = $SiMe_3$) to the unsubstituted ring controls regiochemistry completely.



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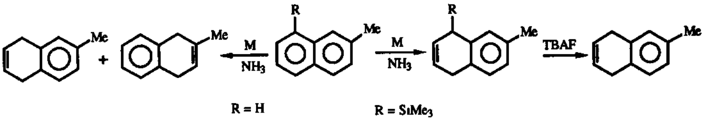
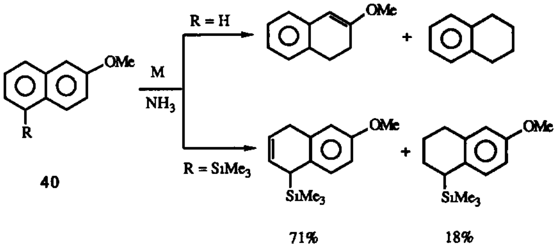


39

The same technique[56] was applied to 2-methoxynaphthalene where normal reduction techniques fail (**40**).[3e] Once again, silicon controlled the reduction although a greater amount of tetrahydro product was formed in this case. Nonetheless 6-methoxy-1,4-dihydronaphthalene was produced in an overall yield of 50–60% by this process.



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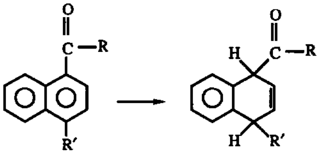
The stereochemical outcome of the reduction of a number of 4-substituted 1-naphthyl ketones and carboxylate esters has also been investigated.[57] There is not much stereoselectivity although we



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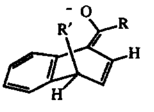
R	R′	cis	trans
O-t-Bu	Me	40	60
O-t-Bu	Et	40	60
Me	Me	60	40
Me	Et	70	30
Me	i-Pr	75	25

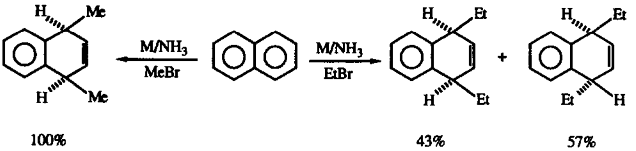
do note a *cis* preference for the ketones which rises to 75% for R′ = *i*-Pr in contrast with *trans* preference for the esters. A possible explanation is that the ester monoanion (enolate **42**, R = O-*t*-Bu) has a relatively flat six-membered ring so that a slight preference for protonation on the side opposite to R′ exists whereas the ketone monoanion (**42**, R = Me) has more enolate character resulting in a somewhat puckered ring. In such a case the *o*-aryl and vinyl protons tend to block underside attack.



Steric interaction (ring puckering) increases with increased enolate character

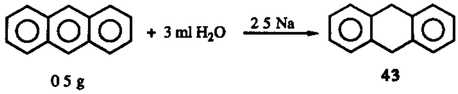
42

Naphthalene can also be reductively dialkylated when Na, but not Li, is used as the electron source.[58] Only monoalkylation is observed in the latter case since the less soluble $LiNH_2$ is not effective in promoting the subsequent deprotonation/alkylation process (see above). It is interesting that the stereochemical outcome goes from stereospecificity with methylation (100% *cis*) to only minor stereoselectivity with ethylation (and excess *trans* at that).[59] Once again, subtle changes in ring geometry are suspected.[59]



6.3. *Anthracenes*

Anthracene is one of the easiest compounds to reduce since it appears to be relatively insensitive to reaction conditions. We have found[15] that, in contrast to the general admonishments,[3] anthracene is converted to 9,10-dihydroanthracene in essentially quantitative yield without prior purification of the ammonia or cosolvent and with a wide variation in metal concentration and stoichiometry



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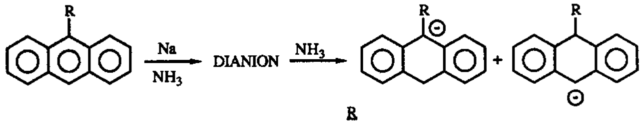
provided short reaction times and rapid quenching are employed. We have since learned[57] that anthracene (0.5 g) in NH_3/THF containing 3 ml H_2O is also quantitatively reduced (i.e. H_2O is present before metal is added—no extra metal above the usual 0.5 mmol excess is employed).

