

Role of Ion-Pair Solvation Complexes in the Protonation Stereospecificity of 10-*tert*-Butyl-9-alkyl-9-metallo-9,10-dihydroanthracenes¹

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Abstract: Diethyl ether solutions of the lithium salt of 10-*tert*-butyl-9-methyl-9,10-dihydroanthracene (Li-3) react with ethanol at 25 or -78° to yield $>99\%$ *cis* hydrocarbon. After the addition of *ca.* 6 equiv of HMPA to diethyl ether solutions of Li-3, reaction with ethanol at -78° yields $>99\%$ *trans* hydrocarbon. Reactions of THF and HMPA solutions of Li-3 with ethanol yield mainly *cis* hydrocarbon and mainly *trans* hydrocarbon, respectively. Parallel solvent effects are observed for protonation of Na-3, Li-4, and Na-4 (4 is the 9-ethyl carbanion). Spectroscopic studies indicate that Li-3 and Li-4 are mixtures of contact and solvent-separated ion pairs in diethyl ether solutions. THF and HMPA solutions of Li-3 and HMPA solutions of Na-3 have identical pmr and visible spectra. Different types of contact ion pairs are present in diethyl ether and THF solutions of Na-3 and Na-4. The -65° pmr spectrum of Li-3 in diethyl ether solution is converted into one virtually identical with those observed in THF and HMPA solution on addition of *ca.* 1.5 equiv of HMPA. This indicates the formation of an HMPA-separated ion pair. Our conclusion from the protonation results is that only when the lithium cation is fully HMPA solvated does stereospecific protonation to *trans* hydrocarbon occur. We call this species a loosely associated ion pair. Our proposal is that the carbanion in structured ion pairs, contact and solvent-separated, shows *cis* stereoselectivity on protonation and that the carbanion in loosely associated ion pairs or free ions shows *trans* stereoselectivity on protonation. The protonation stereoselectivity of the structured ion pairs is probably metal-cation directed, whereas in loose ion pairs product development controls the protonation stereoselectivity.

Recent interest in ion pairing has led to many spectroscopic studies of the alkali metal salts of resonance-stabilized carbanions and organic radical anions.³ The results from these studies have been explained in terms of equilibrium mixtures of different types of ion pairs (eq 1). The less associated ion pairs, loosely



associated ($A^{-} | S | Me^{+}$) and free (A^{-}), are favored by low concentration, low temperature, and small cations. The formation of less associated ion pairs is also favored by strongly coordinating solvents such as the higher glyme ethers,⁴ crown ethers,⁵ and hexamethylphosphoramide (HMPA).⁶ In contrast, less effective coordinating solvents, such as diethyl ether and tetrahydrofuran (THF), favor the formation of more tightly associated ion pairs, contact ($A^{-} \cdot Me^{+}$) and solvent separated ($A^{-} || Me^{+}$).

However, conclusions from spectroscopic studies of resonance-stabilized carbanions can be ambiguous when it comes to the number and relative amounts of ion-pair species present. Only the time-averaged species can be studied by pmr since the rates of equilibrium between ion pairs are rapid compared to the preexchange life-

time.⁷ Electronic spectra can be used to determine concentrations of ion-pair species that have distinguishable spectra,⁸ but distinguishable spectra are not always observed.⁹

Cognizant of these spectroscopic ambiguities, we have studied the influence of the different ion-pair species, or their equilibrium mixtures, as determined spectroscopically on the reactivity of resonance-stabilized carbanions. If different ion-pair species yield different products upon protonation, this might provide a method of differentiating between spectroscopically indistinguishable species. For our experiments, we chose 10-*tert*-butyl-9-alkyl-9-metallo-9,10-dihydroanthracenes and studied the effects of solvent, temperature, and cation on the pmr and visible spectra and the effects of solvent, temperature, cation, and proton donor on the protonation reaction (*cis* or *trans* hydrocarbons can be formed).

The 9,10-dialkyl-9,10-dihydroanthracenes are particularly well suited to a study of this type. Unsubstituted and 10-alkyl-9,10-dihydroanthracene anions have been briefly studied spectroscopically and were found to behave similarly to the structurally similar and well-studied fluorenyl anion.¹⁰ Thus, the general spectroscopic correlations with ion-pair structure found for fluorenyl anion should apply here.^{7,8,11} The desired hydrocarbons can be readily synthesized by known

(1) Portions of this work have been previously presented: E. J. Panek and T. J. Rodgers, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973, No. ORGN-021; E. J. Panek and T. J. Rodgers, Abstracts, 1st Fall Organic Conference of the American Chemical Society, Cape Cod, Mass., Oct 1973, p 42.

(2) National Science Foundation Trainee, 1970-1972.

(3) For reviews see M. Szwarc, "Carbanions, Living Polymers, and Electron Transfer Processes," Interscience, New York, N. Y., 1968; M. Szwarc, Ed., "Ions and Ion Pairs in Organic Reactions," Vol. I, Interscience, New York, N. Y., 1972; J. Smid, *Angew. Chem., Int. Ed. Engl.*, 11, 112 (1972).

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Table I. Proton Magnetic Resonance Data for 1 and 2^a

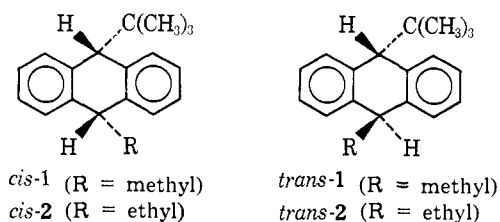
Compd	R ₉ ^b	NOE results ^c		Chemical shifts, ppm			J _{H₁₀, CH₂, or CH₃} , Hz
		H ₉	H ₁₀	H ₉	H ₁₀	CH ₂ CH ₃	
<i>trans</i> -1 ^d	CH ₃	+1	+8	4.07	3.66		6.8
<i>cis</i> -1	CH ₃	+13	+11	4.14	3.77		7.5
<i>trans</i> -2	CH ₃ CH ₂	+5	+12	4.12	3.59	0.64	3.8
<i>cis</i> -2	CH ₃ CH ₂	+12	(Total)	3.73	3.72	1.25	7.5

^a Run at 100 MHz in CCl₄ solutions. ^b R₁₀ = *tert*-butyl for all compounds. ^c Enhancements upon aryl irradiation. ^d Private communication from R. G. Harvey, March 1973.

methods¹² and the configurations of related 9,10-dialkyl-9,10-dihydroanthracenes have been determined.¹²⁻¹⁴

Results

Preparation and Characterization of the Hydrocarbons. Product mixtures containing *cis*- and *trans*-10-*tert*-butyl-9-methyl-9,10-dihydroanthracene (*cis*- and *trans*-1) were prepared by reaction of anthracene with



tert-butyllithium in THF solution at 0° followed by alkylation with iodomethane.¹² Fractional crystallization from absolute ethanol yielded the pure isomers, mp 115.5–117° and mp 125–126°. Similar reactions between anthracene and *tert*-butyllithium followed by alkylation with diethyl sulfate yielded product mixtures containing *cis*- and *trans*-10-*tert*-butyl-9-ethyl-9,10-dihydroanthracene (*cis*- and *trans*-2). Only one isomer, mp 122–124°, could be obtained pure by fractional crystallization. The other isomer of 2, mp 46–48°, was obtained by isomerization of the mp 122–124° isomer *via* lithiation with *n*-butyllithium in THF solution followed by protonation with ethanol (see below).

