Stereochemistry of Metal-Ammonia Ring Reduction of Aryl Carboxylates and Ketones and NMR Conformational Analysis of the Dihydro Aromatic Products

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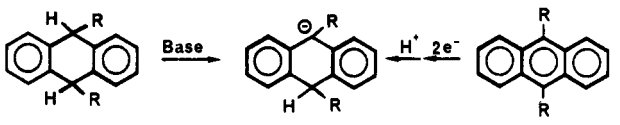
Metal-ammonia ring reductions have been carried out with 9-acetyl-10-alkylanthracenes, 10-alkylanthroate esters, 1-acetyl-4-alkylnaphthalenes, 4-alkylnaphthoate esters, and *p-tert*-butylbenzoic acid. The stereochemistry of these reactions is determined by the protonation of the final monoanion. A model is suggested which involves considerable enolate character, as well as a variation in the extent of ring folding. In general, dihydroanthracene anions are the most highly folded and provide cis products, dihydronaphthalenes have intermediate folding and produce cis/trans mixtures, and *p-tert*-butyldihydrobenzoate dianion is planar and produces trans products. NMR methods for isomer assignment and conformational analyses are also provided.

The protonation (and alkylation) of monoanions derived from dihydroanthracenes, -naphthalenes, and -benzenes has received considerable attention.[1] These anions may be generated by deprotonation of the dihydro aromatics (1) or by electron addition to the fully aromatic compounds (2). In the latter case, these monoanions represent the



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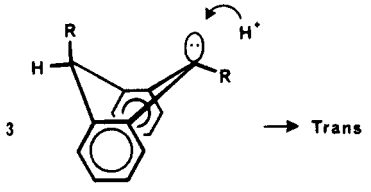
final intermediate in dissolving metal reduction (or reductive alkylation). In either case, it is the protonation (alkylation) of this intermediate that determines stereochemical (cis/trans) outcome.

The most heavily studied case has been the dihydroanthracene system, and early observations[1a-c] of trans products from the protonation of 9-metallo-9,10-dialkyl-9,10-dihydroanthracenes (DHA's) led to the model shown as anion 3. This seemed reasonable, since (1) the DHA ring system was believed to be boat-shaped,[2] and (2) substituents were shown to prefer the pseudoaxial position.[3] In addition, the anion center would require a pseudoaxial geometry to allow overlap with the adjacent aromatic rings. This model needed to be modified, however, when it was learned that protonation of 3 leads to cis products when R_9 and R_{10} are large.[1d-f,n] This provoked explanations involving ion pair phenomena and metal directed protonation.[1s] More recently an sp^2-hybridized anion with variable ring puckering has been suggested.[4,5] Both proton[1s,6] and carbon[4] NMR do seem to support an sp^2 anion. Moreover, variable ring folding in DHA's as well as 1,4-dihydronaphthalenes (DHN's) is suggested by molecular mechanics calculations. In contrast to the concept of rapid boat to boat ring inversions for these dihydro aromatics,[2] molecular mechanics calculations indicate broad potential wells for both DHA and DHN, with planar minima[7] (see Figure 1). Substituents do, of course, cause a change in calculated geometry[7b] although the degree of folding (i.e., angle between the two benzene planes in DHA) is generally much less than the 145° found for the crystalline state of DHA.[8]



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In light of this background, we were interested in investigating the stereochemistry of protonation in a series of such anions where sp^2 hybridization would be promoted by suitable substitution. Since we recently developed methods for the metal-ammonia ring reduction of aryl esters and ketones,[9] we focused on a carbonyl substituent (i.e., enolates) as illustrated. The tendency toward nonplanar structures due to "peri" interactions as well as angle strain[7a] increases in the series dihydrobenzene (DHB) < dihydronaphthalene (DHN) < dihydroanthracene (DHA).

(1) (a) Harvey, R. G.; Arzadon, J.; Urberg, K. *J. Amer. Chem. Soc.* **1969**, *91*, 4535. (b) Harvey, R. G.; Arzadon, L. *Tetrahedron* **1969**, *25*, 4887. (c) Lindow, D. F.; Cortex, C. N.; Harvey, R. G. *J. Amer. Chem. Soc.* **1972**, *94*, 5406. (d) Zieger, H. E.; Schaeffer, D. J.; Padronnaglo, R. M. *Tetrahedron Lett.* **1969**, 5027. (e) Schaeffer, D. J.; Zieger, H. E. *J. Org. Chem.* **1969**, *34*, 3958. (f) Schaeffer, D. J.; Litman, R.; Zieger, H. E. *Chem. Commun.* **1971**, 483. (g) Harvey, R. G.; Davis, C. C. *J. Org. Chem.* **1969**, *34*, 3607. (h) Zieger, H. E.; Gelbaum, L. T. *J. Org. Chem.* **1972**, *37*, 1012. (i) Lapouyade, R.; Mary, M.; Bouas-Laurent, H.; Labandibar, P. J. *Organometal. Chem.* **1972**, *34*, C 25. (j) Panek, E. J.; Rodgers, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 6921. (k) Panek, E. J. *J. Am. Chem. Soc.* **1974**, *96*, 7959. (l) Daney, M.; Lapouyade, R.; Mary, M.; Bouas-Laurent, H. *J. Organomet. Chem.* **1975**, *92*, 267. (m) Fabre, C.; Salem, M. H. A.; Mažaleyrat, J. P.; Tchaplo, A.; Welvart, Z. *Ibid.* **1975**, *87*, 9. (n) Fu, P. P.; Harvey, R. G.; Paschal, J. W.; Rabideau, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 1145. (o) Bank, S.; Bank, J.; Davey, M.; Labrande, B.; Bouas-Laurent, H. *J. Org. Chem.* **1977**, *42*, 4058. (p) Daney, M.; Lapouyade, R.; Bouas-Laurent, H.; *Tetrahedron Lett.* **1978**, 783. (q) Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* **1978**, *43*, 4283. (r) Daney, M.; Labrande, B.; Lapouyade, R.; Bouas-Laurent, H. *J. Organometal. Chem.* **1978**, *159*, 385. (s) Daney, M.; Lapouyade, R. *J. Organomet. Chem.* **1979**, *172*, 385. (t) Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* **1979**, *44*, 2354. (u) Daney, M.; Bouas-Laurent, H.; Calas, B.; Giral, L.; Platzer, N. *J. Organometal. Chem.* **1980**, *188*, 277.