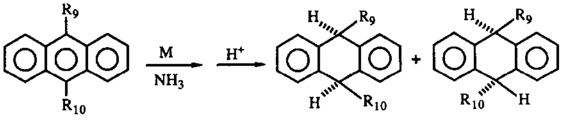
In contrast with naphthalene, the regiochemistry of reduction in anthracenes is not easily affected by substitution. This is due to high electron density at the 9- and 10-positions. However, the site of



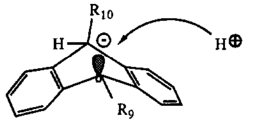
R		
Me	70%	30%
n-Bu	91%	9%
Bz	57%	43%
i-Pr	90%	10%
Ph	100%	0%

initial protonation of the dianion in a series of monosubstituted anthracenes has recently been studied[60] (by methylation of the resulting monoanion), and the results are somewhat surprising since substantial amounts of what might be considered to be the least stable anion are produced. In fact, MNDO calculations predict the 9-R-9-anions to be more stable than their 10-anion counterparts for R = Me, Et and *i*-Pr (and also Ph).[60] The calculations are not so clear on the dianion protonation step, however, since the electron densities are highest at C9 (i.e. predicts the 10-anion) but the HOMO coefficients are largest at C10 (predicts the 9-anion). It has been suggested that these latter values are more important.[61]

The reduction of 9,10-disubstituted anthracenes has attracted considerable attention[3e] since the question of product *cis*/*trans* geometry arises. Harvey *et al.*[62] reported *trans* stereospecificity for a number of cases aside from dimethyl which provided a nearly equal *cis*/*trans* mixture. They suggested a boat-shaped, sp^3 hybridized monoanion (**46**) with R_{10} in a pseudoaxial position and R_9 pseudo-equatorial. Hence, "topside" protonation would produce the *trans* isomer. However, these early studies involved only primary R groups and it was learned later that larger groups (isopropyl, *t*-butyl, etc.) could result in considerable amounts of *cis* products.[63] These results together with the ^{13}C NMR data indicating sp^2 hybridization[41] led us to suggest the model **47** where variable folding of the ring results from the nature of R_9 and R_{10}. Hence modest folding causes the topside of the p-orbital to be more accessible since the bottom lobe is partially blocked by the *ortho*, aryl protons. With large folding, however, the bottom lobe is pushed outward making it more accessible while at the same time the top lobe begins to experience a transannular steric interaction.[64]



44 **45**



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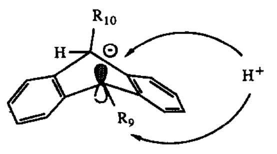
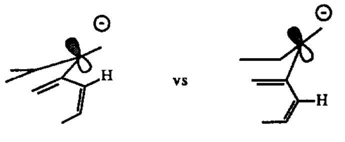
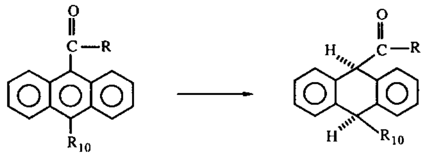


47



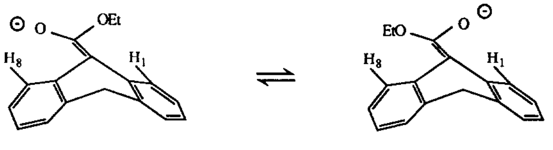
A number of carbonyl derivatives were also investigated and in this case only *cis* products were formed. On the surface this may appear to be in conflict with the above results since acetyl and methyl, for example, are small groups. On closer inspection, however, these results can be explained nicely by the model (**47**).



