γ-Ethyl L-glutamate (Sigma) was recrystallized twice from water–ethanol. Methyl Cellosolve was purified by treatment with alumina and then Na_2CO_3 and was finally distilled from calcium hydride. **Diethyl L-glutamate hydrochloride** (Mann) and buffer salts were commercial products which were used without further purification.

Kinetics. The hydrolysis and/or aminolysis of γ-ethyl glutamate, diethyl glutamate, *O*-acetylserine, and ethyl pyrrolidone-5-carboxylate were studied by measuring the rate of proton release with a Radiometer TTTlc pH-stat, equipped with a PHA 630 scale expander, a SBR 2c titrigraph, and a Metrohm AC 9100 combination electrode. Reactions were initiated by the addition of 10–200 μL of 1 N NaOH to 10 mL of reaction solution which had been previously equilibrated at the desired temperature. The concentration of reactant was ca. 5×10^{-3} M. Carbon dioxide was excluded from the reaction vessel by maintaining a gentle flow of argon or nitrogen (previously bubbled through saturated aqueous NaOH) over the surface of the reaction mixture. Reactions were generally followed to completion (>6 half-lives) except for very slow reactions, which were followed for 2–3 half-lives. Less than 0.4 mL of titrant was used in each case.

First-order rate constants were generally calculated from semilogarithmic plots of (volume of base added at infinite time − volume of base added at time, *t*) vs. time. For very slow reactions, the infinity value was obtained by a modified Guggenheim procedure.[46]

Rate measurements with γ-ethyl glutamate and diethyl glutamate were carried out at 40 °C, in aqueous solution, ionic strength 0.5, maintained with added KCl. In the experiments designed to determine the effects of phosphate buffer on the aminolysis of γ-ethyl glutamate, the ionic strength was kept constant at 0.9, so that phosphate buffers at concentrations up to 0.3 M could be used. The aminolysis of *O*-acetyl serine was studied at 30 °C, $\mu = 0.5$ (KCl). The rates of hydrolysis of ethyl pyrrolidone-5-carboxylate were determined at 40 °C, in 10% acetonitrile–water (v/v), $\mu = 0.5$ (KCl).

The formation of glutamic acid or serine as a result of the hydrolysis of the amino esters was determined after completion of the reaction by assay with ninhydrin.[47] The almost quantitative conversion of *O*-acetyl-L-serine to *N*-acetyl-L-serine was verified by comparison of the optical rotatory dispersion curve of the reaction product ($[\alpha]_{230}$ −1570° ± 100, in the pH range of 8–10) to that of authentic *N*-acetyl-L-serine ($[\alpha]_{230}$ −1590° at pH 8.3).

pK_a values for the amino groups of γ-ethyl glutamate, diethyl glutamate, and *O*-acetylserine were determined under the conditions of the kinetic studies by partial neutralization of the protonated amino group and rapid measurement of the pH (extrapolating the pH readings to zero time, if necessary).

Acknowledgment. We are grateful to Dr. J. A. Shafer (University of Michigan) for providing us with the numerical values of the rate constants for the lactonization of the hydroxy amides **13** and **14**. M.C. was the recipient of a National Research Service Award from the National Institutes of Health.

Registry No. 4, 76529-79-8; ethyl L-pyrrolidone-5-carboxylate, 7149-65-7; L-glutamic acid, 56-86-0; *O*-acetyl-L-serine hydrochloride, 66638-22-0; *N*-acetyl-L-serine, 16354-58-8; γ-ethyl-L-glutamic acid, 1119-33-1; *O*-acetyl-L-serine, 5147-00-2.

(46) Swinbourne, E. S. *J. Chem. Soc.* **1960**, 2371–2372.

(47) Rosen, H. *Arch. Biochem. Biophys.* **1957**, *67*, 10–15.

(48) Narita, K. *Biochim. Biophys. Acta* **1958**, *30*, 352–359.

(49) Akabori, S.; Otani, T. T.; Marshall, R.; Winitz, M.; Greenstein, J. P. *Arch. Biochem. Biophys.* **1959**, *83*, 1–9.

(50) Glushkov, R. G.; Granik, V. G.; Volskova, V. A.; Chernov V. A.; Minakova, S. M. *Pharm. Chem. J. (Engl. Transl.)* **1974**, *7*, 688–690.