(2) For a review, see: Rabideau, P. W. *Acc. Chem. Res.* **1978**, *11*, 141.

(3) (a) Brinkman, A. W.; Gordon, M.; Harvey, R. G.; Rabideau, P. W.; Stothers, J. B.; Ternay, A. L. *J. Am. Chem. Soc.* **1970**, *92*, 5912. (b) Lapouyade, R.; Labandibar, P. *Tetrahedron Lett.* **1970**, 1589.

(4) Rabideau, P. W.; Wetzel, E. M.; Lawrence, J. R.; Husted, C. A. *Tetrahedron Lett.* **1984**, *25*, 31.

(5) Marcinow, J.; Rabideau, P. *Tetrahedron Lett.* **1984**, 5463.

(6) Nicholls, D.; Szwarc, M. *J. Am. Chem. Soc.* **1966**, *88*, 5757.

(7) (a) Lipkowitz, K. B.; Rabideau, P. W.; Raber, D. J.; Hardee, L. E.; Schleyer, P. V. R.; Kos, A. J.; Kahn, R. A. *J. Org. Chem.* **1982**, *47*, 1002. (b) Raber, D. J.; Hardee, L. E.; Rabideau, P. W.; Lipkowitz, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 2843.

(8) Ferrier, W. G.; Iball, J. *Chem. Ind. (London).* **1954**, 1296.

(9) (a) Rabideau, P. W.; Huser, D. L.; Nyikos, S. J. *Tetrahedron Lett.* **1980**, *21*, 1401. (b) Rabideau, P. W.; Young, D. M.; Husted, C. A. *J. Org. Chem.* **1983**, *48*, 4194. (c) Rabideau, P. W.; Wetzel, D. M.; Young, D. M. *J. Org. Chem.* **1984**, *49*, 1544.

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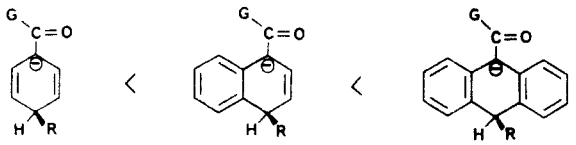
Increasing non-planar structures due to angle strain and "peri" interactions.



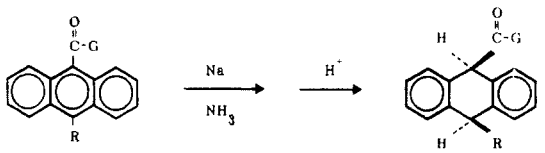
Increasing non-planar structures due to 1,4 steric effects.

R = Me < Et < i-Pr < t-Bu

Moreover, increase in substituent size (Me < Et< *i*-Pr < *t*-Bu) also favors nonplanar structures due to additional nonbonded interactions with the ortho hydrogens. However, transannular steric interactions may also be possible with substituents at the 10 position.[10,11]

Results

We began with the anthracene series since we expected that this system would produce the best results in metal–ammonia reduction.[9] In fact, 9-acetyl DHA's and 9-anthroate esters were smoothly reduced by sodium in ammonia containing an equivalent of water,[12] to produce cis dihydro products (small amounts of trans isomers cannot be completely ruled out).

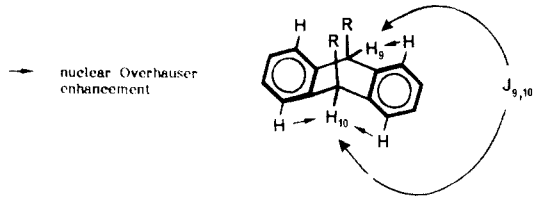


G = OEt, O-t-Bu, Me

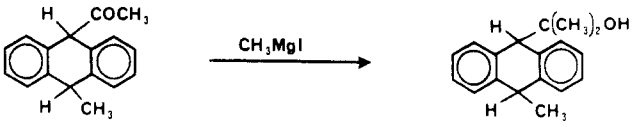
R Me, Et

It was especially important to be sure of correct isomer assignment, and this was approached in the following way for DHA's.

In cis disubstituted DHA's, substituents are pseudoaxial (time averaged) whether one considers a rapid (but unequal) equilibrium between boat conformations,[4,5a] or vibration around a slightly folded structure.[7b] This results in characteristic values for the long-range, homoallylic coupling constants $J_{9,10}$ (usually 0.5 to 1.0 Hz), as well as nuclear Overhauser enhancements at H_9 and H_{10} (illustrated) when the adjacent aromatics are iradiated.[2,5a,1n]



The results summarized in Table I clearly support the cis arrangement. In an effort to provide additional evidence for this assignment, we reacted ketone **4** with methylmagnesium iodide. This produced a product which was identical with authentic **5** previously assigned as cis.[11]



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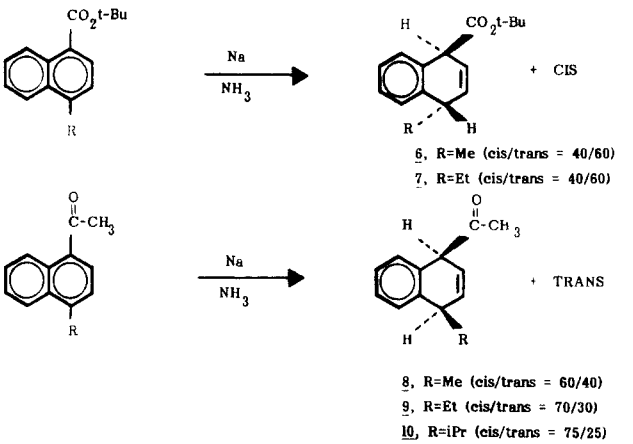
In contrast to metal–ammonia reduction of the anthracene system, the naphthalene derivatives furnished two isomers.