R = OEt, Ot-Bu, Me
R_{10} = Me, Et

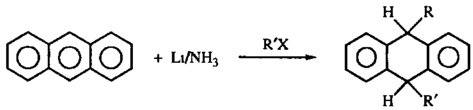
cis only

In fact the carbonyl groups behave as large groups in this case due to their high enolate character. This was demonstrated by the decoalescence of H_1 and H_8 at 0°C indicating the slow interconversion of **48** and **48′**. This structure is highly folded due to the steric interaction of O^-/OEt with H_1/H_8.



48 **48′**

As mentioned above, anthracene undergoes reductive alkylation to furnish 9,10-dialkyl DHAs when the alkyl halide is added last. High *cis* stereoselectivity was found[65] for methylation and ethylation (>80%) and it was also assumed by analogy for isopropylation although the latter reaction was subsequently recognized to favor the *trans* isomer.[63] A considerable number of papers were to follow which dealt with the alkylation of 9-alkyl-10-metallo-9,10-dihydroanthracenes both in ammonia as well as other solvents.[66]



R = Me, Et, i-Pr, etc

We recently suggested[66,67] that alkylation stereochemistry is quite sensitive to geometry changes in the DHA central ring (cf. above discussion on protonation) as well as to a simple steric effect between R and R′X. However, these two effects work in opposition (Fig. 5). Hence ring folding (large R) makes the topside (syn attack) more accessible, and when R′X is small, *cis* products are produced. However if both R and R′X are large (i.e. *i*-Pr) the steric interaction disfavors syn attack and *trans* products predominate.

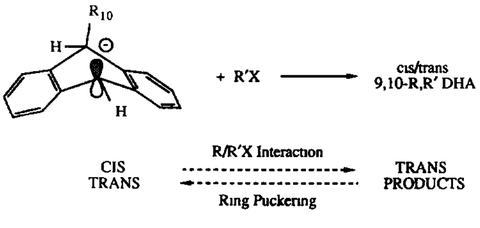
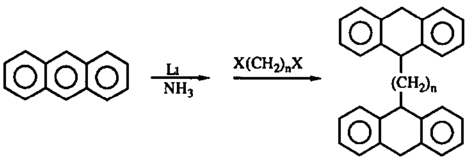


Fig. 5. Alkylation of 9-alkyl-10-metallo-9,10-dihydroanthracene.

Recently Müllen[68] has discussed the reductive alkylation of anthracene using α,ω-dihaloalkanes. The normal lithium–ammonia reduction followed by halide addition produces a dimer (**49**) and eventually polymer products (i.e. amide deprotonation of **49**). Interestingly, similar reaction of the anthracene dilithio salt in THF produces cyclic products (**50**).



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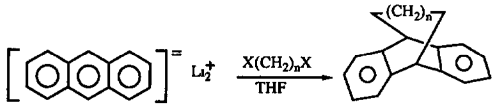
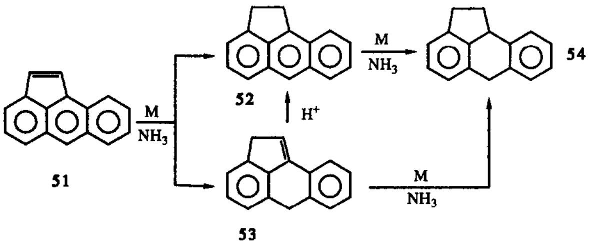
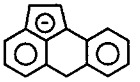


50

We recently[69] examined the reduction behavior of aceanthrylene (**51**) which might be expected to easily reduce all the way to the tetrahydro product **54**. Instead a single dihydro product resulted (**53**) which was isomerized by acid to the known ethano anthracene **52**, and could also be further



reduced to **54**, a compound we have previously obtained by the reduction of **52**. Presumably the reason that reduction does not readily proceed past the initial stage is the formation of the aromatic monoanion **55**.