(51) We have pointed out previously[52] that rate expressions derived for mechanisms such as that of *Scheme* II give rise to identical calculated curves through the use either of a set of constants (P^0, P^-) or of the set ($1 - P^0$, $1 - P^-$). In the present instance, this means that the data of Figure 3B can equally well fit eq 12 with the assumption that $P^0 \simeq 0$ and $P^- = 0.985$. This assumption, however, is equivalent to saying that the neutral intermediate T^0 breaks down exclusively to amide ($k_3' \gg k_2'$) and T^- gives mainly amine, which is contrary to earlier results with closely related systems.[3,10,32]

(52) Hershfield, R.; Schmir, G. L. *J. Am. Chem. Soc.* **1973**, *95*, 7359–7369.

Metal–Ammonia Reduction: Effect of Methyl Substituents and a Question Concerning Protonation Sites in Dianions

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Received October 28, 1980

The effect of substituents on Birch reductions and other metal–ammonia processes has received considerable attention. Since the intermediate(s) is negatively charged, activation and orientation effects have been dealt with in terms of electron donation or withdrawal of substituents. The methyl group displays somewhat irregular behavior in naphthalenes and biphenyls, and an explanation is offered in terms of methyl location on a charge-bearing or non-charage-bearing carbon in the intermediates. The observation is also made that protonation of dianions (produced by electron addition) always seems to lead to the most stable monoanion. Reasons for this are discussed.

The addition of alkali metals to aromatic compounds in liquid anhydrous ammonia, a reaction known generally as the Birch reduction,[1] provides an important method for the reduction of aromatic rings. Initial electron addition produces a radical anion, which in the case of many benzene derivatives requires the presence of a proton source (e.g., alcohol) to shift the equilibrium to the right (Scheme I, lower path). In the case of polynuclear compounds (and some highly activated benzenes), a second electron addition may take place to produce a dianion which is highly basic,[2] and except for cases of unusual stability (e.g., aromatic dianions, etc.), protonation by ammonia then takes place to produce a monoanion[3] (Scheme I, upper path). If this monoanion is sufficiently delocalized (usually two pathways are necessary such as

(1) (a) Birch, A. J. *Q. Rev., Chem. Soc.* **1950**, *4*, 69. (b) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Los Angeles, CA, 1972. (c) Harvey, R. G. *Synthesis* **1970**, *4*, 161.

(2) Szwarc, M., Ed. "Ions and Ion Pairs in Organic Reactions"; Wiley-Interscience: New York, 1972.

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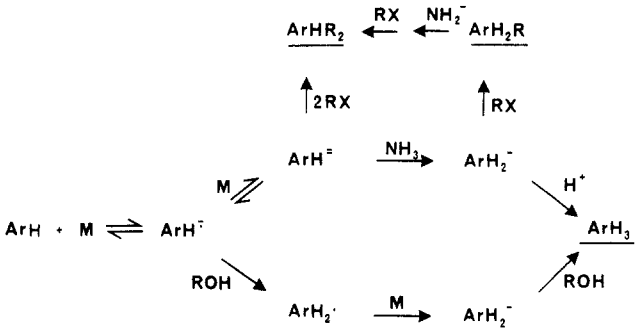
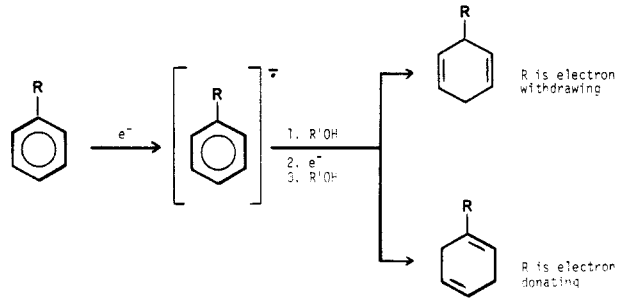
Scheme I



