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Stereochemistry of 9,10-Dialkyl-9,10-dihydroanthracene and 9-Alkyl-10-lithio-9,10-dihydroanthracene

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Abstract: The stereochemistry of alkylation of 9-alkyl-10-lithio-9,10-dihydroanthracene (**2**) by alkyl halides is shown to be primarily dependent upon the steric requirements of the alkyl groups, with large groups in either reactant favoring trans stereoselectivity. Other factors (temperature, halide, solvent) influence more the yield than the stereochemistry. The steric assignments are based principally upon nmr analysis including measurement of nuclear Overhauser enhancement and homoallylic coupling constants. The latter techniques demonstrate existence of the 9,10-dialkyl-9,10-dihydroanthracene (**3**) ring system in a flattened boat structure with bulky groups such as *tert*-butyl and isopropyl preferentially occupying the pseudoaxial position. Evidence is presented for ring flattening as a consequence of transannular steric interaction and for preferred conformations due to restricted rotation of alkyl groups. A unified mechanistic scheme is proposed to explain the stereochemistry of the anions of **2** and **3**. Both are postulated to exist as an equilibrium mixture of ions and ion pairs (contact and solvent separated) with the dihydro ring in a flattened boat conformation and the 9-alkyl groups in a preferred axial orientation. The stereochemistry of the following reaction types is accounted for by this general mechanistic concept: (1) reduction of 9,10-dialkylanthracene and reductive alkylation of anthracene in liquid ammonia; (2) alkylation and protonation of **2** in organic solvents; and (3) epimerization of **3** with the alkyllithium–TMEDA reagent.

Previous studies have established rather remarkable steric preference in the alkylation and protonation of the monoanions and dianions of 9,10-dihydroanthracene (DHA). Thus, reduction of a series of 9,10-dialkylanthracenes[2a] and 7,12-dimethylbenz[*a*]anthracenes[2b] with lithium in liquid ammonia proceeded stereospecifically to provide the corresponding *trans*-9,10-dialkyl-DHA and *trans*-7,12-dialkyl-7,12-dihydrobenz[*a*]anthracenes, respectively. Alkylation of the anthracene dianion generated in analogous manner was initially demonstrated to exhibit cis stereoselectivity;[3,4] subsequently, however, diisopropylation was shown to provide *trans*-9,10-diisopropyl-DHA.[5] Alkylation of 9-alkyl-10-lithio-DHA in organic solvents has led to conflicting stereochemical results[6,8,9] which are difficult to interpret due to differences (halide, temperature, method of generation of anion, solvent, etc.) in the experimental procedures employed. The more fundamental problems underlying these observations concern the stereochemical properties of the 9-alkyl-9,10-dihydro-10-anthryl anion and the 9,10-dialkyl-DHA ring system, concerning which very little is known. Also the intimate details of the mechanism of these alkylations, particularly the role of ion-pair complexes and the possible importance of alternative mechanisms involving electron transfer[6c] or halogen–metal exchange[6b,10] are unexplored.

We now report a systematic study of the alkylation of 9-alkyl-10-lithio-DHA. Objectives of this investigation are: (1) to determine the role of steric and other experimental factors on the stereochemistry of product structure; and (2) to analyze by nmr spectroscopy the conformational properties of the 9,10-dialkyl-DHA ring system.

Results

Alkylation of the 9-alkyl-10-lithio-DHA (**2**) was selected for study since this is the product-determining step for both dianion and monoanion reactions. In initial experiments, the monoanions were generated through addition of the appropriate alkyllithium reagent to anthracene.[8] Although this procedure proved satisfactory for the primary alkyl groups,[11] conversions were somewhat lower, and product mixtures were more complex with the isopropyl- and *tert*-butyllithium compounds. The most efficient and general route to **2** proved to be metalation of 9-alkyl-DHA with *n*-butyllithium in THF at −30°; the pure 9-alkyl-DHA precursors (except 9-*tert*-butyl-DHA)[12] were themselves obtained *via* similar metalation and alkylation of DHA.[8,14]

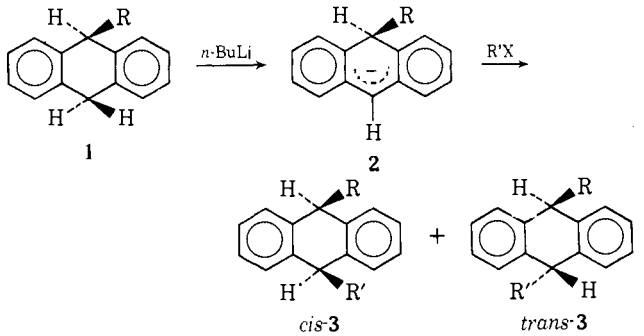
Alkylations of 9-isopropyl- and 9-*tert*-butyl-10-lithio-DHA (**2a,b**) were conducted with a series of alkyl halides R′X (R′ = Me, Et, *i*-Pr, *t*-Bu; X = Cl, Br, I) under standard conditions in THF at −78 and 0°. The results are summarized in Tables I and II.