The configurations and preferred conformations of these hydrocarbons were assigned by pmr methods. Nuclear Overhauser enhancements (NOE) have been used for determination of the configurations and preferred conformations of 9,10-dialkyl-¹³ and 9-alkyl-9,10-dihydroanthracenes.¹⁵ Irradiation of the peri aromatic protons leads to greater enhancement of the quasi-equatorial protons than the quasi-axial protons at C₉ and C₁₀ if the preferred conformation is a boat.^{13,15} Application of this technique to the isomers of 1 and 2 gave results (Table I) which allowed the unambiguous assignment of the mp 115.5–117° isomer of 1 and the mp 122–124° isomer of 2 as the *trans* isomers.¹⁶ The

much greater enhancement of the C₁₀ protons for the *trans* isomers implies that the preferred conformation is a boat with the *tert*-butyl group in a quasi-axial position. Additional pmr evidence which supports these assignments is that irradiation of the *tert*-butyl group of *cis*-1 leads to an 18% enhancement of H₁₀ and no detectable enhancement of H₉. The lower field chemical shift of the methyl protons of the ethyl group of *cis*-2 compared to *trans*-2 is consistent with the assignments. Steric interactions between the *tert*-butyl and ethyl groups in *cis*-2 will make conformations which have the methyl group over the aromatic rings less favorable for *cis*-2 than *trans*-2. Thus the methyl group will not be shielded as much in *cis*-2.

The relative rates of lithiation of *cis*-1 and *trans*-1 were determined by competition experiments. A mixture of 0.047 *N cis*-1 and 0.062 *N trans*-1 was reacted with 0.31 *N n*-butyllithium in diethyl ether solution at room temperature. After 8 hr, 83% of the *cis*-1 was lithiated, but only 8% of the *trans*-1 was lithiated. Pseudo-first-order plots of the rates of lithiation indicated that the relative rates of lithiation for *cis*- and *trans*-1 are 20:1, respectively. Analysis of the products obtained upon quenching portions of this solution with dimethyl sulfate and deuterium oxide showed that lithiation occurred only at C₉. The rates of lithiation in diethyl ether solution for both isomers of 2 were much slower than the corresponding rates for the isomers of 1. The rate of lithiation of *cis*-2 is *ca.* six times greater than that of *trans*-2.

Preparation and Spectra of the Carbanions. *cis*- and *trans*-1 and *cis*- and *trans*-2 all react rapidly with *n*-butyllithium in THF, HMPA, and diethyl ether-HMPA mixture solutions to form 10-*tert*-butyl-9-lithio-9-methyl-9,10-dihydroanthracene (Li-3) and 10-*tert*-butyl-9-ethyl-9-lithio-9,10-dihydroanthracene (Li-4), respectively. In diethyl ether solution, it is more convenient because of their greater reactivities to use *cis*-1 and *cis*-2 for the preparation of Li-3 and Li-4. The corresponding sodium compounds, Na-3 and Na-4, are prepared by reaction of a hexane suspension of *n*-butylsodium with *cis*-1 and *trans*-2, respectively.¹⁷

The visible spectra of the carbanions show the expected shifts of the absorptions to lower energies as the solvent is changed from diethyl ether to THF to HMPA (Table II). These changes are indicative of the decreasing interactions between the metal cation and the carbanion as the coordinating ability of the solvent increases. All of the absorption bands, except those for Li-3 and Li-4 in diethyl ether solution, were relatively sharp, single bands. The lower energy transitions for the sodium salts in diethyl ether solution indi-

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 (14) R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *J. Amer. Chem. Soc.*, **91**, 4535 (1969).
 (15) A. W. Brinkmann, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **92**, 5912 (1970).
 (16) Similar results have been obtained for these four compounds and seven related ones by Professor P. W. Rabideau. We thank Professor Rabideau for sharing these results with us prior to publication: P. P. Fu, R. G. Harvey, J. W. Paschal, and P. W. Rabideau, *J. Amer. Chem. Soc.*, submitted for publication.

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Table II. Visible Spectra of Dihydroanthracene Anions at Room Temperature

Carbanion	λ_{\max} , nm		
	Ether	THF	HMPA
Li-3	444 464 (sh)	464	464
Na-3	456	461	464
Li-4	442 465 (sh)	466	465
Na-4	454	461	465

cate that the larger sodium cation cannot approach the carbanion as closely as the smaller lithium cation can. The changes observed upon going to THF solution show that the more readily coordinated lithium cation is effectively moved further from the carbanion and thus perturbs its electronic transition less than the sodium cation. The shoulders observed for Li-3 and Li-4 in diethyl ether solution are presumably from solvated ion-pair species similar to those formed in THF solution. Since the sodium and lithium salts have the same absorption position in solutions containing the strongly coordinating HMPA, it is reasonable to assume that the cation is only loosely associated with the carbanion, if at all, in this solvent.

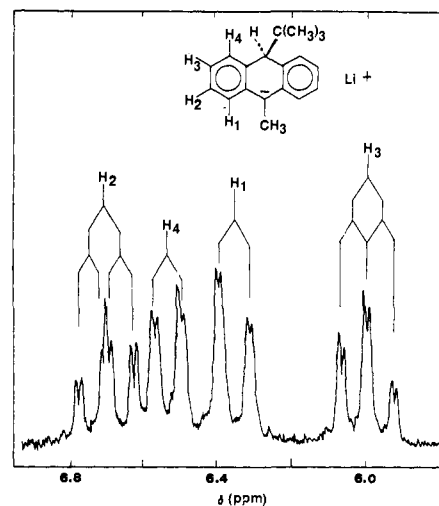
The pmr spectra of the carbanions as functions of solvent and metal cation show the same pattern of changes seen in the visible spectra (Table III). The

Table III. Apparent Chemical Shifts of the Aromatic Protons of Dihydroanthracene Anions^a