6, R=Me (cis/trans = 40/60)
7, R=Et (cis/trans = 40/60)

8, R=Me (cis/trans = 60/40)
9, R=Et (cis/trans = 70/30)
10, R=iPr (cis/trans = 75/25)

We have previously encountered difficulties in separating 1,4-dihydronaphthalene isomers, and the compounds studied herein did not prove to be an exception. For example, the reduction of *tert*-butyl 4-methyl-1-naphthoate produced two isomers (by NMR) which could not be separated on several $^1/_4$ in. glpc columns although separation on a capillary column was achieved. Due to these difficulties, structural analysis was carried out with a purified mixture of cis/trans isomers.

There has been a considerable amount of interest, and controversy, with the NMR analysis of these dihydro aromatics.[2,14-16] (Important proton NMR coupling constants are illustrated below for **14** and **15**.) The use of spin decoupling techniques to remove vinyl coupling, together with the addition of $Eu(fod)_3$ to separate overlapping resonances, allowed the measurement of the homoallylic coupling constants ($J_{1,4}$) for each DHN isomer. These values, which are provided in Table II , can provide a method for isomer assignment as well as the determination of preferred conformations.[16b] From the previously studied 1-R DHN derivatives [**11**, R = CD_2OH; **12**, R = CO_2H; **13**, R = $C(CH_3)_2OH$] as well as some rigid boat structures,[15] it is apparent that $J_{1,4}$(cis) varies from small values for dipseudoequatorial relationships (e.g., 1.8 Hz for **13**) in "highly puckered" boat conformations, to moderate values in nearly planar geometries (3.5 and 3.8 for **11** and **12**, respectively), to rather large values in (rigid) dipseudoaxial relationships (8.5 Hz).[15] This latter arrangement is, of course, unexpected in flexible systems since cis substituents are not known to be dispseudoequatorial. In contrast to this potentially wide range of values (1.8–8.5 Hz) for $J_{1,4}$(cis), the values for $J_{1,4}$(trans) vary only slightly (3.0–4.4 Hz) over the full range of geometry changes. Hence in cases where there is a significant difference between $J_{1,4}$(cis) and $J_{1,4}$(trans) (see Table II), assignment of the smaller value as the cis isomer is probably safe. However,

(10) A nuclear Overhauser enhancement was observed between the *t*-Bu and H_{10} in an NMR study of 9-*tert*-butyl DHA. See ref 3.

(11) Cho, H.; Harvey, R. G.; Rabideau, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 1140.

(12) The use of water is important in some cases,[9] especially when dimerization may occur. This appears less important when the 10-position is blocked, and in this case anhydrous conditions work well. See Experimental Section for details.

(13) (a) Birch, A. J.; Rao, G. Subba. *Advances in Organic Chemistry, Methods and Results*; Taylor, E. C., Ed.; Wiley-Interscience: New York, 1972. (b) Smith, H. *Chemistry in Nonaqueous Ionizing Solvents*; Jander, G., Spandau, H., Addison, C. C., Ed., Interscience: New York, 1963; Vol. I, Part 2. (c) Harvey, R. G. *Synthesis*. **1970**, 161.

(14) (14) Rabideau, P. W.; Wetzel, D. M. *J Org. Chem.* **1982**, *47*, 3993.

(15) Rabideau, P. W.; Burkholder, E. G.; Yates, M. J.; Paschal, J. W. *J. Am. Chem. Soc.* **1977**, *99*,, 3596.

(16) (a) Rabideau, P. W.; Paschal, J. W.; Marshall, J. L. *J. Chem. Soc., Perkin Trans. 2* **1977**, 842, and references therein. (b) Holy, N. L.; Vail, H. P.; Nejad, A.-H.; Huang, S.-J.; Marshall, J. L.; Saracoglu, O.; McDaniel, C. R., Jr. *J. Org. Chem.* **1980**, *45*, 4271.

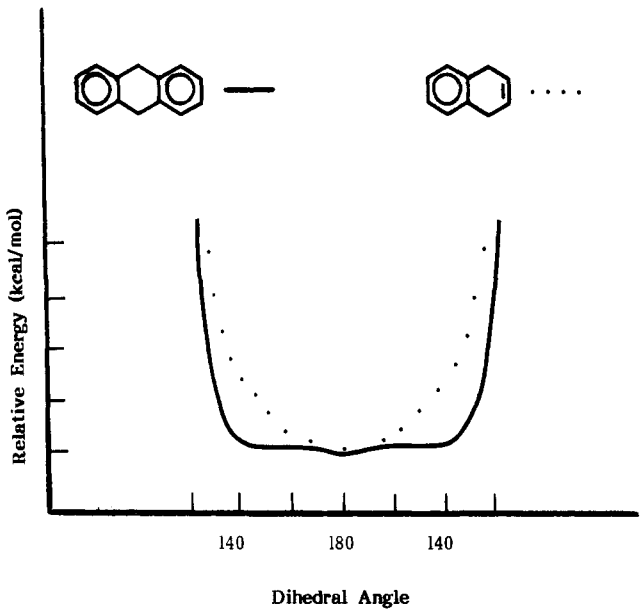
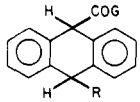


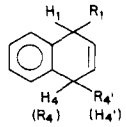
Figure 1. MMI energy profile of 9,10-dihydroanthracene (solid) and 1,4-dihydronaphthalene (dots).

Table I. NMR Homoallylic Coupling Constants and NOE Results for DHA Systems[a]

	G	R	$J_{9,10}$, Hz	NOE enhancement, % H_9	NOE enhancement, % H_{10}
	*t*-Bu	Me	0.9	13	8
	t-Bu	Et	0.6	23	7
	Me	Me	1.1	20	15
	Me	Et	–[b]	18	18

[a] Run at 90 MHz on deoxygenated samples in $CDCl_3$. [b] Less than 0.5 Hz (not resolvable).