The stereochemical assignments of the *cis*- and *trans*-9,10-dialkyl-DHA (**3**) products were approached with considerable caution in view of the unreliability of previous chemical and physical criteria (*cf.* Discussion). Thus, *cis*- and *trans*-9,10-dimethyl-,[16] *cis*-9-ethyl-10-methyl-,[17,2] and

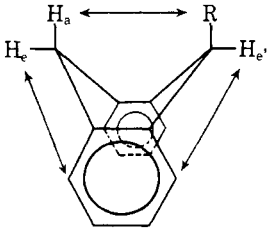
Table I. Alkylation of 9-Isopropyl-DHA by Alkyl Halides[a]

R′X	T, °C	Solvent	Yield, %[b] 1 (R = i-Pr)	3 (cis/trans)
CH_3Cl	−78	THF	32	62 (100/0)
CH_3Br	−78	THF	4	91 (100/0)
CH_3Br	0	THF-HMPA[c]	8	92 (100/0)
CH_3I	−78	THF	28	64 (100/0)
CH_3I	0	THF-HMPA[c]	5	82 (100/0)
C_2H_5Br	−78	THF	4	93 (72/28)
C_2H_5Br	0	THF	12	83 (74/26)
C_2H_5Br	0	THF-HMPA[c]	15	84 (66/34)
C_2H_5I	−78	THF	16	80 (69/31)
C_2H_5I	0	THF	17	79 (75/25)
i-PrBr	−78	THF	7	92 (25/75)
i-PrBr	0	THF	39	57 (26/74)
i-PrBr	0	THF-HMPA[c]	50	50 (28/72)
i-PrI	0	THF	18	80 (23/77)
i-PrI	0	THF-ether[d]	17	68 (26/74)

[a] All experiments were conducted in THF (100 ml) with 2.22 g (10 mmol) of 1 and 10.5 mmol of n-butyllithium, except where noted otherwise. [b] Yields are based on glpc and nmr data and represent product percentage composition rather than isolated yields of pure products. [c] These reactions were conducted on half the usual scale, and THF and HMPA in 1:3 ratio were employed as solvent. [d] The solvent was THF (75 ml) and ethyl ether (75 ml).



trans-9,10-diisopropyl-DHA[3,5] all have at one time been erroneously assigned and subsequently corrected. Nmr analysis, utilized to limited extent in previous studies in this area, provides the most convenient direct experimental probe of molecular structure and conformation. In an earlier study,[13] nmr analysis of the closely related 9-alkyl-DHA demonstrated existence of this ring system in a nonplanar boat structure with the 9-alkyl group preferentially occupying a pseudo-axial position (see structure below).



⟷ signifies NOE

This analysis was based primarily on coupling constants and nuclear Overhauser enhancements (NOE). Thus, by decoupling the aromatic signal, the homoallylic coupling constants $J_{a,e'}$ and $J_{e,e'}$ can be resolved and compared with the expected values ($J_{aa} \approx 2.5$, $J_{ae} \approx 1.5$, and $J_{ee} \approx 0.5$ Hz),[18] and these data can be utilized to determine the conformational preferences of the substituent. The conclusions based on these data were confirmed by nuclear Overhauser

Table II. Alkylation of 9-*tert*-Butyl-DHA by Alkyl Halides at 0°

R′X	% yield[a] 3 (cis/trans)	1 (R = t-Bu)
CH_3Br	72 (48/52)	27
C_2H_5Br	80 (18/82)	19
i-PrBr	91 (3/97)	8
t-BuBr	18 (0/100)	75
CH_3I	50 (42/58)	39
C_2H_5I	80 (30/70)	18
i-PrI	82 (2/98)	16

[a] Small amounts of anthracene (0–5%) and an unknown product (0–2% for bromides, 1–9% for iodides) were also detected by glpc analysis.

experiments, in that irradiation of the aromatic signal produced an enhancement of the integrated areas of the H_e and $H_{e'}$ signals but not H_a. Similarly the irradiation of large R groups (*tert*-butyl, isopropyl) caused an enhancement of H_a but not H_e.