Scheme II

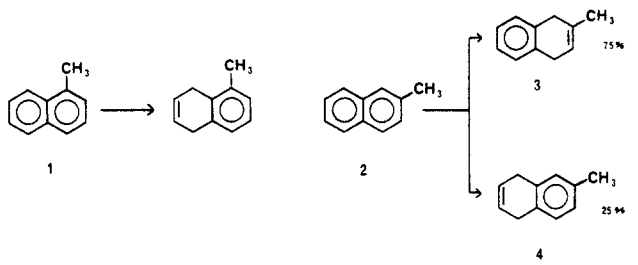


doubly benzylic, etc.[3]), it is resistant to a second protonation by ammonia and can be alkylated or protonated by the addition of suitable reagents (RX, ROH, H_2O, NH_4Cl, etc.). Secondary proton abstraction can produce substantial amounts of dialkylation (or higher) in these "reductive alkylation" reactions,[1c,3] although the reaction can be cleanly limited to monoalkylation with common polynuclear compounds by inverse quenching techniques.

In the case of polynuclear compounds an alternate scheme could be presented involving the protonation of a radical anion by ammonia and hence not involving a dianion at all. We reject this pathway since (1) it is known that these compounds easily add a second electron to produce a dianion, and, more importantly, (2) the radical anions are known not to be very basic.[2] In fact, they are considered less basic than the monoanions,[2] and since these monoanions are not protonated by ammonia under these conditions, the radical anions can be expected not to be protonated either.

The effect of substitution on both rate and orientation of benzene derivatives has received considerable attention. Since the intermediate in this reaction is a radical anion, it has been commonly accepted[1] that electron-withdrawing substituents will activate the ring and direct orientation so that the ring carbon bearing the substituent will also bear a hydrogen in the product. Conversely, an electron-donating substituent should deactivate the ring and cause orientation away from the substituent (Scheme II). There are certain observations, however, that appear to challenge this concept: (1) anisole is reported to react 3.28 times faster than benzene,[4] (2) *p*-(trimethylsilyl)toluene reduces to give the 2,5-product,[5] and (3) 2-methylnaphthalene is reported to reduce exclusively in the methylated ring.[6] In this paper, we will focus our attention on the effect of a methyl group on reduction and reductive alkylation processes.

Scheme III



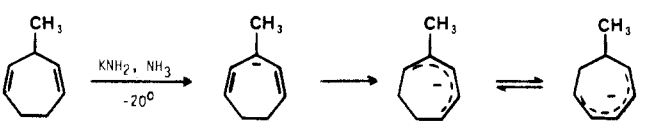
It appeared rather unusual to us that 1-methylnaphthalene (1) would reduce only in the nonmethylated ring, whereas the 2-methyl isomer (**2**, Scheme III) would react exclusively in the substituted ring. Thus, we repeated the reduction of these compounds under conditions recently shown to be optimum for the reduction of naphthalene itself,[3] and although **1** provides only a single product, the presence of a second isomer was indicated for **2**. Separation by gas chromatography was unsuccessful, but both proton and carbon NMR indicated the presence of a second isomer.

The major component (75%) had a slightly broadened singlet at 1.8 ppm in the proton NMR, and the lesser product (25%) had a sharp singlet at 2.3 ppm. These signals were assigned as allylic and benzylic methyl resonances, respectively, and hence structures **3** and **4**. Nonetheless, our results do confirm the apparent enhancement of reduction by a β-methyl substituent with the opposite effect observed with an α-methyl group.

The effect of methyl substitutents on delocalized carbanions has been recently considered by several investigators. Olah et al.[8] reported that deprotonation of **5** leads

5 6 7

to **6** and **7** (together with some toluene) in a molar ratio of 1.5:2.5. The predominance of **7** may indicate that methyl is less destabilizing (if destabilizing at all) when on a position which does not bear much negative charge in the delocalized anion. However, the question of simple kinetic acidity differences at positions 3 and 6 in **5** prevents drawing such conclusions. Staley et al.[9] did in fact conclude that a methyl is destabilizing on a charge-bearing carbon in anion **9** due to its rapid conversion to **10**.[10] The fact that **10** exists in equilibrium with **11** at 0 °C (2:3, respectively) may also indicate a slight destabilizing effect for the methyl even on a carbon relatively free of negative charge.