Carbanion	Temp, °C	Solvent	δ , ppm, aromatic protons ^b			
			1	2	3	4
Li-3	30	Ether	6.35	6.70	6.00	6.53
	-65	Ether	6.27	6.65	5.94	6.46
	30	THF	6.12	6.48	5.72	6.31
	-65	THF	6.04	6.43	5.68	6.24
Na-3	30	HMPA	6.10	6.48	5.72	6.30
	30	Ether	6.41	6.73	6.00	6.60
	30	THF	6.31	6.67	5.90	6.51
Li-4	30	HMPA	6.10	6.48	5.72	6.30
	30	Ether	6.49	6.71	6.05	6.57
	30	THF	6.24	6.46	5.72	6.32
	30	HMPA	6.22	6.43	5.71	6.29

^a Relative to internal tetramethylsilane. These shifts are independent of concentration over the range 0.1–0.8 *N*. ^b See Figure 1 for the numbering of the aromatic protons.

spectra were readily interpreted and the aromatic protons were assigned by inspection and spin decoupling (Figure 1). Some of the spectra were fit by computer simulation to obtain more accurate chemical shifts and coupling constants (see Experimental Section). The aromatic protons are shifted upfield in the order HMPA \sim THF $>$ diethyl ether for the lithium salts and HMPA $>$ THF $>$ diethyl ether for the sodium salts. The tighter the association between the metal cation and the carbanion, the less charge delocalization there will be on the carbanion, which will lead to smaller upfield shifts of the aromatic protons.^{7,11} Thus the extent of interaction between the metal cation and the carbanion follows the order ether $>$ THF \sim HMPA for the lithium salts and ether $>$ THF $>$ HMPA for the sodium salts. The identical pmr spectra obtained for Li-3 and Na-3 in HMPA solutions confirm the

**Figure 1.** The pmr spectrum of the aromatic protons of Li-3 in diethyl ether solution at +30°.

conclusion that the metal cations are interacting only weakly, if at all, with the carbanion in this strongly coordinating solvent. Free ions are formed in dilute HMPA solutions of lithium, sodium, or potassium salts of anthracene radical anion.⁶ Thus Li-3 or Li-4 and Na-3 or Na-4 are probably free ions or loosely associated ion pairs in HMPA solution. The spectra obtained for Na-3 and Na-4 in diethyl ether and THF solutions and for Li-3 and Li-4 in diethyl ether solutions are consistent with contact or solvated contact ion-pair species as the major or only species present. The minor species detected by visible spectra in diethyl ether solutions of Li-3 and Li-4 appears identical with the species detected in THF solutions of Li-3 and Li-4. This species is most likely a solvent-separated ion pair but could be a loosely associated ion pair or free ion. Free ions and solvent-separated ion pairs are also spectroscopically indistinguishable for 9-fluorenyl and 9-substituted-9-fluorenyl anions.^{8,18}

Pmr spectra of Li-3 in diethyl ether–HMPA solvent mixtures at +30 and -65° were taken in an attempt to determine the stoichiometries of complexes formed between Li-3 and HMPA. Plots of the chemical shift of H₃ vs. the HMPA to Li-3 ratio at -65 and +30° show that HMPA readily complexes with Li-3 and that the complex formation constant is greater at -65° (Figure 2).¹⁹ The chemical shifts of the aromatic protons are virtually identical with those obtained in pure HMPA solution at ratios of HMPA to Li-3 greater than ca. 1.5 at -65° and ca. 4 at +30°. The concentration of HMPA in these mixture solutions is low enough (up to ca. 0.8 *M*) that it is not changing the bulk properties of the solution to any appreciable extent.²⁰ Thus the presence of only small amounts of HMPA can change the structures of the ion pairs of Li-3 initially present in diethyl ether solution.¹⁶ The “break point” in the plot for the -65° experiments at a HMPA to Li-3 ratio of ca. 1.5 suggests that the initially formed complex has 1:1 stoichiometry. The detection of two different types of HMPA ($\Delta\delta \sim 0.1$ ppm) at -65° at HMPA to Li-3 ratios up to ca. 1.5 allows us to calculate a forma-

(18) L. L. Chan and J. Smid, *J. Amer. Chem. Soc.*, **90**, 4654 (1968).

(19) Similar plots of the chemical shifts of H₁, H₂, and H₄ vs. the HMPA to Li-3 ratio yield identical results.

(20) E. J. Panek, *J. Amer. Chem. Soc.*, **95**, 8460 (1973).

Table IV. Per Cent Yield of *cis*-1 Formed on Protonation of 3^a

Cation Solvent Temp, °C	Ether		Li			Na		
	25	-78	THF	-78	HMPA	25	THF	HMPA
Proton donor								
2-Methyl-2-propanol	>99	>99	95	84	16			
Ethanol	>99	>99	90	77	23	>99	94	22
Triethylammonium trifluoroacetate	>99				70			
1-Propyne	94		85		20			
Hydrogen chloride	95	95	84	70				

^a These are relative yields determined by glpc and are the average of at least two reactions. The product yields are not affected over a concentration range of 0.1–0.3 *N* for the carbanion, nor are they a function of the amount or method of addition of the proton donor. In some cases, *n*-tetracosane was used as an internal glpc standard, and the absolute yields were $\geq 95\%$.

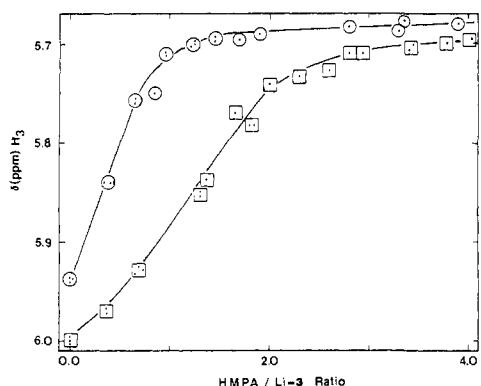


Figure 2. The influence of added HMPA on the apparent chemical shift of H₃ of Li-3 in diethyl ether solution at +30° (□) and -65° (○).

tion constant for a 1:1 complex. Assuming the upfield HMPA signal is due to complexed HMPA held over the shielding region of the aromatic rings,^{11b} the formation constant is calculated to be *ca.* 20. The single type of HMPA observed after the addition of 4 equiv or more of HMPA has a chemical shift slightly downfield of the apparently free HMPA observed when smaller quantities were added. This possibly indicates that the HMPA–lithium cation complex is now further away from the carbanion since the HMPA is no longer being shielded. In similar experiments with THF–HMPA mixture solutions at +30 and -65°, straight-line plots of the chemical shift of H₃ *vs.* the HMPA:Li-3 ratio with essentially zero slope are obtained.¹⁹ This re-emphasizes the similarity of the spectral properties of Li-3 in THF and HMPA solutions.