These same techniques have now been applied to the conformational analysis of the 9,10-dialkyl-DHA compounds in Tables I and II,[19] and the nmr data are listed in Table III. In the case of the 9-isopropyl-10-ethyl isomers, one isomer showed a small homoallylic coupling constant (*i.e.*, $J_{cc'}$) and significant and equal NOE's (18%) at both meso hydrogens when the aromatic signal was irradiated. Hence, it was assigned as the cis isomer with both groups preferentially populating the pseudo-axial positions. The other isomer showed a larger $J_{9,10}$ value, a significant NOE (16%) from the aromatics to H_9, and a small NOE (4%) to 10, all of which are consistent with a trans assignment. This latter NOE suggests that ring inversion is occurring, but that the isopropyl group exhibits a strong preference for the pseudo-axial position with the ethyl group more often pseudo-equatorial.

In the *tert*-butyl series, analysis of the *cis*- and *trans*-9-*tert*-butyl-10-methyl and 9-*tert*-butyl-10-ethyl derivatives was carried out in the same manner with additional confirmation of the trans isomers accomplished by significant NOE's from the *tert*-butyl groups to the pseudo-axial protons at C-10. There were no NOE's from the aryl protons to H_{10} with either of the trans isomers, however, which suggests that neither methyl or ethyl groups are able to compete with the *tert*-butyl group for the pseudo-axial position. Similarly, the *cis*- and *trans*-9-*tert*-butyl-10-isopropyl derivatives were easily discerned by the NOE results, again confirming a strong preference for the conformation with the bulky *tert*-butyl group in the pseudo-axial position.

The nmr spectra of *cis*- and *trans*-9,10-di-*tert*-butyl-9,10-dihydroanthracenes have been previously reported[7,20] with isomer assignments postulated primarily on the basis of chemical-shift information. We have been able to confirm these assignments with confidence, based on the NOE data which indicate proximity of the H_9H_{10} protons to the aromatic protons in only one isomer (*i.e.*, cis). The rather small NOE (2%) from the aryl protons to H_9H_{10} in the trans isomer may suggest some ring "flattening," but the magnitude is too low to conclude this with confidence. It is also interesting to note that the trans isomer shows a larger *tert*-butyl/H_9H_{10} NOE (14 *vs.* 10), which may reflect an "across the ring" contribution which is possible only for the trans arrangement.

From the data in Tables I and II, the size of the entering alkyl group is evidently a predominant factor in determining product stereochemistry. In the isopropyl series, the cis/trans ratio decreases (Me > Et > i-Pr) as the steric demands of the alkyl groups increase, with isomer ratios ranging from pure cis for methyl to 3:1 trans for isopropyl. In

Table III. Nuclear Magnetic Resonance[a] Spectral Data for the 9,10-Dialkyl-9,10-dihydroanthracenes