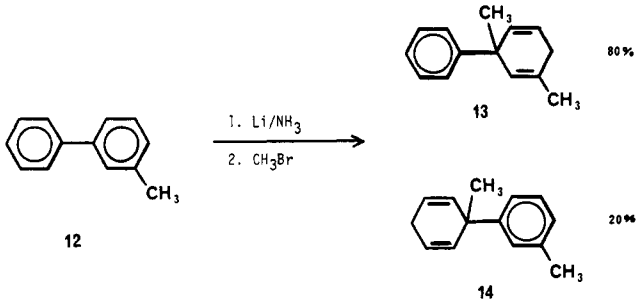


8 9 10 11

(3) Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* **1978**, *43*, 4283.
(4) Krapcho, A. P.; Bothner-By, A. A. *J. Am. Chem. Soc.* **1959**, *81*, 3658.
(5) Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Chem. Soc., Perkin Trans. 1* **1975**, 470. This effect may be steric in origin.
(6) Hückel, W.; Wartini, M. *Justus Liebigs Ann. Chem.* **1965**, *686*, 40.
(7) Isomer **4** is reported to be formed in 6% yield by the sodium/alcohol reduction of **2**.[6]
(8) Olah, G. A.; Asensio, G.; Mayr, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 4347.
(9) Staley, S. W.; Linkowski, G. E.; Fox, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 4818.
(10) Kloosterziel, H.; van Drunen, J. A. A. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1471.

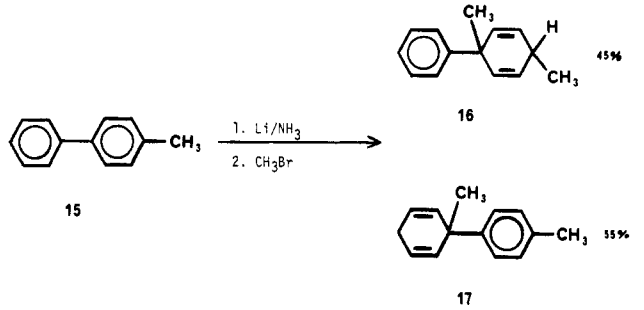
Since methyl groups are known to be stabilizing on sp^2 carbons (e.g., olefins), lack of deactivation, or even activation, may not be unreasonable for a methyl substitutent on a highly olefinic carbon in a delocalized carbanion. This would provide an attractive explanation for naphthalenes **1** and **2**, since the β-position should be olefinic but relatively free of excess negative charge.

To further investigate the effect of a methyl group on a relatively non-charge-bearing carbon during reduction, we considered 3-methylbiphenyl. In this case, due to potential problems with the stability of products[11] (rearomatization, etc.), we methylated the reduction mixture to produce the more stable 1-(or 1′-)methyl derivatives. The reaction was carried out under conditions known to give only monomethylation with biphenyl,[11] and this resulted in two major products (80:20). Both carbon-13 NMR and mass spectra confirmed the incorporation of only one additional methyl group into **12**. The presence of two vinyl



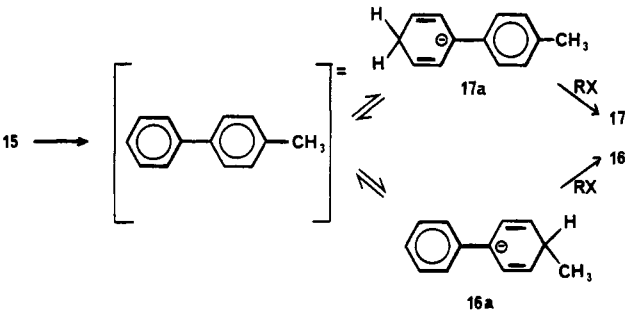
signals in a 2:1 ratio as well as an allylic methyl in proton NMR confirmed the identity of the major isomer as **13**. Thus once again, the major product involves reduction in the ring bearing the original methyl group, and this would appear to corroborate our results and interpretation with the naphthalenes.