Protonation of the Carbanions. The products of reaction of the carbanions with proton donors in diethyl ether, THF, or HMPA solutions depend primarily upon the reaction solvent. The other variables studied (proton donor, method of protonation, metal cation, temperature, and carbanion) exert much smaller influences on the product distributions (Tables IV and V). The *cis* hydrocarbon is the exclusive or major product formed in diethyl ether or THF solutions. The *trans* hydrocarbon is the major product in HMPA solutions. The protonations were done three different ways: the neat proton donor was added to the carbanion solution; a solution of the proton donor was added to the carbanion solution (same solvent); and the carbanion solution was added to a solution of the proton donor (same solvent). For example, a THF solution of Li-3 when quenched with 2-methyl-2-

Table V. Per Cent Yield of *cis*-2 Formed on Protonation of 4 at Room Temperature^a

Cation Solvent	Li			Na
	Ether	THF	HMPA	THF
Proton donor				
2-Methyl-2-propanol	>99	94		
Ethanol	>99	76	20	74
Triethylammonium trifluoroacetate	>99	77		80

^a See footnote *a*, Table IV.

propanol at room temperature yields 95, 96, and 95% of *cis*-1 by the three methods in turn. Thus the method of protonation has no influence on the product distribution. The proton donors used represent a wide range of *pK_a*'s (triethylammonium ~ 10 ,²¹ ethanol ~ 18 , 2-methyl-2-propanol ~ 19 , 1-propyne ~ 25) and acid types (positive nitrogen, oxygen, and carbon). They can also be classed as those that can coordinate to the metal cation, ethanol and 2-methyl-2-propanol, and those that are not expected to coordinate to the metal cation, hydrogen chloride, 1-propyne, and triethylammonium. Protonation of Li-3 with hydrogen chloride or 1-propyne in diethyl ether or THF solutions yields less *cis*-1 than does protonation with ethanol or 2-methyl-2-propanol. This suggests that the metal cation coordinating ability of the proton donor has an influence on the protonation stereoselectivity in these solvents. The similarity of the per cent *cis*-1 obtained on protonation of Li-3 in HMPA solution by 2-methyl-2-propanol, 1-propyne, and ethanol suggests that the metal cation coordinating ability of the proton donor has no influence on the protonation stereoselectivity in HMPA solution.

The influence of HMPA on the protonation results was studied in more detail by protonating Li-3 with ethanol in diethyl ether–HMPA mixture solutions at room temperature and -78° (Table VI). Plots of the per cent *trans*-1 obtained *vs.* the HMPA:Li-3 ratio are qualitatively similar to the pmr results obtained in ether–HMPA mixture solutions (Figure 3). Even the qualitative temperature dependence is the same. We feel this similarity demonstrates that the effect of HMPA on the protonation reactions is, as in the pmr results, due to coordination of the lithium cation by HMPA and the resulting change in the ion-pair structures. Additional support for this hypothesis is the fact that

(21) The *pK_a* of triethylammonium ion is 9.0 in dimethyl sulfoxide solution, 10.7 in aqueous solution, and 18.5 in acetonitrile solution: I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *J. Amer. Chem. Soc.*, **90**, 23 (1968).

Table VI. Per Cent Yield of *trans*-1 Formed on Ethanolysis of Li-3 in Diethyl Ether-HMPA Mixture Solutions

25°				78°			
HMPA:Li-3 ^a	Yield	HMPA:Li-3 ^a	Yield	HMPA:Li-3 ^a	Yield	HMPA:Li-3 ^a	Yield
0.0	<0.5	7.12	71.2	0.0	<0.5	1.74	87.6
0.24	7.6	10.0	75.0	0.22	8.0	2.09	93.0
1.91	46.8	18.0	82.8	0.27	12.4	2.97	96.5
3.00	50.3	50	84.8	0.71	38.2	4.00	98.3
3.69	57.0			0.86	59.2	4.54	99.1
6.90	72.5			1.00	66.2	6.50	>99.5
				1.31	79.6	9.00	>99.5

^a The HMPA:Li-3 ratio was determined by integration of the pmr spectrum. These values are accurate to ca. 5% up to a ratio of 10. The higher ratios are less accurate. These are relative yields determined by glpc.

no *cis* isomer is detected in the -78° reactions when 6.5 equiv of HMPA is added. A typical coordination number for lithium cation is four.^{4b} Thus, only when the lithium cation is fully solvated by HMPA is there *trans* stereospecificity on protonation.

This conclusion was confirmed by examining the effect of small amounts of HMPA on the protonation of Li-3 with 2-methyl-2-propanol in THF solution at room temperature. The results are: 0 equiv HMPA, 5% *trans*-1; 10 equiv, 20%; 18 equiv, 34%; 36 equiv, 69%. Comparison of these results with the results in Table VI indicates that the bulk amount of HMPA present in THF and diethyl ether solutions does not determine the yield of *trans*-1. Rather, the yield of *trans*-1 reflects the amount of HMPA coordination to the lithium cation that has occurred. Since THF is a better coordinating agent than diethyl ether, it is not unexpected that HMPA competes with diethyl ether better than it does with THF for coordination sites at the lithium cation. The extent of coordination of HMPA to Li-3 in THF solution could not be determined spectroscopically since Li-3 has identical pmr and visible spectra in THF and HMPA solutions. These results also imply that HMPA-proton donor interactions are not a necessary condition for formation of *trans* hydrocarbon.

The formation of mainly *cis* hydrocarbon in diethyl ether solution is not due to equilibration of the hydrocarbons during the quenches. The relative rates of lithiation of *cis*- and *trans*-1 (20:1) indicate that any *trans*-1 formed would be more resistant to remetalation than *cis*-1.

The results of protonation of Li-3 (and likewise Li-4) formed from either *cis*- or *trans*-1 (or 2) in diethyl ether, THF, or HMPA solutions are identical. Identical visible and pmr spectra were also obtained for Li-3 (or Li-4) formed from either stereoisomeric precursor in these solvents. Thus the carbanions have no memory of their precursors which means that the lithium cation can change sides of the carbanion, and C₉ must be planar at least part of the time. The similarity of the protonation results and the visible spectra of Na-3 (obtained from *cis*-1) and of Na-4 (obtained from *trans*-2) suggests that Na-3 and Na-4 also have no memory of the stereoisomer of their precursors.