Compd				NOE results			Chemical shifts in ppm (coupling constants in Hz)								
R_9	R_{10}	Isomer assign	$J_{9,10}$, Hz[b]	Irrad	Obsd	Inc, %	$-CH_3$	$-CH_2CH_3$	$-CH_2CH_3$	$-CH(CH_3)_2$	$-CH(CH_3)_2$	$-C(CH_3)_3$	H_9	H_{10}	Aromatic[c]
$(CH_3)_2CH-$	CH_3CH_2-	Cis	<0.3	Aryl	H_9	18		1.74 (m)	1.18	1.60 (m)	0.94		3.28	3.60	7.05 (m)
				Aryl	H_{10}	18			(t, 7.5)		(d, 7.0)		(d, 9.2)	(d, 8.0)	
$(CH_3)_2CH-$	CH_3CH_2-	Trans	1.1	Aryl	H_9	16		2.40 (m)	0.78	1.85 (m)	0.75		3.5	3.96	7.10 (m)
				Aryl	H_{10}	4			(t, 7.8)		(d, 6.9)		(d, 7.8)	(t, 4.5)	
$(CH_3)_3C-$	CH_3-	Cis	1.3	Aryl	H_9	12	1.78					0.90 (s)	3.71 (s)	4.08	7.15 (m)
				Aryl	H_{10}	10	(d, 7.8)							(q, 7.8)	
$(CH_3)_3C-$	CH_3-	Trans	1.2	Aryl	H_9[d]	17	1.68								
				$(CH_3)_3C-$	H_{10}	18	(d, 7.0)					0.87 (s)	3.61 (s)	4.00 (q, 7.0)	7.25 (m)
$(CH_3)_3C-$	CH_3CH_2-	Cis	1.3[e]	Aryl	H_9H_{10}[f]	15	1.96 (m)	1.24 (t, 7.1)				0.89 (s)	3.71 (s)	3.72 (t, 7.3)	7.10 (m)
$(CH_3)_3C-$	CH_3CH_2-	Trans	1.2	Aryl	H_9[d]	14		2.48 (m)	0.63			0.80 (s)	3.61 (s)	4.09	7.30 (m)
				$(CH_3)_3C-$	H_{10}	20			(t, 7.0)					(t, 4.1)	
				$(CH_3)_3C-$	H_9	20									
$(CH_3)_3C-$	$(CH_3)_2CH-$	Cis	g	Aryl	H_9	11				1.90 (m)	1.07	0.98	3.84 (s)	3.32	7.05 (m)
				Aryl	H_{10}	13					(d, 7.5)			(d, 9.9)	
$(CH_3)_3C-$	$(CH_3)_2CH-$	Trans	1.2	Aryl	H_9[d]	8				2.96 (m)	1.22	0.82 (s)	3.59 (s)	4.00	7.10 (m)
				$(CH_3)_3C-$	H_{10}	21					(d, 7.0)			(bd, 2.6)	
				$(CH_3)_3C-$	H_9	13									
$(CH_3)_3C-$	$(CH_3)_3C-$	Cis		Aryl	H_9H_{10}	8						1.04 (s)	3.97 (s)		7.08 (m)
				$(CH_3)_3C-$	H_9H_{10}	10									
$(CH_3)_3C-$	$(CH_3)_3C-$	Trans		Aryl	H_9H_{10}	2[h]						1.13 (s)	3.83 (s)		7.12 (m)
				$(CH_3)_3C-$	H_9H_{10}	14									
$(CH_3)_3C-$[i]	$(CH_3)_3C-$[i]	Cis		Aryl (9, 10)[i]	H_1H_4[i]	8						0.85 (s)	H_1H_4, 3.25	(d, 1.95)	7.40 (m)
				$(CH_3)_3C-$	H_1H_4	11							H_2H_3, 6.10	(d, 1.95)	7.61 (s)[j]
				$(CH_3)_3C-$	H_9H_{10}	9									

[a] Run at 100 MHz in CS_2. [b] These coupling constants become observable when the aromatic signal is decoupled. [c] Given as center of multiplet. In all cases, the trans isomers gave a more complex aromatic multiplet. [d] No significant enhancement at H_{10}. [e] Some uncertainty due to signal overlap. [f] Could not be determined independently due to signal overlap. [g] Coupling not resolvable. [h] Of questionable significance. [i] A 1,4-dihydroanthracene, $R_1 = R_4 = (CH_3)_3C-$. [j] Overlapping on the low-field half of the AA'B B' spectrum centered at 7.40.

the *tert*-butyl series, a similar trend is evident with the cis/trans ratio for the alkyl bromides declining from 1:1 for methyl through 1:4 for ethyl, and 1:32 for isopropyl to 100% trans for *tert*-butyl. Steric interaction between the substituent in the 9 position and the entering group is clearly importantly involved since in analogous reactions, the percentage of the trans isomer is generally greater in the *tert*-butyl series than in the isopropyl series. These results are in accord with additional examples not included in Tables I and II. Thus, analogous alkylation of **1** (R = Et) with ethyl or methyl bromide under the same conditions afforded stereospecifically (*i.e.*, ≥95% by nmr) the corresponding *cis*-9,10-diethyl- and *cis*-9-ethyl-10-methyl-DHA compounds.

The nature of the halogen atom appears to influence product stereochemistry to only minor extent. Thus, methylation of **1** (R = *i*-Pr) led to stereospecific cis alkylation independent of the halide (Cl, Br, I). Similarly, ethylation and isopropylation of the same monoanion under similar conditions provided essentially the same cis/trans ratio of products with either bromide or iodide. However, the nature of the halide did affect the yields, with the optimum yields generally being associated with the bromides.[15] Similarly, temperature had little effect on the cis/trans ratio with no significant difference apparent between reactions conducted at −78 or at 0°.