Table II. Homoallylic Coupling Constants (Hz) for DHN Derivatives[a]

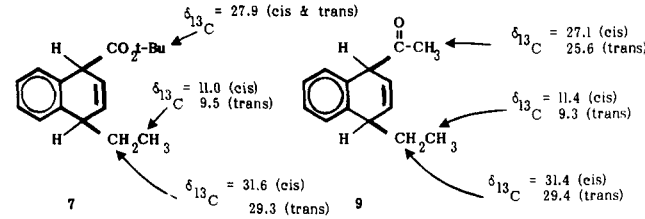
	compd	R_1	$R_4(R_{4'})$	$J_{1,4}$, cis	$J_{1,4'}$, trans
	**6**	CO_2-*t*-Bu	Me	3.0	3.8
	7	CO_2-*t*-Bu	Et	3.1	3.1
	8	$COCH_3$	Me	4.0	3.9
	9	$COCH_3$	Et	3.6	4.2
	10	$COCH_3$	*i*-Pr	3.0	3.8
	11[b]	CD_2OH	H	3.5	3.7
	12[b]	CO_2H	H	3.8	4.4
	13[b]	$C(CH_3)_2OH$	H	1.8	3.0

[a] Measured in the presence of Eu(fod)$_3$. [b] Data taken from ref 15.

an important result of this study, given the rather wide usage of homoallylic coupling constants for these systems, is that this method fails in some cases. For example, compounds **7** and **8** have essentially identical values for both isomers.

Additional coupling constants, if they can be measured, will also provide information about geometries. *tert*-Butyl 4-ethyl-1,4-dihydro-1-naphthoate (**7**) serves as an example. In the presence of Eu(fod)$_3$, the vinyl region for the cis/trans mixture of **7** appeared as an apparent singlet superimposed on a complex AB pattern. Integration indicated that the AB pattern represented the major isomer. Eu(fod)$_3$ also produced separate resonances for $H_{4'}$, although we did not know which was which.[17] We suspected that the downfield signal [i.e., moving fastest with incremental additions of Eu(fod)$_3$] was $H_{4'}$ of the trans isomer, since this proton is on the same side as the coordination site for the shift reagent in the trans case. Double irradiation of this signal produced decoupling of the AB vinyl system whereas irradiation of the upfield signal (H_4) produced no effect. Further evidence that the downfield ("fastest moving") C_4H, and in turn the vinyl AB pattern, belonged to the trans isomer is as follows. With decoupling of $H_{4'}$, we were able to measure $J_{1,2}$ = 3.1 Hz (and $J_{1,3}$ = 2.2 Hz).[17] In puckered systems of known geometry, $J_{1,2}$ is ca. 5 Hz when H_1 is pseudoequatorial, and ca. 1.5 Hz when H_1 is pseudoaxial. Hence the value of 3.1 is roughly in between and suggests a planar (or nearly so) geometry. This geometry is only expected for the trans isomer.

Our final approach involved an examination of ^1H and ^{13}C NMR chemical shifts. In the 9,10-dihydroanthracene system, it has been noted that the CH_3 of a trans ethyl group (i.e., 9-Et-10-R-DHA) absorbs at higher field in ^1H NMR.[18] This is due to the fact that the ethyl group is more pseudoequatorial in trans derivatives (as compared to cis dipseudoaxial) bringing it closer to the faces of the benzene rings (shielding region). In ^{13}C NMR, trans methyl groups also absorb at higher field, in this case due to a γ steric effect.[19] We have found a similar effect for ethyl groups, and a comparison of *cis*- and *trans*-9,10-diethyl DHA shows upfield shifts of 3.4 and 8.5 ppm for the CH_2 and CH_3 (respectively) of the trans isomer. This appears to be a general method for distinguishing between many cis and trans isomers in the DHA system. We expected that these same effects should be observed in the DHN system except to a lesser extent due to the absence of one aromatic ring. We have examined the CH_3 resonances for a series of cis and trans DHN's containing CH_3 and CH_2CH_3 substituents (and in one case $CH(CH_3)_2$), and in all cases where resonances were clearly resolved, the CH_3 appeared at higher field in both ^1H and ^{13}C NMR for the trans isomers and at lower field for the cis isomers. This appears to hold for other resonances as well, as illustrated for ^{13}C shifts **7** and **9**. In summary, we feel that we have



demonstrated the general utility of four NMR techniques for isomer assignment in dihydro aromatic compounds. They are (1) use and potential misuse of homoallylic coupling constants, (2) vicinal and allylic coupling constants, (3) the fact that hydrogens across the ring move downfield fastest when on the same side as a group which will coordinate Eu(fod)$_3$, and (4) the upfield ^1H and ^{13}C shifts of trans substituent groups (relative to cis).

Our investigations with the benzene series was limited to substituted benzoic acids since the ring reduction of the corresponding esters and ketones does not proceed well.[9] Although the reduction of some 4-alkylbenzoic acids has been reported,[20] isomer assignments were not made. Moreover, 1,4-dihydrobenzoic acid, together with its 2,6-

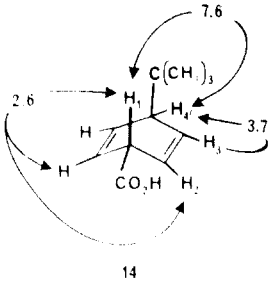
(17) The assumption is that the H_2 vinyl moves downfield faster than the H_3 vinyl in the presence of Eu(fod)$_3$. This has been shown to be the case for DHN and DHB derivatives.[2,15]

(18) Panek, E. J. *J. Am. Chem. Soc.* **1974**, *96*, 7959.
(19) Dalling, D. K.; Zilm, K. W.; Grant, D. M.; Heeschen, W. A.; Horton, W. J.; Pugmire, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 4817.
(20) Van Bekkum, H.; Van Den Bosch, C. B.; Van Minnenpathius, G.; DeMos, J. C.; Van Wijk, A. M. *Rec. Trav. Chim. Pays-Bas*, **1971**, *90*, 137.

and 3,5-dimethyl derivatives, have been the subject of conformational studies,[2,16a] and so a 4-alkyl derivative provides an interesting case in this respect. Metal–ammonia reduction of 4-*tert*-butylbenzoic acid proved to be especially useful since only one isomer was formed. Isomer assignment as well as conformational analysis follows.