Discussion

The spectra indicate that different types of ion pairs for 3 or 4 are present in most of the solutions studied. Spectroscopically, the environments of Li-3 and Li-4 in THF, HMPA, or diethyl ether-HMPA mixture solutions (containing enough HMPA) are identical. How-

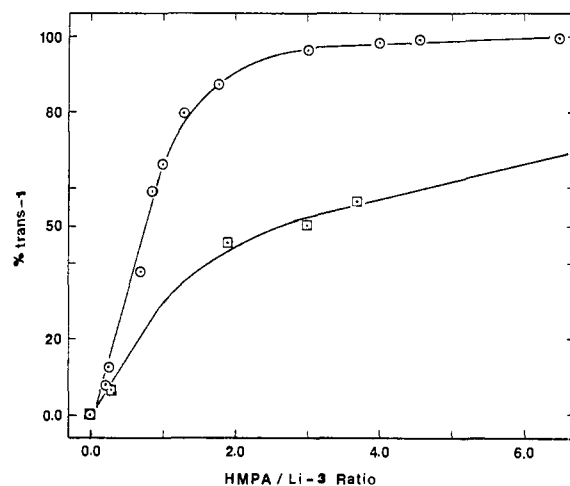
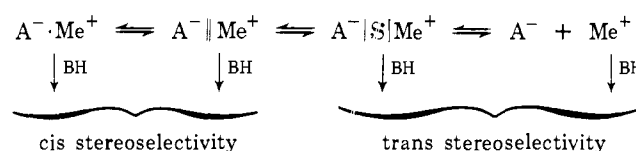


Figure 3. The influence of added HMPA on the yield of *trans*-1 on reaction of Li-3 with ethanol in diethyl ether solution at +25° (□) and -78° (○).

ever, in the presence of enough HMPA to coordinately saturate the metal cation the protonation stereoselectivities are different for the HMPA containing solutions. Thus these spectroscopically indistinguishable environments are chemically distinguishable. The effect of HMPA could be primarily due to changed ion-pair structure upon coordination of HMPA to the metal cation.

Our explanation of the protonation results is that the loosely associated ion pairs ($A^-\cdot S|Me^+$) and free ions (A^-) preferentially form *trans* hydrocarbon on protonation and that the more structured ion pairs, contact ($A^-\cdot Me^+$) and solvent-separated ($A^-\parallel Me^+$), preferentially form *cis* hydrocarbon on protonation (Scheme I). The loosely associated ion pairs are the fully

Scheme I



HMPA-solvated species formed in diethyl ether-HMPA mixture solutions of Li-3. Free ions are not expected under these conditions,¹⁸ and the pmr results suggest this species is different geometrically from solvent-separated ion pairs.

Another possible explanation is that the carbanions exist as aggregates in diethyl ether and THF solutions and as monomers in HMPA and diethyl ether-HMPA

mixture solutions. The aggregates would form *cis* hydrocarbon and the monomers would form *trans* hydrocarbon upon protonation. Although we have not measured the extent of aggregation of these carbanions, 1-naphthylmethyl- and 2-naphthylmethyl-lithium, which could stack better into aggregates than these substituted dihydroanthracene anions, are monomeric in diethyl ether solution at similar concentrations.^{7b} Thus, these dihydroanthracene anions should also be monomeric so that explanations based on differing protonation stereoselectivities for differing states of aggregation should not apply.

The observed *cis* stereoselectivity for protonation of **3** and **4** in diethyl ether and THF solutions is easily rationalized by Scheme I. Contact and solvent-separated are the only or the predominant ion-pair species present. Protonation, especially by alcohols and water, of carbanions in contact ion-pair species occurs *syn* to the metal cation.²² This product control is the result of coordination of the alcohol to the metal cation prior to protonation of the carbanion. Formation of *cis* hydrocarbon on protonation of **3** or **4** requires protonation *trans* to the *tert*-butyl group. The stereoisomer of the contact ion pairs of **3** and **4** which has the partially solvated metal cation *trans* to the *tert*-butyl group will lead to formation of *cis* hydrocarbon by protonation *syn* to the metal cation. Protonation of the carbanion in contact ion pairs is probably preceded by coordination of the proton donor to the metal cation, when possible, since Li-**3** in diethyl ether solution stereospecifically yields *cis*-**1** on protonation by the alcohols. However, hydrogen chloride and 1-propyne, which are not expected to coordinate to the metal cation, give only stereoselective formation of *cis*-**1**. The *cis* stereoselectivity observed with these noncoordinating proton donors is due to the instability of free ions in diethyl ether and THF solutions.¹⁸ Thus protonation *syn* to the metal cation will preferentially occur so that the anion of the proton donor can readily form a contact or solvent-separated ion pair. Protonation by triethylammonium ion is probably preceded by ion exchange with the metal cation to form the *trans* stereoisomer of this new ion pair. Transfer of the proton will now lead to *cis* hydrocarbon. The formation of 70% *cis*-**1** on reaction of Li-**3** with triethylammonium ions in HMPA solutions indicates that, even in the highly polar HMPA solutions, the ammonium ion prefers to approach the carbanion by the pathway that leads to intermediates resembling contact ion pairs. The solvent-separated ion pairs of **3** and **4** probably have the same general structure as the contact ion pairs and react in a similar fashion.

The proposed *trans* positions of the *tert*-butyl group and the partially solvated metal cation in contact ion pairs of **3** and **4** are consistent with the crystal and molecular structure of 9-fluorenyllithium bisquinclidine.²³ The lithium cation is located *ca.* 2 Å above the ring plane and 1.1 Å in front of the carbanion and is bonded to C₉, C₁₀, and C₁ by an asymmetric three-centered bond (closer to C₉ than C₁). One of the quinclidine molecules is held over the fluorenyl

(22) See, for example, D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter 3.

(23) J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Amer. Chem. Soc.*, **94**, 7339 (1972).

carbanion. If the lithium cation in contact ion pairs of **3** or **4** assumes a position similar to that in fluorenyllithium, severe steric interaction between one of the solvent molecules coordinated to the lithium cation and a *cis tert*-butyl group should inhibit formation of the *cis* stereoisomer of the ion pair. The *trans* stereoisomer of the ion pair will not have this interaction and should be formed preferentially.

Solvent effects on the stereoselectivity of protonation reactions of 9,10-dihydroanthracene anions, similar to those reported here, have been observed by others. 9,10-Diethylantracene is reduced by lithium in liquid ammonia¹⁴ or in a HMPA-THF mixture solution (1:4)²⁴ to *trans*-9,10-diethyl-9,10-dihydroanthracene. Reduction by sodium or lithium in HMPA-THF mixture solutions of composition 3:2 and 7:1, respectively, yields *cis*-9,10-diethyl-9,10-dihydroanthracene.²⁴ The final and stereoisomer determining step in these reductions is protonation of 9,10-diethyl-9-metallo-9,10-dihydroanthracene. The reactions of deuterium oxide with 10-*n*-butyl-9-lithio-9,10-dihydroanthracene²⁵ in diethyl ether solution and 10-*tert*-butyl-,²⁶ 10-isopropyl-,²⁶ or 10-ethyl-9-lithio-9,10-dihydroanthracene^{26,27} in THF solution all lead to *ca.* 50:50 mixtures of *cis*- and *trans*-10-alkyl-9-deutero-9,10-dihydroanthracene. Reaction of deuterium oxide with the three latter anions in THF-HMPA mixture solutions (3:2) yields the *cis*-10-alkyl-9-deutero-9,10-dihydroanthracenes.²⁶ It should be noted that high concentrations of HMPA favor protonation *cis* to the *tert*-butyl group just as in our experiments.