The order of introduction of the alkyl group into the meso region of the dihydroanthracene ring system, however, markedly affected the cis/trans ratio. While ethylation of the 9-isopropyl-DHA monoanion (**2**, R = *i*-Pr) gave a 3:1 cis/trans ratio, isopropylation of the 9-ethyl-DHA anion (**2**, R = Et) afforded a contrary 1:4 cis/trans ratio. A possible explanation is that product distribution reflects differences in the position of equilibria between types of ion pairs or free ions; a greater degree of dissociation might be anticipated[21] for **2** having the larger group (R = *i*-Pr) than for **2** (R = Et). Accordingly, several experiments to test this hypothesis were conducted in the strongly dissociating solvent hexamethylphosphoramide (HMPA). However, reaction of **2** (R = *i*-Pr) with methyl, ethyl, and isopropyl bromides furnished the corresponding *cis*- and *trans*-9,10-dialkyl-DHA compounds in virtually unchanged ratio from that found in THF alone. Therefore, *it appears that ion-pair association is not an important determinant of product stereochemistry for alkylation under the conditions employed.* These results contrast with the finding of Lapouyade, et al.,[22] and Panek and Rodgers[23] who observed a strong solvent effect with HMPA in the reaction of **2** with D_2O. Thus, while deuteration is sensitive to the degree of association, alkylation appears relatively insensitive, at least for the compounds studied (*cf.* Discussion).

Epimerization of *trans*-9-*tert*-butyl-10-alkyl-DHA with *n*-butyllithium-TMEDA[14,24] indicated a strong general preference for the cis isomers (Table IV) based on the percentage conversion in a 1-hr period (or longer in the case of *tert*-butyl). The rate of epimerization was inversely related to the size of the 10-alkyl substituent. Although no attempt was made to determine the isomer ratio at equilibrium, it is clear from the data that with sufficient time even the di-*tert*-butyl compound exists preferentially in the cis isomeric form. This fact is of considerable synthetic utility in permitting convenient preparation of the otherwise difficultly accessible cis isomers in the *tert*-butyl series.

Table IV. Epimerization of *trans*-9-*tert*-Butyl-10-alkyl-DHA[a]

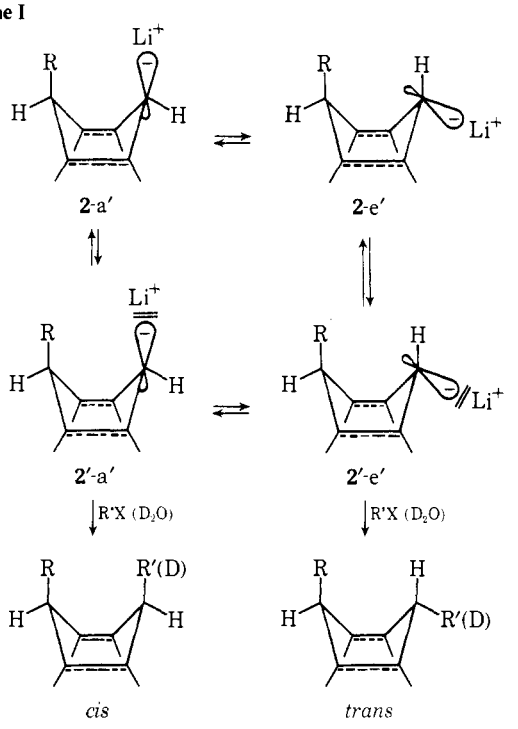
R	Time, hr	% Trans	% Cis
CH_3	1	5	95
C_2H_5	1	10	90
i-Pr[b]	1	30	70
i-Pr	24	0	100
t-Bu	1	90	10
t-Bu	5	56	44
t-Bu	21	42	58
t-Bu[c]	21	0	100

[a] Experiments were conducted with 1–3 mmol of the hydrocarbon in dry cyclohexane (10 ml) and TMEDA (1–3 × 4 mmol) to which was added a solution of *n*-butyllithium (1–3 × 4 mmol) in hexane. Reaction mixtures were quenched with water, except as noted, and analyzed by glpc and nmr. [b] A similar experiment quenched with D_2O afforded a product in which the deuterium was incorporated in only the cis isomer indicative of exclusive cis protonation of the anionic intermediate. [c] Reaction was carried out with 0.48 mmol of the hydrocarbon. HMPA (6 ml) was added after the stated reaction period and the solution stirred at 35° for an additional 30 min, then quenched with ethanol. Similar reaction quenched with NH_4Cl gave the same result.