Since the behavior of 3-methylbiphenyl parallels the observations with 2-methylnaphthalene, it seemed that 4-methylbiphenyl should resemble 1-methylnaphthalene and only reduce in the nonmethylated ring (i.e., since the methyl is on a charge-bearing carbon). We were quite surprised to learn that the reductive methylation of **15**



gives two products in nearly equal amounts (55:45). Once again, gas chromatography/mass spectroscopy indicated these products to be dimethyldihydrobiphenyls, and the appearance of a methyl doublet with a vinyl singlet[12] of intensity 4 confirmed the presence of the unexpected isomer **16**.[13]

Scheme IV



The reductive methylation of biphenyls[11] proceeds by an electron addition/protonation process, which ultimately produces a monoanion that is resistant to protonation by ammonia and can be alkylated. Hence, we regarded the formation of **16** as remarkable for several reasons. It provides reduction in a ring in which the methyl group is situated on a carbon that would ordinarily bear a considerable amount of the charge in the intermediate dianion (or radical anion), and this appears inconsistent with our results with the methylnaphthalenes. Similarly, HMO theory[14] indicates that initial protonation of the dianion (or radical anion) should occur at the position of highest electron density, which is certainly not the position bearing the methyl group.[14a] Furthermore, this concept has considerable experimental verification since it has been generally accepted that protonation does not usually occur at methylated carbons.[15]

In a sense, our results seem more consistent with the early proposal of Barton[16] that predicts formation of the most stable product. In this case, protonation of the dianion proceeds to produce the most stable monoanion. That is, in **17a** (Scheme IV) the "benzylic" anion has a *p*-methyl substituent which is, of course, destabilizing.[17] However, protonation at the carbon bearing this methyl group effectively removes it from interaction with the resultant anionic center (i.e., **16a**). Hence, the question is raised as to whether protonation of a dianion does indeed take place at the most electronegative site or rather whether protonation produces the most stable anion. We should note that in most systems studied, including the common polynuclear hydrocarbons, protonation at the most electronegative site in the dianion *also* results in the most stable monoanion, so that usually these two concepts are not brought into conflict.

It is possible, of course, that protonation does take place faster at the 4′-position with **15** (i.e., **17a**) but that both **16a** and **17a** are in equilibrium with the dianion. This would allow the buildup of **16a** as a thermodynamic product and, provided protonation of **16a** is comparable in rate to the protonation of **17a**, would account for the observation. Since the protonation rate of **16a** may be slower than **17a** on simple steric grounds, this would also account for the substantial amount of **17** from the less

(11) Lindow, D. F.; Cortez, C. N.; Harvey, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 5406.

(12) The appearance of "nonequivalent" vinyl protons as a singlet is quite common in 1,4-cyclohexadienes. For a review of the NMR characteristics of these compounds, see: Rabideau, P. W. *Acc. Chem. Res.* **1978**, *11*, 141.

(13) Cis/trans assignment not made. A slight doubling of the methyl doublet (only) suggests the possibility of both isomers. If so, they are not separated by GC, and insufficient sample (trapped from GC) prohibited confirmation by carbon-13 NMR.

(14) (a) Streitwieser, A., Jr.; Suzuki, S. *Tetrahedron* **1961**, *16*, 153. (b) Zimmerman, H. E. *Ibid.* **1961**, *16*, 169. (c) Birch, A. J.; Hinde, A. L.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 3370.

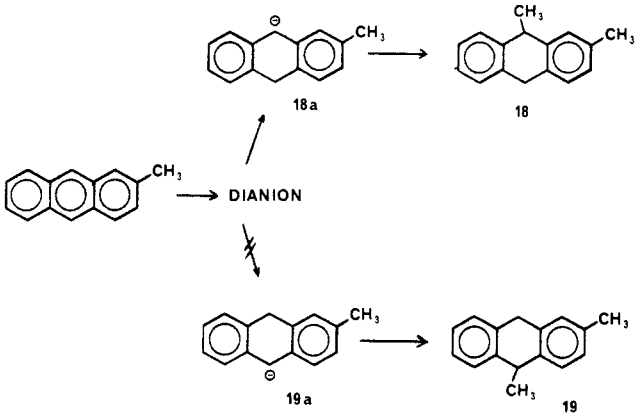
(15) Birch, A. J.; Rao, G. Subba "Advances in Organic Chemistry, Methods and Results"; Taylor, E. C., Ed.; Wiley-Interscience: New York, 1972.

(16) Barton, D. H. R.; Robinson, C. H. *J. Chem. Soc.* **1954**, 3045.