The normal NMR spectrum of 4-*tert*-butyl-1,4-dihydrobenzoic acid (**14**) at either 90 or 300 MHz is not very informative since the vinyl protons appear more or less as a singlet [i.e., accidental equivalance of $H_2(H_6)$ and $H_3(H_5)$], and H_1 and H_4 appear as poorly resolved doublets. The addition of 6–8 drops of pyridine, however, resulted in a considerable increase in detail including the appearance of the vinyls as an pattern with a considerable amount of additional complexity. The pyridine causes a ca. 0.12 ppm downfield shift of H_2 and possibly a slight upfield shift of H_3. Double irradiation of $H_{4'}$ (the upfield doublet) produced a vinyl AB pattern with each of the four resonances further split into doublets representing $J_{1,2}$ and $J_{1,3}$. Irradiation of H_1 afforded a similar pattern allowing the measurement of $J_{2,4'}$. Moreover, it is the value of $J_{3,4'}$ (3.7 Hz) which allowed assignment of H_2 and H_3 since this value is too large for allylic coupling and must be assigned as vicinal. Double irradiation of the vinyls produced two doublets of H_1 and $H_{4'}$ and $J_{1,4'}$ was easily measured. Since $J_{1,2}$ does not equal $J_{3,4'}$ and $J_{1,3}$ does not equal $J_{2,4'}$, a completely planar structure, whether cis or trans, can be ruled out. As a consequence, the homoallylic coupling constant value of 7.6 Hz rules out a cis relatiohship, since ${}^5J_{\text{homoallyic}}$ (cis) for a nonplanar system would be much smaller than 7.6 for a dipseudoaxial arrangement of substituents or larger for a dipseudoequatorial relationship.[14,21]

The NMR coupling constants for **14** compare quite closely with our recent values for **15**[14] which we suggested as a "flattened boat" geometry due to a comparison of the data with both planar and rigid boat model systems. If



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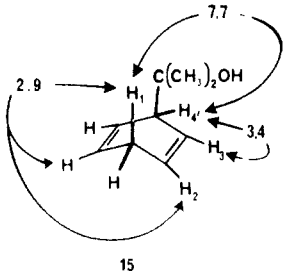

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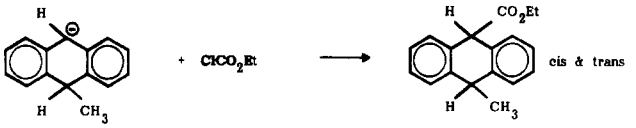
14 is also a "flattened boat", the trans arrangement means that one group must be slightly pseudoaxial, and the other slightly pseudoequatorial. This raised an important question since substituent preference has been somewhat controversial in DHB's.[14,22] Comparison of the NMR coupling with model systems, however, provides an easy resolution. For example, $J_{1,2}$ ($J_{3,4}$, $J_{3,4'}$) has a value of ca. 3.0 Hz for the planar state. This value increases to ca. 5.5 Hz as H_1 becomes pseudoequatorial (i.e., H_1 and H_2 more coplanar) and drops to ca. 2.5 or less as H_1 becomes pseudoaxial. Hence in **14** the fact that $J_{1,2}$ (2.6) < $J_{3,4'}$ (3.7) indicates that H_1 is pseudoaxial and $H_{4'}$ is psueodoequatorial. This, of course, means that the larger *tert*-butyl group is pseudoaxial. The allylic coupling $J_{1,3}$ (2.3 Hz) confirms this assignment since it is larger (maximum for a 90° relationship) than expected for a planar system (1.5 Hz). At any rate, although the nonplanarity of **14** is easily established, the coupling constant values are generally much closer to the planar state than full boat (rigid) geometries. So it seems that the "flattened boat" geometry best describes **14** and **15**, and we suspect that this will be a common conformational pattern for DHB's.

Discussion

Two concerns must be addressed before the stereochemistry of protonation can be considered. (1) Are the products really kinetic, or do they result from a secondary isomerization after the initial protonation step? After all, product geometry is determined by the configuration at an "α carbon" which has two additional unsaturated substituents. (2) What is the extent of enolate character? This is important since in DHA's, for example, it is not possible for the enolate double bond and both aromatic rings to all lie in the same plane. This would necessitate nonplanar structures.

We have ruled out the possibility of isomerization in dihydrobenzenes and dihydronaphthalenes since it is likely that any epimerization would be accompanied by double bond migration, and none was observed. We recently studied the reversible (i.e., equilibrium) protonation/deprotonation of these systems and found that double bond migration to form the conjugated derivatives is quite facile.[23] Hence we turned our attention to DHA's on this question since double bond migration is not possible.