The same explanation should hold for the preferential protonations of **3** and **4** and the 10-alkyl-9-lithio-9,10-dihydroanthracenes²⁶ by alcohols or water *cis* to the 10-alkyl group in HMPA containing solutions. Others have explained the protonation^{24,26} and alkylation¹³ reactions of dihydroanthracene anions in terms of stereospecific reactions of nonplanar *cis* and *trans* stereoisomeric forms of the carbanion. The effect of HMPA on the protonation stereoselectivity of the 10-alkyl-9-lithio-9,10-dihydroanthracenes is proposed to be the result of selective formation of the *cis* stereoisomer of the carbanion in the solvent-separated ion pairs formed by HMPA.²⁶ Models indicate that bending the carbanion so that the *tert*-butyl group occupies a quasi-axial position should favor approach of the proton donor *trans* to the *tert*-butyl group more than for a planar carbanion. We believe the carbanions are essentially flat and have discussed above how the metal cation can direct protonation of the contact and solvent-separated ion pairs of **3** and **4** in diethyl ether and THF solution. It is clear the fully HMPA-coordinated metal cation does not direct the protonation reaction in this fashion. For example, 80% *trans*-**1** is formed on protonation of Li-**3** in HMPA solutions by the alcohols or 1-propyne.²⁸ One possible

(24) R. Lapouyade, P. Labandibar, and H. Bouas-Laurent, *Tetrahedron Lett.*, 979 (1971).

(25) H. J. S. Winkler, R. Bollinger, and H. Winkler, *J. Org. Chem.*, **32**, 1700 (1967).

(26) R. Lapouyade, M. Mary, H. Bovas-Laurent, and P. Labandibar, *J. Organometal. Chem.*, **34**, C25 (1972).

(27) D. J. Schaeffer and H. E. Zieger, *J. Org. Chem.*, **34**, 3958 (1969).

(28) Potassium ion complexed by dicyclohexyl-18-crown-6 cannot direct the protonation by *tert*-butyl alcohol of the carbanion formed from optically active 4-biphenylphenylmethoxymethane.²⁹

(29) W. D. Kollmeyer and D. J. Cram, *J. Amer. Chem. Soc.*, **90**, 1779 (1968); J. N. Roitman and D. J. Cram, *ibid.*, **93**, 2231 (1971).

explanation is that the HMPA-metal cation complex is blocking approach of the proton donor trans to the *tert*-butyl group. Our pmr data indicate that the coordinated HMPA is not close enough to the aromatic rings of the carbanion to be shielded. Thus the HMPA-metal cation complex is not close enough to the carbanion to block approach to one of its faces. Another explanation of the observed protonation stereoselectivity is that the proton donor and the *tert*-butyl group (or other 10-alkyl group) prefer to be in quasi-axial positions in the transition state for protonation. This driving force is overcome in the protonation of the contact and solvent-separated ion pairs by interactions between the proton donor and the metal cation.

The effect of other good complexing agents, glyme ethers and crown ethers, on the protonation and alkylation reactions of **3** and **4**, as well as the results of experiments designed to determine the geometries of carbanions similar to **3** and **4** in solution, will be reported later.

Experimental Section

General Methods. All reactions involving organometallic compounds were carried out under atmospheres of prepurified nitrogen or Grade A helium using standard techniques. Ether was distilled from lithium aluminum hydride under a nitrogen atmosphere immediately before use. THF was distilled from a dark purple solution of sodium benzophenone dianion under a nitrogen atmosphere immediately before use. Hexane was scrubbed with concentrated sulfuric acid to remove olefinic impurities and distilled from a suspension of sodium benzophenone ketyl under a nitrogen atmosphere immediately before use. HMPA was vacuum distilled from sodium and stored under vacuum. It was vacuum distilled from sodium again immediately before use. Melting points were obtained using a Laboratory Devices Mel-Temp capillary melting point apparatus and are uncorrected. Pmr spectra of the hydrocarbons were run as carbon tetrachloride solutions on JEOL MH-100 or C-60HL spectrometers; chemical shifts are reported in parts per million downfield from tetramethylsilane and coupling constants in hertz. NOE and $J_{C_{95}-H_{10}}$ measurements were obtained on sealed, degassed solutions in carbon tetrachloride on a JEOL C-60HL spectrometer operated in the frequency sweep mode. The NOE results are the difference in the average of four integrations obtained for irradiation at the aryl protons and for irradiation at 5 ppm downfield from the aryl protons. Results were obtained at two similar H_2 intensities. Pmr spectra of the carbanions were run at concentrations over the range 0.1 *N*–0.8 *N* on a JEOL MH-100 spectrometer; chemical shifts are the average of at least two upfield and downfield sweeps. Benzene was often used as a secondary internal standard in these experiments. Its chemical shift from internal tetramethylsilane was independent of any of the variables studied. Probe temperatures were measured using methanol and ethylene glycol samples. Visible spectra were recorded on a Cary 14 spectrometer at room temperature. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Analytical glpc analyses were performed on a Perkin-Elmer Model 810 instrument equipped with flame ionization detectors. All components in the reaction mixtures from **3** could be separated using a 6-ft 10% DEGS on 80–100 mesh Chromosorb W(AW) column operating at 140°. The components in the reaction mixtures from **4** could be separated using a 10-ft 10% SE-30 on 80–100 mesh Chromosorb W column operating at 210°. Compounds could be identified by pmr spectra of the crude reaction mixtures since the reactions were so clean.

Concentrations of organolithium reagent solutions were determined by the Gilman double-titration method with 1,2-dibromoethane.³⁰ The alkyllithium reagents were purchased from Lithium Corporation of American as hydrocarbon solutions. Solutions of *n*-butyllithium in diethyl ether and THF were prepared by distilling the hexane from the *n*-butyllithium in a side-arm flask attached to a nitrogen-vacuum manifold. The resulting liquid *n*-butyllithium was dissolved in the appropriate volume of cooled (–78°) THF or diethyl ether.