Discussion

The foregoing results are explicable in terms of a unified mechanism now proposed to accommodate all the available evidence concerning the stereochemistry of the 9-alkyl- and 9,10-dialkyl-DHA anions. In this concept, the 9,10-substituted-DHA anionic intermediates are considered to exist as an equilibrium mixture of ions[25] **2**-a′,e′ and ion pairs **2′**-a′,e′ (contact and solvent separated) with the dihydro ring in a flattened boat conformation and the 9-alkyl group in the preferred axial (a′) orientation (Scheme I). The set of inverted conformers (not depicted) analogous to **2**-a′,e′ and **2′**-a′,e′ in which the group R is equatorial is expected to make a significant contribution only when the size of the group is quite small. This is a consequence of the substantial steric interaction with the adjacent peri hydrogens anticipated for groups larger than methyl.[13] The angle of deviation of the central ring from planarity may be expected to be a compromise between opposing factors. Thus, orbital overlap of the anion should favor planarity for an sp^2 hybrid orbital, while internal ring strain, steric interaction of substituent groups with the peri hydrogens, and ion-pair association[26] should exert a contrary effect. The stereochemistry of the products of both protonation and alkylation of **2** may

Scheme I



be expected to be influenced by (1) the position of the equilibria involving **2**-a′,e′ and **2′**-a′,e′, (2) the relative rates of reaction of each of these species, and (3) the steric demands of the alkyl groups concerned.

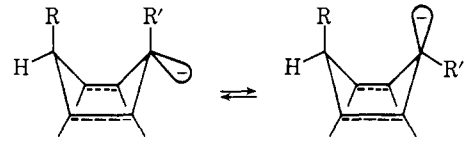
The predominant role of the steric factor in determining the stereochemistry of the products of alkylation is clearly indicated by the results reported herein. As the 9-alkyl group of **2** increases in size, ethylation affords a decreasing proportion of the cis isomer ranging from 95% for R = Et, through 75% for R = *i*-Pr to 20% for R = *t*-Bu. A similar effect is evident in comparison of the data in Tables I and II; the precentage trans is in all cases greater for R = *t*-Bu than for R = *i*-Pr. These results may be interpreted equally well in terms of two variations of the general mechanistic scheme, the one involving only axial anionic intermediates (**2**-a′ and **2′**-a′), the other involving both axial and equatorial intermediates (**2**-e′ and **2′**-e′). In the latter mechanism (Scheme I), the observed increase in the ratio of trans products as the size of R increases is interpreted as a consequence of the steric demands of the 9-alkyl group forcing attack to occur increasingly from the more accessible equatorial (e′) direction (*i.e.*, **2**-e′ rather than **2**-a′). That the equilibrium **2**-a′ ⇌ **2**-e′ is not shifted to the right by increase in the size of R is indicated by the essential constancy of the cis/trans ratio on deuteration in this same series.[22] Conversely, when R is maintained constant, and R′ increases in steric dimensions, the percentage of trans isomer in the product also rises dramatically (Tables I and II). This effect is similarly interpreted as a consequence of the increasing bulk of the attacking reagent hindering approach to the crowded upper face of **2** more than to the relatively open equatorial side. Indeed, the steric demands of the alkyl halide appear to be more important than those of the 9-alkyl group as evidenced by the greater trans preference exhibited by isopropylation of **2** (R = Et) (80% trans) than by ethylation of **2** (R = *i*-Pr) (25% trans); this is not unreasonable since the 9-alkyl group is four carbon atoms removed from the site of reaction. A similar, though less dramatic, reversal of steric preference was observed[9] in comparison of isopropylation of **2** (R = Me) (60% trans) and methylation of **2** (R = *i*-Pr) (10% trans). The relatively low cis/trans ratio (40/60) obtained from isopropylation of **2** (R = Me) reflects the probability that **2** (R = Me) exists partially in the inverted form in which the alkyl group is in the equatorial orientation.[13,27]

Since no significant solvent effect on product stereochemistry was detected for alkylation of **2** (R = *i*-Pr) in HMPA compared with THF, either the reactivity of the ion pairs and free ions is equivalent in this respect, which seems improbable and contrary to general observation,[28] or alkylation occurs on only one of these species, which the independence of solvent would indicate to be the less associated form (*i.e.*, **2′**-a′ and **2′**-e′ in Scheme I).