This was regarded as a serious problem with the DHA's since (1) they are the most acidic in our series, and (2) the cis isomers are, in fact, the most stable.[24] In view of this latter point, we were not able to generate a mixture of isomers from our reaction products. However, reaction of anion **16** with ethyl chloroformate did produce both isomers. This mixutre of isomers was then dissolved in THF/NH_3 and −78 °C and subsequently poured into dilute ammonium chloride solution to simulate our reaction conditions. This did not result in any significant amount of isomerization.[25]



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The second question dealt with the extent of enolate character, and again, we decided to examine the ^1H NMR spectrum of the anion generated by deprotonation of ethyl 9,10-dihydroanthroate. The expected dynamics of this system are shown in Figure 2. If there is considerable enolate character, this should lead to inverting boat conformations (path A in Figure 2) of the type observed for the related isopropylidene DHA.[26] We would also expect some rotational barrier (i.e., double bond character) around the C_9/carbonyl bond. This is represented by pathway B. Unfortunately, precipitation occurred before we could reach a temperature low enough to cause coalescence of $H_9/H_{9'}$. However, H_1 and H_8 did undergo coalescence below 0 °C resulting in two separate signals at lower tem-

(21) Molecular mechanics calculations predict the dipseudoaxial arrangement for 1,4-dimethyl-1,4-dihydrobenzene, but dipseudoequatorial for 1,4-di-*tert*-butyl-1,4-dihydrobenzene.[22]

(22) Rabideau, P. W.; Lipkowitz, K. B.; Nachbar, R. B., Jr. *J. Am. Chem. Soc.*, **1984**, *106*, 3119.

(23) Rabideau, P. W.; Huser, D. L. *J. Org. Chem.* **1983**, *48*, 4266.

(24) (a) Mathieu, J.; *Ann. Chim.* **1945**, *20* 215. Rigaudy, J. *Ibid.* *1950*, *5*, 398. (b) The cis compounds are also more stable in 10-alkyl-9-nitro-DHA's. See: Bartoli, G.; Bosco, M.; Dal Pozzo, R.; Sgarabotto, P. *J. Chem. Soc., Perkin Trans 2*, *1982*, 929.

(25) Sodium–ammonia reduction of ethyl 10-methylanthroate produces only the cis isomer.

(26) Cho, H.; Harvey, R. G.; Rabideau, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 1140.

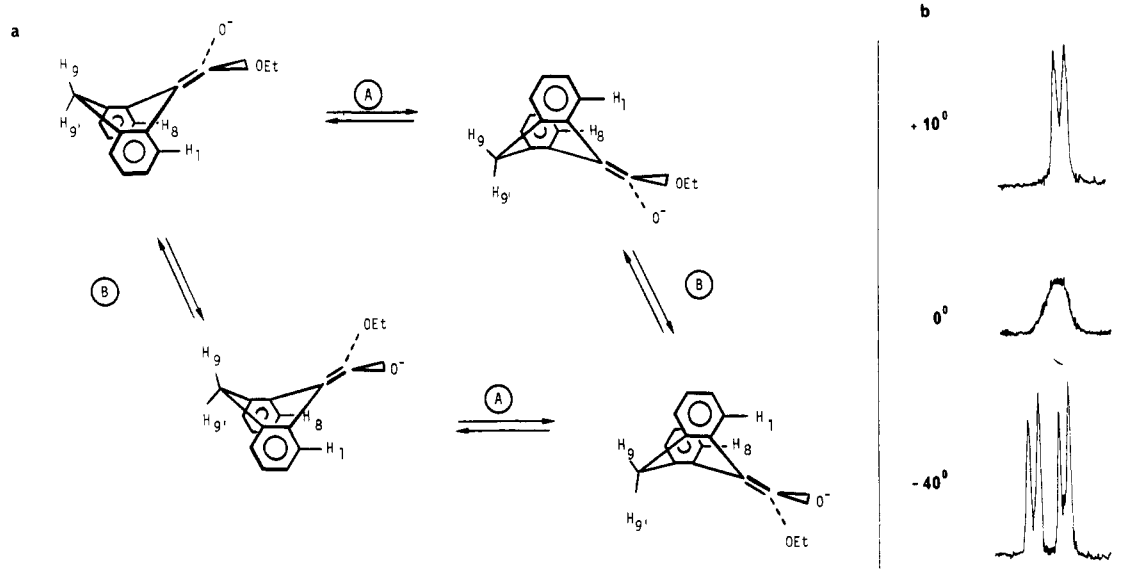
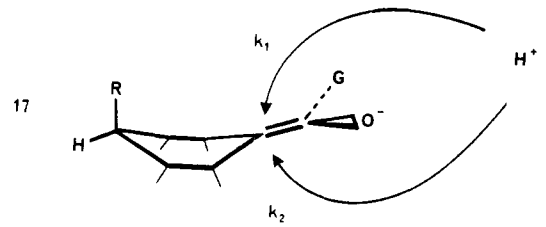


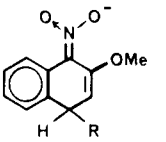
Figure 2. (a) Dynamic processes for ethyl 10-lithio-9,10-dihydroanthroate. Path A represents ring inversion: path B represents bond rotation. (b) Variable temperature NMR (THF-d_8) of H_1 H_8 region.

peratures (Figure 2b). Symmetry requirements for this observation do, in fact, indicate slow rotation around the C_9/carbonyl bond and therefore considerable enolate character.

Hence, we have established nonplanar structures with considerable enolate character. This leads us to suggest a model for protonation shown as structure **17**. We envision intermolecular protonation at carbon[27] (even if preceded by protonation at oxygen) from the least hindered side.[28] If there were very little ring folding in **17**, as one might expect in the dihydrobenzoate (DHB) series, then protonation could occur from either side[27] but the R group produces a transannular steric effect retarding k_1. This would produce trans products as is observed with 4-*tert*-butylbenzoic acid. Substantial folding, as with DHA's, would eventually make the underside lobe of the C_{10} p orbital accessible and together with an increase in the transannular steric effect, should favor k_2 (i.e., cis products). Hence this model would seem to provide a reasonable explanation for both the DHB's and DHA's.



We would expect the DHN system to be intermediate in ring folding, and hence the resulting mixture of both cis and trans products is not surprising. However, the changeover from cis predominance with the ketones to trans with the esters must be addressed. We propose that the ketones result in a more folded structure due to higher enolate character and/or greater steric interaction.[29] This is consistent with an earlier study involving the protonation of 2-methoxy-1,4-dihydronaphthalene-1-nitronate anion[31] (**18**). In this case even larger amounts of cis products were



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obtained (e.g., 85% for R = Me, 99% for R = Bz) no doubt due to high double bond characther at C-1 plus additional interference caused by the adjacent methoxy group. It is also suggested that the cis/trans ratio should be more sensitive to the size of R in more highly folded structures and that does seem to be the case for **18** as well as ketones **8–11**. Unfortunately, synthetic problems limited our study with the esters, but the two systems studied showed essentially no difference in isomer ratio in contrast to the ketones.