(17) Streitwieser, A., Jr.; Murdoch, J. R.; Häfelinger, G.; Chang, C. J. *J. Am. Chem. Soc.* **1973**, *95*, 4248.

(18) Barnett, E. de B.; Goodway, N. F. *J. Chem. Soc.* **1929**, 1754. This procedure was modified in that ring closure was effected by an intramolecular Friedel–Crafts reaction of the acid chloride in benzene with an $SnCl_4$ catalyst.

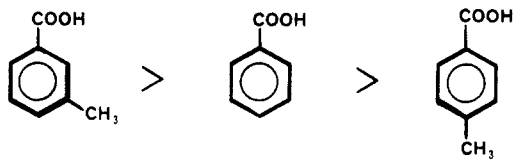
Scheme V



stable monoanion. However, experiments have been done to detect any equilibrium between biphenyl monoanion and dianion in ammonia, and these workers[11] concluded that it does not take place.

To find further support for the effect of a *p*-methyl substituent in the formation of a monoanion, we considered the reductive methylation of 2-methylanthracene. In this case, protonation of the dianion may produce **18a** or **19a** (Scheme V), the latter being a *p*-methylbenzyl anion type. In fact, comparison with an authentic sample, produced by simple reduction of 2,9-dimethylanthracene, indicates that only **18** is produced. Once again, the nature of the intermediate monoanion influences the outcome of the reaction.

A final consideration of the effect of a methyl group on relative rates did not produce dramatic results in competitive reactions. The difference in rates appears relatively small in considering benzoic and *m*- and *p*-toluic acids. However, when reacted with a limited amount of sodium in ammonia in a competition experiment, *m*-toluic was slightly more reactive than benzoic acid, whereas the para isomer was less reactive. Since the carboxylate group is known to be quite activating and produces 1,4 reduction, however, this does appear to confirm the differences in the effect of methyl with regard to its presence on a charge-bearing or relatively non-charge-bearing carbon.

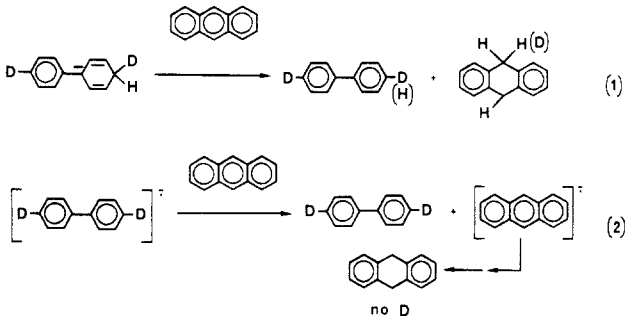


Discussion

This paper provides two important conclusions. The first indicates that a methyl substituent may not be simply categorized with regard to its effect on reactivity and regioselectivity in reduction reactions. The second, and most important, however, deals with the suggestion that protonation of dianion intermediates occurs at the site which produces the most stable monoanion, not necessarily the site of highest electron density. Since this notion is perhaps contrary to current thought, it deserves careful consideration.

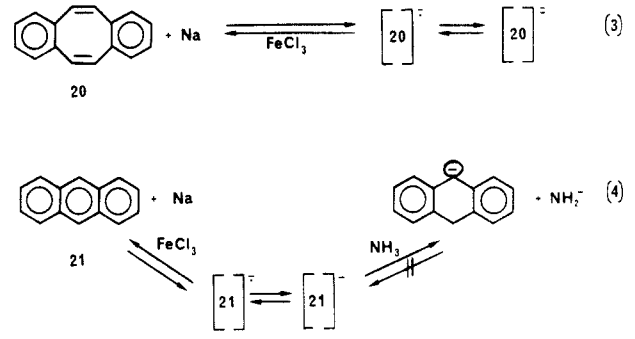
With this in mind, it is important that the following three points be firmly established: (1) that the intermediates are monoanions and not dianions or radical anions; (2) that these intermediate monoanions are not in equilibrium; (3) that alkylation occurs by nucleophilic substitution (with monoanions) and not electron transfer (with radical anions).

Harvey and co-workers[11] have shown that the intermediate in the metal–ammonia reduction of 4,4′-dideuteriobiphenyl transfers a deuterium (consistent with $k_H/k_D \approx 5.5$) to anthracene. This is consistent with a hydride transfer from a monoanion but not with electron transfer



from a radical anion or dianion (eq 2), since in this latter case no deuterium should be incorporated into the final dihydroanthracene product.