(30) H. Gilman, F. K. Cartledge, and S. Y. Sim, *J. Organometal. Chem.*, **1**, 8 (1963).

cis- and *trans*-10-*tert*-butyl-9-methyl-9,10-dihydroanthracene were prepared by reaction of a suspension of 7.1 g (40 mmol) of anthracene in 200 ml of THF with 30 ml of 2.0 *N* *tert*-butyllithium (60 mmol) in *n*-pentane solution while cooling in an ice-salt bath.¹² The resulting dark blue solution was stirred for 45 min, while being cooled in the ice-salt bath before being quenched with 14.2 g (100 mmol) of freshly distilled iodomethane. The crude reaction mixture was partitioned between ether (ca. 200 ml) and water (ca. 100 ml). Then the ether layer was dried (magnesium sulfate) and the ether removed by rotary evaporator to yield 9.9 g of crude product. Glpc analysis showed that at least four products in addition to *cis*- and *trans*-**1** were formed. *cis*-**1** is the major product present.

The crude reaction mixture was dissolved in 30 ml of absolute ethanol and allowed to cool to room temperature. Further recrystallization from absolute ethanol of the crystals formed yielded 1.03 g of *cis*-**1**: mp 125–126°; pmr (CCl₄) δ 7.05–7.30 (8 H, aryl), 4.14 (d, J = 1.3 Hz, of q, J = 7.5 Hz, 1 H, H₉), 3.77 (d, J = 1.3 Hz, 1 H, H₁₀), 1.77 (d, J = 7.5 Hz, CH₃), 0.88 (s, 9 H, C(CH₃)₃).

Anal. Calcd for C₁₉H₂₂: C, 91.14; H, 8.86. Found: C, 90.90; H, 9.06.

trans-**1** (0.24 g) was obtained from the mother liquor of the first crystallization by reducing the volume of the ethanol: mp 115.5–117° (lit.³¹ mp 115.5–117°); pmr (CCl₄) δ 7.38–7.56 (2 H, aryl), 7.18–7.38 (6 H, aryl), 4.07 (d, J = 1.1 Hz, of q, J = 6.8 Hz, 1 H, H₉), 3.66 (d, J = 1.1 Hz, 1 H, H₁₀), 1.74 (d, J = 6.8 Hz, 3 H, CH₃), 0.92 (s, 9 H, C(CH₃)₃).

Anal. Calcd for C₁₉H₂₂: C, 91.14; H, 8.86. Found: C, 91.10; H, 9.01.

The material remaining after the purification of *cis*-**1** (5.2 g) was a mixture of *cis*- and *trans*-**1** and was useful for most of the reactions studied.

trans-10-*tert*-Butyl-9-ethyl-9,10-dihydroanthracene was prepared by the same method as *cis*- and *trans*-**1**, except 12.5 g (100 mmol) of diethyl sulfate was used for alkylation. Glpc analysis of the crude reaction mixture showed two products in addition to *cis*- and *trans*-**2**. *trans*-**2** (2.1 g) was isolated by fractional crystallization from absolute ethanol: mp 122–124°; pmr (CCl₄) δ 7.30–7.50 (2 H, aryl), 7.00–7.28 (6 H, aryl), 4.12 (d, J = 1.1 Hz, of q, J = 3.8 Hz, 1 H, H₉), 3.59 (d, J = 1.1 Hz, 1 H, H₁₀), 2.46 (d, J = 3.8 Hz, of q, J = 7.2 Hz, 2 H, CH₂), 0.80 (s, 9 H, C(CH₃)₃), 0.64 (t, J = 7.2 Hz, 3 H, CH₃).

Anal. Calcd for C₂₀H₂₄: C, 90.85; H, 9.15. Found: C, 90.80; H, 8.99.

cis-10-*tert*-Butyl-9-ethyl-9,10-dihydroanthracene was prepared by treating a solution of 0.663 g (2.53 mmol) of *trans*-**2** in 20 ml of THF with 6.0 ml of 1.6 *N* *n*-butyllithium in hexane (9.6 mmol) while cooling with an ice bath. The bright red reaction mixture was stirred for 4 hr while being cooled and then quenched with water. Glpc analysis showed 86% *cis*-**2** and 14% *trans*-**2** were present in the crude reaction mixture. Work-up, followed by chromatography on alumina with hexane, yielded pure *cis*-**2**, 0.50 g (76% yield): mp 46–48°; pmr (CCl₄) δ 7.25–7.00 (8 H, aryl), 3.72 (1 H, H₁₀), 3.73 (d, J = 1.2 Hz, of t, J = 7.5 Hz, 1 H, H₉), 2.00 (q, J = 7.5 Hz, 2 H, CH₂), 1.25 (t, J = 7.5 Hz, 3 H, CH₃), 0.92 (s, 9 H, C(CH₃)₃).

Anal. Calcd for C₂₀H₂₄: C, 90.85; H, 9.15. Found: C, 90.86; H, 9.04.

The relative rates of lithiation of *cis*- and *trans*-**1** by *n*-butyllithium in diethyl ether solution were determined by glpc analysis of aliquots of the reaction mixture that had been quenched with dimethyl sulfate.³² In a 12-ml centrifuge tube sealed with a No-Air stopper and flushed with nitrogen was prepared an ether solution of concentrations 0.047 *N* *cis*-**1**, 0.063 *N* *trans*-**1**, 0.104 *N* *n*-tetradecane, and 0.31 *N* *n*-butyllithium. The concentrations decreased with time as follows: 75 min, 0.028 *N* *cis*-**1**, 0.061 *N* *trans*-**1**; 150 min, 0.019 *N* *cis*-**1**, 0.060 *N* *trans*-**1**; 490 min, 0.008 *N* *cis*-**1**, 0.058 *N* *trans*-**1**. Pseudo-first-order rate plots indicated that *cis*-**1** was reacting 20 times faster than *trans*-**1**. A similar experiment in a THF-hexane mixture solution with initial concentrations of 0.041 *N* *cis*-**1**, 0.057 *N* *trans*-**1**, 0.098 *N* *n*-tetradecane, and 0.32 *N* *n*-butyllithium gave these results: 4.0 min, 0.00009 *N* *cis*-**1**, 0.045 *N* *trans*-**1**; 12.0 min, no detectable *cis*-**1**, 0.034 *N* *trans*-**1**. In pure THF solutions with comparable concentrations of reactants, both *cis*- and *trans*-**1** were completely lithiated within 15 min.

(31) Footnote *d*, Table I, and ref 12.

(32) The product formed is 10-*tert*-butyl-9,9-dimethyl-9,10-dihydroanthracene. Satisfactory spectra and analytical data ($\pm 0.2\%$ for C, H) were obtained.