Experimental Section

General Procedure for Metal–Ammonia Reduction. The compound to be reduced is dissolved in 1 part THF and added to 2 parts ammonia at −78 °C (or −33 °C where specified) followed by the addition of 1.5 equiv of water and finally 2.5 equiv of sodium metal in small pieces. The reaction mixture is stirred for 20 min after the metal is dissolved and then poured quickly (or pumped through a glass tube) onto cooled, dilute, aqueous ammonium chloride. (Caution: this must be done carefully to avoid frothing.)

***cis*-9-Acetyl-10-methyl-9,10-dihydroanthracene (4).** 9-Acetyl-10-methylanthracene[32] (0.50 g, 2.0 mmol) was reacted with Na/NH_3 at −33 °C according to the general procedure to give *cis*-9-acetyl-10-methyl-9,10-dihydroanthracene as white crystals which were recrystallized from methanol: mp 114–116 °C; (0.31 g, 1.2 mmol, 62%); NMR (CCl_4) δ 1.5 (d, 3 H), 2.0 (s, 3), 4.1 (complex m, 1), 4.8 (bs, 1), 7.2 (complex s, 8).

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.41; H, 6.83. Found: C, 86.32; H, 6.88.

***cis*-9-Acetyl-10-ethyl-9,10-dihydroanthracene.** 9-Acetyl-10-ethylanthracene[33] (0.40 g, 1.6 mmol) was reacted with Na/NH_3 at −33 °C according to the general procedure to give white crystals

(27) Capon, B.; Zucco, C. *J. Am. Chem. Soc.* **1982**, *104*, 7567.
(28) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1968**, *90*, 6091.
(29) The *tert*-butyl group is large, of course, but its presence as OR effectively removes it from the site of steric interference. For example, the "A-value" for CH_2CH_3 is 2.1, but OCH_2CH_3 is only 1.0.[30]
(30) Eliel, E. L. "Stereochemistry of Carbon Compounds", McGraw-Hill: New York, 1962, p. 236.
(31) Baccolini, G.; Bartoli, G.; Bosco, M.; Dalpozzo, R. *J. Chem. Soc. Perkin Trans 2*, **1984**, 363.
(32) Prepared from 9-methylanthracene by Friedel–Crafts acylation. see: Merritt, C.; Braun, C. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, pp. 8–10.
(33) Prepared from 9-ethylanthracene by Friedel–Crafts acylation. See reference in note 32.

of *cis*-9-acetyl-10-ethyl-9,10-dihydroanthracene which were recrystallized from methanol: mp 99–100 °C (0.26 g, 1.0 mmol, 66%); NMR (CCl_4) δ 1.0 (t, 3 H), 1.6 (m, 2), 2.1 (s, 3), 1.3 (t, 1), 4.7 (s, 1), 7.2 (complex s, 8).

Anal. Calcd. for $C_{18}H_{18}O$: C, 86,36; H, 7.25. Found: C, 86.46; H, 7.28.

***cis*-Ethyl 10-Methyl-9,10-dihydro-9-anthroate.** 9-Methyl-9,10-dihydroanthracene was reacted with *n*-butyllithium in THF at 0 °C for 20 min. The reaction mixture was inverse quenched into a large excess of freshly distilled ethylchloroformate in THF to give *cis*- and *trans*-ethyl 10-methyl-9,10-dihydro-9-anthroate. Chromatography on silica (28-200 mesh) with 95% petroleum ether and 5% ethyl acetate eluent gave the ester in the second fraction. The yellow oil was microdistilled for analysis: NMR (CCl_4) δ 1.1 (t, 3 H), 1.4–1.6 (m, 3), 4.1 (q, 3), 4.8 (s, 1), 7.2 (m, 8).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.16; H, 6.83. Found: C; 81.26; H, 6.87.

***cis*-*tert*-Butyl 10-Methyl-9,10-dihydro-9-anthroate.** *tert*-Butyl 10-methyl anthroate[34] (0.50 g, 1.7 mmol) was reacted with Na/NH_3 at −33 °C according to the general procedure. *cis*-*tert*-Butyl 10-methyl-9,10-dihydro-9-anthroate was obtained as a pale yellow oil and was microdistilled (0.40 g, 1.4 mmol, 80%). NMR (CCl_4): δ 1.3 (s, 9 H), 1.5 (d, 3), 3.7 (m, 1), 4.7 (s, 1), 7.2 (m, 8).

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.63; H, 7.48. Found: C, 81.72; H, 7.54.

***cis*-*tert*-Butyl 10-Ethyl-9,10-dihydro-9-anthroate.** *tert*-Butyl 10-ethylanthroate[35] (0.45 g, 1.5 mmole was reacted with Na/NH_3 at −33 °C according to the general procedure to give *cis*-*tert*-Butyl 10-ethyl-9,10-dihydro-9-anthroate, a yellow oil, which was microdistilled. (0.36 g, 1.2 mmol, 79%). NMR (CCl_4): δ 0.90 (t, 3 H), 1.3 (s, 9), 1.7 (t, 2), 3.6 (t, 1), 4.7 (s, 1), 7.2 (complex s, 8).

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.91; H, 7.97.

1-Acetyl-4-methyl-1,4-dihydronaphthalene (8). 1-Acetyl-4-methylnaphthalene[36] (0.50 g, 2.7 mmol) was reacted with Na/NH_3 according to the general procedure to give a colorless oil which was a mixture of *cis*- and *trans*-1-acetyl-4-methyl-1,4-dihydronaphthalene (see Table II). The mixture was microdistilled. (0.43 g, 2.3 mmol, 86%). NMR (CCl_4): δ 1.3 (d, 3 H), 2.8 (d, 3), 3.4 (m, 1), 4.2 (m, 1), 5.6–6.1 (m, 2), 7.1 (m, 4).