The fact that 4,4′-dideuteriobiphenyl can be reduced with no loss of deuterium also suggests that the monoanion is not in any equilibrium with dianion or NH_2^-/NH_3. This was also demonstrated for anthracene by Rabideau and Burkholder.[3] Hence, addition of $FeCl_3$ to a sodium–ammonia solution of dibenzo[*a*,*e*]cyclooctatetraene (aromatic dianion) drives the equilibrium back to the left by catalyzing the reaction of sodium with ammonia and thus removing it from the system, resulting in the recovery of starting material. However, the addition of $FeCl_3$ to sodium–ammonia solutions of anthracene has no effect, and only 9,10-dihydroanthracene is produced with no recovery of starting material (eq 4). Once again this suggests an irreversible protonation by ammonia.



Finally, as amplified in several reviews,[19] alkylation of radical anions takes place by an electron-transfer process. Although we feel that radical anions are ruled out here for the reasons presented above, it may be reassuring to note that the products herein are not consistent with such electron-transfer processes. In such cases, one should expect a significant amount of bimolecular reduction[19a] which would lead to substantial amounts of unreduced (and alkylated unreduced) products. In these reductive alkylations, it is not uncommon to recover no unreduced materials at all. In addition, the stereochemical results of reductive alkylation appear similar to results involving the generation of monoanions in ammonia by proton-abstraction reactions. Moreover, a kinetic study by Bank et al.[20] dealing with the alkylation of dihydroanthracene monoanion in THF suggests that the behavior of this system is normal as compared to that of other anions

(19) (a) Garst, J. F. *Acc. Chem. Res.* **1971**, *4*, 400. (b) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.
(20) Bank, S.; Bank, J.; Daney, M.; Labrande, B.; Bouas-Laurent, H. *J. Org. Chem.* **1977**, *42*, 4058.

presumed to alkylate by substitution processes (at least with primary alkyl halides).

Experimental Section

NMR spectra were obtained on Varian EM-390 and CFT-20 spectrometers and mass spectra with a Hewlett-Packard gas chromatography/mass spectroscopy system. Microanalyses were performed by Galbraith Laboratories, Inc.

Metal–Ammonia Reduction. General Procedure. Excess (1.5–2 equiv) metal (Na or Li) is added to the aromatic compound in ammonia/THF (2:1) at reflux (or −78 °C). After 10–30 min, the reaction is inverse[3] quenched into dilute ammonium chloride solution, and the product is isolated by ether extraction.

Metal–Ammonia Reductive Methylation. The metal–ammonia solution is prepared as above except that (1) methyl bromide gas is passed in (normal quench), or (2) the reaction mixture is pumped into methyl iodide in THF (inverse quench). This is followed by addition of aqueous ammonium chloride and ether extraction.

1-Methyl- and 2-methylnaphthalene were reduced with sodium according to the general procedure to produce 8-methyl- and 2-methyl-1,4-dihydronaphthalenes as indicated previously.[6] The presence of a second isomer in the latter case is discussed in the body of this paper.

Reductive Methylation of 4-Methylbiphenyl. Lithium wire (0.08 g) was added to 4-methylbiphenyl (0.5 g) in THF (15 mL) and ammonia (40 mL) at reflux. After 30 min, methyl bromide gas was passed in until the deep color was discharged. The reaction mixture was then treated with aqueous NH_4Cl followed by ether extractions. GC showed two major products (45:55) confirmed by gas chromatography/mass spectroscopy to be dimethyldihydrobiphenyls [*m/e* 184 (M), 169 (loss of CH_3)]. The first peak was trapped off to afford 1,4-dimethyl-1,4-dihydrobiphenyl (**16**): NMR ($CDCl_3$) δ 7.2 (m, 5 aryl), 5.6 (d, 4 vinyl), 2.75 (q, 1), 1.5 (s, 3), 1.13 (d, 3). The second peak was 1,4′-dimethyl-1,4-dihydrobiphenyl (**17**): NMR ($CDCl_3$) δ 7.06 (AB q, 4), 5.03 (s, 4), 2.69 (m, 2), 2.31 (s, 3), 1.5 (s, 3). Because of difficulties in obtaining suitable analytical samples from the GC for elemental analysis, the above reaction mixture was subjected to microdistillation (bp 140 °C) and a combined sample of **16** and **17** was analyzed.