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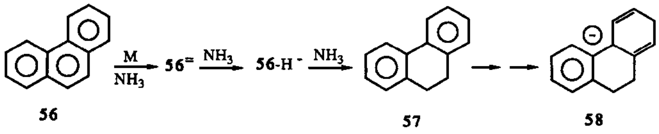
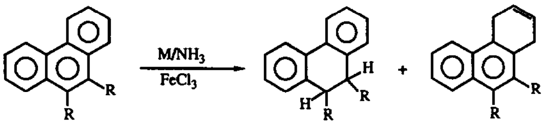
6.4. *Phenanthrenes*

The reduction of phenanthrene (**56**)[70] is complicated by the fact that even the monoanion in this

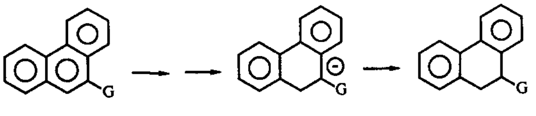


case is protonated by ammonia and so the initial product, 9,10-dihydrophenanthrene (**57**), is further reduced until the "stable" monoanion **58** finally results (as evidenced by its methylation[44] and NMR[17] behavior). However the presence of iron salts greatly attenuates this overreduction and so 9-Me, 9-Et, 9,10-diMe and 9,10-diEt derivatives provide reasonable (70–85%) yields of 9,10-dihydro product (**60**). Interestingly in contrast to anthracene, dialkyl substitution in phenanthrene (**60** R = Me or Et) causes some amount of reduction in the adjacent ring (i.e. ~10% **61**).



59 60 61

With a single stabilizing substituent, however, phenanthrenes may be reduced in high yield (>90%) without the use of iron salts.[45] This is presumably due to the additional stabilization of the monoanion **62**.

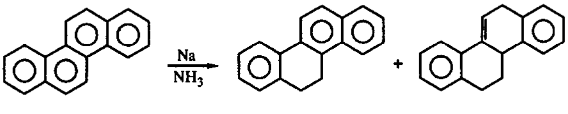


G = CN, CO_2R, Ph, Me_3Si

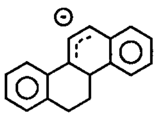
62

6.5. *Compounds with four fused rings*

Like phenanthrene, the reduction of chrysene (**63**) is also difficult to control. However by using Na over Li or Ca, and adding it in pieces slowly, Harvey[70] was able to achieve good yields of **64**. Once again the problem appears to be protonation by ammonia until the monoanion **66** is finally formed.

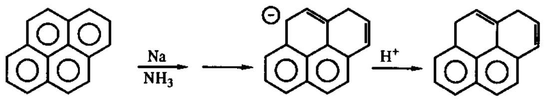


63 64, 82% 65, 9%



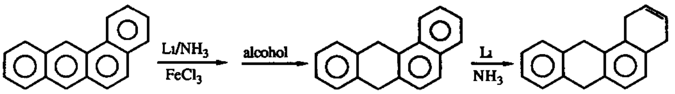
66

Pyrene (**67**) is an interesting case since five different dihydro products are possible (and equivalent by HMO theory).[71] In fact, a single product (**69**) is produced. Once again a monoanion is the persistent intermediate in ammonia as demonstrated by NMR.[72]



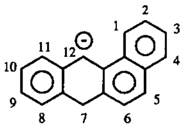
67 68 69

Harvey and Urberg[73] investigated the reduction of benz[a]anthracene (**70**) and encountered some difficulty in controlling the reaction to stop at **71**. Ultimately they found that the use of $FeCl_3$

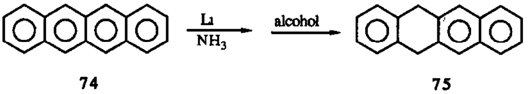


70 71 72

and extended reaction periods gave good results. The conversion of **71** to **72** on the other hand proceeded nicely and did not require the use of iron salts. This case is quite instructive. The problem is the use of alcohol in the quench.[74] Based on our earlier discussion one would expect that the use of Na at −78°C for short reaction periods would produce **73** as a stable monoanionic species (or alternatively, the 7-anion). However, if **73** is protonated in the presence of active metal (i.e. use of alcohol cosolvents), then the product (**71**) is itself easily reduced. The isomeric tetracene (**74**) undergoes similar reduction to produce **75** in 80% yield. In this case, however, no problem with overreduction was noted.[62]