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H 7.58. Found: C, 83.56; H, 7.63.

1-Acetyl-4-ethyl-1,4-dihydronaphthalene (9). 1-Acetyl-4-ethylnaphthalene[37] (0.50 g, 2.2 mmol) was reacted with Na/NH_3 according to the general procedure to give *cis*- and *trans*-1-acetyl-4-ethyl-1,4-dihydronaphthalene (see Table II), a colorless oil, which was microdistilled. (0.44 g, 1.9 mmol, 88%). NMR (CCl_4): δ 0.5–1.0 (two triplets, 3 H), 1.6–1.9 (overlapping methyl from acetyl and methylene from ethyl group, 5), 3.2–3.5 (m, 1), 4.2 (m, 1) 5.9 (m, 2), 7.1 (m, 4).

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.73; H, 8.13.

1-Acetyl-4-isopropyl-1,4-dihydronaphthalene (10). 1-Acetyl-4-isopropylnaphthalene[38] (0.50 g, 2.4 mmol) was reacted with Na/NH_3 according to the general procedure to give *cis*- and *trans*-1-acetyl-4-isopropyl-1,4-dihydronaphthalene (see Table II), a colorless oil, which was microdistilled. (0.39 g, 1.9 mmol, 79%). NMR (CCl_4): δ 0.5–1.1 (two sets of doublets, 6 H), 1.7-2.2 (two singlets from acetyls overlapping with one H from isopropyl group, 4), 3.3 (m, 1), 4.2 (m, 1), 6.0 (m, 2), 7.1 (m, 4).

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.37; H, 8.79.

***tert*-Butyl 4-Methyl-1,4-dihydro-1-naphthoate (6).** *tert*-Butyl 4-methylnaphthoate[39] (0.50 g, 2.0 mmol) was reacted with Na/NH_3 accordig to the general procedure to give *cis*- and *trans*-*tert*-butyl 4-methyl-1,4-dihydro-1-naphthoate (see Table II), a colorless oil, which was microdistilled. (0.41 g, 1.6 mmol, 82%). NMR (CCl_4): δ 1.2–1.5 (overlapping *tert*-butyl and methyl signals, 12 H), 3.4 (m, 1), 4.2 (m, 1), 5.8 (m, 2), 7.1 (m, 4).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65, H, 8.25. Found: C, 78.40; H, 8.21.

***tert*-Butyl 4-Ethyl-1,4-dihydro-1-naphthoate (7).** *tert*-Butyl 4-ethyl-1-naphthoate[40] (0.50 g, 2.0 mmol) was reacted with Na/NH_3 according to the general procedure to give *cis*- and *trans*-*tert*-butyl 4-ethyl-1,4-dihydro-1-naphthoate (see Table II), a yellow oil, which was microdistilled. (0.40 g, 1.6 mmol, 80%). NMR (CCl_4): δ 0.5–0.9 (overlapping triplets from methyl on ethyl group, 3 H), 1.3–1.9 (overlapping *tert*-butyl singlets and methylenes from ethyl group, 11), 3.1–3.4 (m, 1), 4.1 (m, 1), 6.8 (m, 2), 7.1 (m, 4).

Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.02; H, 8.60. Found C, 79.22; H, 8.53.

***trans*-*p*-*tert*-Butyl-1,4-dihydrobenzoic Acid (14).** Commercial *p*-*tert*-butylbenzoic acid[41] was reacted with Na/NH_3 at −33 °C according to the general procedure, but NO water was added. After quenching, the ammonia was boiled off and the reaction mixture was cooled at 0 °C and acidified with dilute HCl. The aqueous solution was then extracted with ether, and the ether layer was washed with cold water, dried over $MgSO_4$, and evaporated. The resulting yellow oil was triturated with COLD methanol to yield white crystals of *trans*-*p*-*tert*-butyl-1,4-dihydrobenzoic acid: mp 85–87 °C (0.35 g, 2.0 mmol, 70%); NMR (CCl_4) δ 0.9 (s, 9 H), 2.4 (m, 1), 3.5–3.8 (m, 1), 5.9 (m, 4), 10.7 (s, 1).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.29; H, 8.97. Found C, 73.20; H, 8.79.

Acknowledgment. We gratefully acknowledge support from the U.S. Department of Energy, Office of Basic Energy Science, as well as technical assistance from D. Michael Young.

(34) 9-Methylanthracene was reacted with oxalyl chloride in a general procedure to furnish the carboxylic acid precursor. See: Fieser, W.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. I, p. 769. Esterification was achieved using trifluoroacetic anhydride and *tert*-butyl alcohol. See: Panish, R. C.; Stock, L. *J. Org. Chem.* **1965**, *30*, 927.

(35) Prepared from 9-ethylanthracene according to references in note 34.

(36) Prepared from 1-methylnaphthalene by Friedel–Crafts acylation. See reference in note 32.

(37) Prepared from 1-ethylnaphthalene by Friedel–Crafts acylation. See reference in not 32.

(38) 1-Isopropylnaphthalene was prepared by isopropyl Grignard addition to α-tetralone and subsequent dehydration–rearomatization by heating with sulfur. Acylation was done according to the reference in note 32.

(39) 1-Methylnaphthalene was reacted with oxalyl chloride and subsequently esterified with trifluoracetic anhydride and *tert*-butyl alcohol according to general procedures. See note 34.

(40) The Grignard reagent from 1-bromo-4-ethylnaphthalene was carbonated to give the acid. Esterification was accomplished using *tert*-butoxide. See: Kaiser, E.; Woodruff, R. *J. Org. Chem.* **1970**, *35*, 1199.

(41) *p*-*tert*-Butylbenzoic acid was first recrystallized from methanol by the addition of a small amount of water.