Table VII. Best Fit Aromatic Chemical Shifts (δ , ppm) and Coupling Constants (Hz) at 30°^a

Compd	Solvent	δ_1	δ_2	δ_3	δ_4	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$
Li-3	Ether	6.35	6.69	6.00	6.53	8.1	1.3	6.9	1.5	7.1
Li-3	Ether plus 1.5 equiv of HMPA	6.22	6.56	5.85	6.40	8.2	1.3	6.9	1.5	7.0
Li-3	THF	6.11	6.47	5.72	6.31	8.2	1.3	6.8	1.6	6.8
Li-3	HMPA	6.12	6.48	5.72	6.30	8.0	1.1	6.8	1.6	7.1

^a $J_{1,4}$ could not be resolved. Varying the value of $J_{1,4}$ by ± 0.35 Hz changed the magnitude of the other coupling constants < 0.1 Hz.

The relative rates of lithiation of *cis*-1 and *cis*- and *trans*-2 were determined by pmr integration of the hydrocarbon and carbanion absorbances at various times. Solutions were prepared from 0.1 mmol of the hydrocarbon and 0.40 ml of 0.75 *N* *n*-butyllithium (0.30 mmol) in 5-mm nmr tubes sealed with No-Air stoppers and flushed with nitrogen. Pseudo-first-order rate plots yielded the following rate ratios: *cis*-2 to *trans*-2 equals 6:1; *cis*-1 to *cis*-2 equals 10:1; *cis*-1 to *trans*-2 equals 57:1. The rate ratio *trans*-1 to *trans*-2 is calculated to be 3:1.

Visible spectra of the carbanions were recorded in a quartz epr flat cell attached to a Y cell.²⁰ The assembly was flushed with dry nitrogen and charged with 0.75 ml of 0.05 *N* *n*-butyllithium and 25 μ l of 5×10^{-3} *M* solutions of 1 or 2 in the desired solvent to obtain the spectra of Li-3 or Li-4. The spectra of Na-3 and Na-4 were obtained on solutions made by adding 10-25 μ l of *ca.* 0.1 *N* solutions to 0.75 ml of the desired solvent in the cell. The inside of the assembly was dried by sacrificing *ca.* 0.5 ml of the 0.1 *N* solutions.

The sodium salts of 3 and 4 were obtained by reacting *ca.* 1.5 mmol of *n*-butylsodium with 250 mg (1.0 mmol) of *cis*-1 or 262 mg (1.0 mmol) of *trans*-2, respectively, in 10 ml of *n*-hexane with stirring at room temperature in tubes sealed with Teflon stopcocks. Pmr analysis of the hexane solutions showed that *cis*-1 reacted within 6 hr but that *trans*-2 needed 2 days for complete reaction. The suspensions of Na-3 or Na-4 were transferred by forced siphon through a stainless steel cannula to a side-arm flask attached to a nitrogen-vacuum manifold. The hexane was distilled off, and the compounds were made up to *ca.* 0.1 *N* solutions in the desired solvents. These solutions were transferred by cannula to dry, nitrogen-flushed nmr tubes or centrifuge tubes capped with No-Air stoppers.

Diethyl ether and THF solutions of Li-3 and Li-4 for nmr spectra were prepared by reacting 1 or 2 with *n*-butyllithium in nmr tubes that had been flushed with nitrogen and capped with No-Air stoppers. In a typical preparation, 25 mg (0.1 mmol) of *cis*-1 was reacted with 0.35 ml of 0.3 *N* *n*-butyllithium (0.1 mmol) in diethyl ether solution.

HMPA solutions of Li-3 and Li-4 were prepared by reacting HMPA solutions of 1 or 2 with *n*-butyllithium in hexane solution in a flask attached to a nitrogen-vacuum manifold. For example, 0.151 g (0.6 mmol) of 1 dissolved in 6.0 ml of HMPA was added to 0.5 ml of 1.6 *N* *n*-butyllithium (0.8 mmol) in hexane, and hexane was pumped off. The solution was transferred by cannula to dry, nitrogen-flushed nmr tubes or centrifuge tubes capped with No-Air stoppers.

The protonation reactions were usually done with *ca.* 0.1 *N* solutions of 3 or 4, prepared as described above with *n*-tetradecane

usually added to the solutions. For each series of protonation reactions, at least one aliquot of the solution was quenched with dimethyl sulfate (for 3)³² or diethyl sulfate (for 4).³³ One milliliter aliquots of the *ca.* 0.1 *N* solutions were quenched by adding 50 ml of ethanol, 2-methyl-2-propanol, or triethylammonium trifluoroacetate; by adding 1.0 ml of 0.25 *N* solutions of ethanol, 2-methyl-2-propanol, or triethylammonium trifluoroacetate in the same solvent as 3 or 4; or by adding these quenching solutions to the solutions of 3 or 4. To quench with hydrogen chloride and 1-propyne, 1.0-ml aliquots of the solutions of 3 or 4 were added to 5.0 ml of the same solvent saturated with the reagent.

Triethylammonium trifluoroacetate was prepared by reacting a solution of 20.0 g (0.198 mol) of triethylamine (freshly distilled from CaH_2) in 50 ml of *n*-hexane with 18.0 g (0.158 mol) of trifluoroacetic acid at room temperature. A light yellow liquid separated out immediately. The excess triethylamine was removed by pumping 1 day at *ca.* 0.1 mm: pmr (CDCl_3) δ 11.40 (s, 1 H), 3.12 (q, $J = 6.0$ Hz, 6 H), 1.30 (t, $J = 6.0$ Hz, 9 H).

The diethyl ether-HMPA mixture solution experiments of Li-3 were done as outlined above, except only *ca.* 0.9 equiv of *n*-butyllithium was added to ensure the absence of excess *n*-butyllithium. The unreacted *cis*-1 did not interfere with the pmr spectra of Li-3 and was corrected for in the protonation reactions by dimethyl sulfate quenches and the use of *n*-tetradecane as an internal glpc standard. HMPA was added by microliter syringe, and the HMPA:Li-3 ratio was determined by pmr integration. Ethanol was added by microliter syringe in the protonation reactions.

Computer simulation of some pmr spectra of Li-3 were done to determine if there was a correlation between ion-pair structure and the magnitude of the aromatic proton coupling constants.³⁴ No apparent correlation was observed. The best fit data, rounded off to reflect the reproducibility observed for different samples, are summarized in Table VII.

Acknowledgment. The Tulane University Chemistry Department and Computer Laboratory are thanked for their support. The nmr spectrometers were purchased with funds supplied mainly by the Gulf Foundation.

(33) The product formed is 10-*tert*-butyl-9,9-diethyl-9,10-dihydroanthracene. Satisfactory spectra and analytical data ($\pm 0.2\%$ for C, H) were obtained.

(34) LAOCOON III written by A. A. Bothner-By and S. M. Castellano was used. The program was obtained from the Quantum Chemistry Program Exchange, University of Indiana.