Anal. Calcd for $C_{14}H_{16}$: C, 91.30; H, 8.70. Found: C, 91.46; H, 8.54.

Reductive Methylation of 3-Methylbiphenyl. The procedure was similar to that above. The first peak trapped (80%) was 1,3-dimethyl-1,4-dihydrobiphenyl (**13**): NMR ($CDCl_3$) δ 7.21 (m, 5 aryl), 5.66 (m, 2 vinyl), 5.33 (m, 1 vinyl), 2.59 (m, 2), 1.75 (s, 3), 1.48 (s, 3). The second (20%) was 4,3′-dimethyl-1,4-dihydrobiphenyl (**14**): NMR ($CDCl_3$) δ 7.1 (m, 4), 5.61 (s, 4), 2.63 (m, 2), 2.28 (s, 3), 1.43 (s, 3). Furthermore, ^{13}C NMR of **14** showed three upfield singlets (37.08, 34.34, 29.59 ppm) with proton decoupling that yielded a triplet, a doublet, and a triplet under off-resonance conditions, consistent with CH_3, CH_2, and CH_3.

Reductive Methylation of 2-Methylanthracene. 2-Methylanthracene (0.3 g) was dissolved in THF (20 mL) and added to ammonia (50 mL) at reflux. Sodium (0.09 g) was then added, and after 15 min, the reaction mixture was pumped into 8 mL of methyl iodide in 10 mL of THF. The major reduction product (>80%) was shown to be 2,9-dimethyl-9,10-dihydroanthracene (**18**) by comparison with an authentic sample obtained by the reduction of 2,9-dimethylanthracene:[18] mp 70–70.5 °C; NMR ($CDCl_3$) δ 7.15 (m, 7), 3.9 (m, 3), 2.3 (s, 3), 1.35 (d, 3).

Anal. Calcd for $C_{16}H_{16}$: C, 92.31; H, 7.69. Found: C, 92.31; H, 7.99.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences. Partial funding of the EM-390 NMR spectrometer was provided by the National Science Foundation (Grant No. CHE 79-16449). We thank Mrs. Elizabeth Solow for performing gas chromatographic/mass spectroscopic analyses.

Registry No. **2**, 91-57-6; **3**, 2717-43-3; **4**, 2717-46-6; **12**, 643-93-6; **13**, 76613-02-0; **14**, 76613-03-1; **15**, 644-08-6; **16**, 76613-04-2; **17**, 76613-05-3; **18**, 76613-06-4; 2-methylanthracene, 613-12-7.

Reactions of Tris(dialkylamino)phosphines with Carbonyl Compounds

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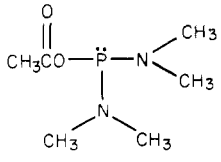
Received October 10, 1980

The reactions of hexamethylphosphorous triamide and some cyclic analogues with anhydrides, acid chlorides, and esters are reported. A mechanism is postulated which involves nucleophilic attack of trivalent phosphorus upon the carbonyl carbon, followed by phosphorane formation and a concerted fragmentation to products.

As a continuation of our studies of the nucleophilic reactions of phosphorodiamidites[1,2] we undertook a study of the reactions of bis(dimethylamino)phosphinous ethanoic anhydride (1). While compounds of this general type



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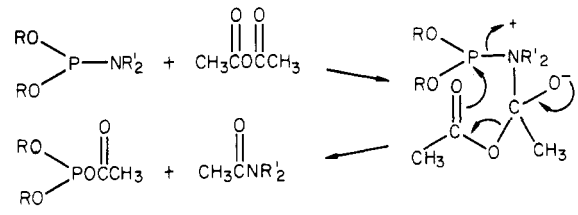
have been reported in the literature,[3] syntheses and in particular purification of this type of compound are made difficult by the thermal lability of the product. A novel synthesis of a closely related compound was reported by Kabachnik et al. in 1963[4] (eq 1). This paper reports the

Scheme I



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