In the alternative mechanism, the cis products are considered to arise through axial attack on the major lobe of the anion orbital cis to the 9-alkyl group, while axial attack from the opposite face on the minor lobe of the same anion orbital affords the trans products. Increased size of either alkyl group involved should, as a consequence of steric interaction, favor transaxial attack, which is consistent with the experimental results. This mechanism provides the simplest interpretation of the results of alkylation and is additionally attractive in that attack of very bulky groups, such as *tert*-butyl, from the relatively open transaxial direction is more acceptable than approach from the sterically hindered equatorial direction; it is also consistent with a planar intermediate. However, it is less satisfactory than the former scheme in accounting for the results of protonation of the related 9,10-dialkyl-DHA monoanion in reduction and epimerization experiments, as will be shown. Spectroscopic studies analogous to those of Panek and Rodgers[23] on the related 9-*tert*-butyl-10-methyl- and 9-*tert*-butyl-10-ethyl-DHA monoanions might provide evidence regarding the number of ionic species in solution; however, these are beyond the scope of the present investigation.

This same general mechanism is also applicable to the reductive 1,4-dialkylation of anthracene, benz[*a*]anthracene, and dibenz[*a,h*]anthracene with alkali metals and alkyl halides in liquid ammonia.[2,3] In these reactions, the sequence of electron addition and alkylation[29] is considered to be irrelevant to the determination of product stereochemistry since this is determined in the final step, which is alkylation of the monoalkylmonoanion equivalent or analogous to **2**. Although it might be anticipated that the differences in solvation of the anionic intermediates in ammonia and in ethereal solvents might influence product structure to some extent, the experimental findings do not appear to bear this out. Thus, reductive dialkylation of anthracene with methyl, ethyl, *n*-butyl, and benzyl halides and reductive dimethylation of 1,4-dimethylanthracene, benz[*a*]anthracene, and dibenz[*a,h*]anthracene afford cis products with high stereoselectivity, in agreement with the proposed mechanism. On the other hand, reductive diisopropylation of anthracene by the same method furnished *trans*-9,10-diisopropyl-DHA,[5] also in accord with the proposed mechanism but contrary to our earlier assumption.[3] Therefore, although the number of examples of this reaction reported to date is still small, the stereochemistry of all those known is in accord with the suggested mechanism.

Similar concepts are also applicable to the epimerization of 9,10-dialkyl-DHA described herein and to the observed highly regiospecific and stereoselective trans reduction of 9,10-dialkylanthracene and 7,12-dialkylbenz[*a*]anthracenes by alkali metals in liquid ammonia.[2,4] In both processes, product stereochemistry is presumably determined in the final protonation step involving a common intermediate, the 9,10-dialkyl-DHA monoanion 4 or its analog. The



4-e′ ⇌ 4-a′

latter which differs from **2** only in the presence of an alkyl group in the 10 position (for simplicity in representation, ion-pair structures are omitted) is presumably free to adopt a preferred conformation with the 9-alkyl group (R) in the axial position to minimize steric interaction.

Since metal–ammonia reduction of 9,10-dialkylanthracene and 7,12-dimethylbenz[*a*]anthracenes has been found to generally proceed with trans stereospecificity,[2] product structure may be accounted for by preferential protonation on an intermediate of the type 4-a′. On the other hand, the closely related epimerization of *trans*-9-*tert*-butyl-10-alkyl-DHA (Table IV) and *trans*-9-isopropyl-10-alkyl-DHA with *n*-butyllithium–TMEDA exhibited cis stereoselectivity, indicative of preferential protonation of an intermediate of the type **4**-e′. *Thus, protonation of apparently the same monoanion proceeds with opposite stereoselectivity in these two reactions!* It should be pointed out, however, that most of the examples of reduction of the anthracene ring system investigated[2] to date have been restricted to derivatives bearing primary alkyl groups (ethyl, *n*-butyl, benzyl). It is noteworthy that analogous reduction of 9-isopropyl-10-ethylanthracene reported herein affords the corresponding dihydro derivative containing a substantial proportion of the

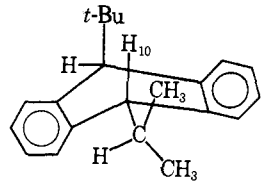
cis isomer (26%). Although this might suggest that where R and R′ are sufficiently large to favor strongly **4**-e′ over **4**-a′ preferential cis reduction may be anticipated, 9,10-diisopropylanthracene has been found to undergo reduction to the trans isomer.[14,30] Obviously, further investigation will be required to resolve the question of steric effects on metal-ammonia reduction.