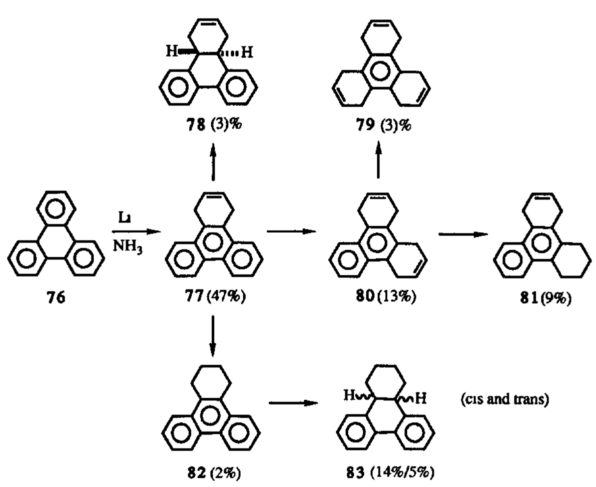


73

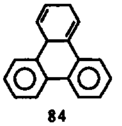


Formally triphenylene (**76**) has four fused rings although the center ring is more or less empty. At least eight products have been isolated from its lithium–ammonia reduction with **77** as the major product (47% ; a yield of 67% was obtained by a decrease in the amount of lithium used) together with a number of additional tetra- and hexahydro compounds (**78**–**83**).[75] The origin of each of these latter products shown in Scheme 6 is easily understood: **77** either reduces as a phenanthrene, or undergoes isomerization/reduction like a naphthalene. Similar "naphthalene like" behavior of **80** accounts for **79** and **81**.

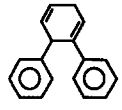
The formation of **77** itself, however, is somewhat of a puzzle. MNDO calculations suggest that the triphenylene dianion should protonate at the β-position which would afford **84**.[75] Such "biphenyl



Scheme 6.

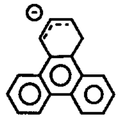


84



30

type" behavior was discussed above for *o*-terphenyl (**30**). This may indeed be a case where monoanion stability is the controlling factor[29] since protonation at the α-position produces an anion (**85**) with greater phenanthrene type character[76] than that resulting from β-protonation (**86**).



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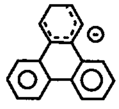

86

7. CONCLUSION

The reduction of polynuclear aromatics containing two to four rings (and maybe higher) by alkali metals in ammonia produces highly basic dianions which are protonated by ammonia to afford monoanions. In most cases, the monoanions will persist in ammonia until a stronger proton source is added, but this is not without exception (e.g. phenanthrene). The monoanions are most resistant to protonation when sodium is used instead of lithium, and at lower temperatures [lower temperatures favor solvent separated ion pairs which protonate more slowly (but alkylate faster)].

Although necessary for benzene and most of its derivatives except highly activated ones, alcohols should not be used as cosolvents or quenching agents since the neutral compounds so produced will themselves be reduced by any excess metal present. Of course the excess metal (and some excess metal always appears to be necessary) can be destroyed by $FeCl_3$ in which case alcohols can be used. However, this requires a longer reaction period which is not necessary if good quenching agents are used. Reverse quench into aq. NH_4Cl produces a very fast quenching procedure which may be useful for especially sensitive substrates.

Reductive alkylation may also be achieved by adding alkyl halides or sulfates to the metal–ammonia solutions of polynuclear aromatics. However the number of alkyl groups incorporated may vary from one to more than two depending on the circumstances. If the neutral compound produced by alkylation of the monoanion has acidic hydrogens (e.g. doubly benzylic), then amide ion deprotonation can result in a second alkylation. Moreover this process can repeat. It is less likely with lithium over sodium or potassium due to the experimentally observed, decreased kinetic basicity of lithium amide which may be due to decreased solubility.

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[38] Generally the dianions that have been studied by NMR show diatropic or paratropic ring currents which suggest planarity. This may not always be true, however.

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