On the other hand, the results of the epimerization experiments are, without exception, entirely consistent with the proposed mechanism. Since the lithium-TMEDA complexes of **4** are likely to be tightly associated in cyclohexane, and since cis stereoselectivity is generally observed independent of the size of the 10-alkyl group, protonation of the complex apparently occurs with the same steric preference in all cases. This may mean that the lithium-TMEDA complex of **4** exists in solution as a single conformer (presumably **4**-e′) in all cases, or that complexes derived from both **4**-a′ and **4**-e′ are present in equilibrium, but that protonation occurs selectively on the latter. Panek and Rodgers report[23] that treatment of the lithium salt of **4** (R = *t*-Bu, R′ = CH_3) in diethyl ether with ethanol yields the cis isomer, while similar reaction in the presence of HMPA affords the trans isomer. In our investigation, the products are accounted for in terms of protonation of the different ionic species present in these solutions. In HMPA, the less associated anion present can adopt the more stable **4**-a′ conformation with ease due to the minimal steric interference offered by the methyl group, while in diethyl ether, the ion pair with the solvated lithium cation exists more comfortably in the **4**-e′ conformation. In this concept it would be predicted that if R′ were sufficiently large, even the dissociated anion should exist in the **4**-e′ form and afford the cis product on protonation. In confirmation of this prediction, epimerization of **3** (R = R′ = *t*-Bu) with the alkyllithium-TMEDA reagent followed by addition of HMPA to permit equilibration of the resulting anionic intermediates before protonation gave a somewhat *decreased* percentage of the trans isomer.

Alternative mechanisms for alkylation appear less generally satisfactory. Thus, halogen-metal exchange has been suggested by Zieger and Gelbaum[9] as an alternative to SN2 displacement. In this interpretation, rapid coupling of 9-halo-10-alkyl-DHA and the alkyllithium formed initially leads to the observed products. This pathway cannot be general since alkyl chlorides which are known to participate to very limited extent in halogen-metal exchange[32] can, under appropriate conditions, provide high yields of alkylated products. For example, reaction of **2** (R = *i*-Pr) with isopropyl chloride in THF gave 9,10-diisopropyl-DHA (80%). Also reductive isopropylation of anthracene[3] employing this same halide proceeded smoothly to furnish 9,10-diisopropyl-DHA (70%) and 9,9,10-triisopropyl-DHA (18%).

The nmr data in Table III on more careful inspection reveal several interesting facts concerning the structure of the 9,10-dialkyl-DHA molecules. Thus, the coupling constants of the isopropyl methine protons to the adjacent H_{10} protons of 9-*tert*-butyl-10-isopropyl-DHA are widely different in the two isomeric forms. In the cis isomer, J = 9.9 Hz, which is very large for this type of vicinal coupling, and in the trans isomer, J = 2.6 Hz, which is extremely small. A preferred conformation for the trans isomer such as that indicated below seems reasonable from inspection of the model, and the dihedral angle approaching 90° between the isopropyl methine and H_{10} does explain the small coupling constant. Furthermore, the proximity of the isopropyl methine to the plane of the benzene ring provides an explanation for the significant (>1 ppm), downfield shift of this proton.

Similar effects were also noted in 9-isopropyl-10-ethyl-DHA and 9-*tert*-butyl-10-ethyl-DHA. In the former,



the coupling constant from H_{10} to the methylene protons of the ethyl group is 8.0 Hz in the cis isomer but only 4.5 Hz for the trans. In the latter, the coupling constant from H_{10} to the methylene protons is 7.3 Hz in the cis isomer but only 4.1 in the trans isomer. These results are similarly interpreted as a consequence of a preferred rotational conformation in the trans isomers.

Preferred rotation of substituents is also suggested in many of the cis isomers. For example, in the case of the *cis*-9-isopropyl derivatives, large coupling constants were observed from the isopropyl methine proton to the adjacent meso proton (9.2 and 9.9 for 10-ethyl and 10-*tert*-butyl, respectively). Similarly, large values observed for *cis*-9,10-diisopropyl-9,10-dihydroanthracene have been interpreted to be a result of a preferred conformation of the isopropyl substituents caused by steric interactions between the two groups.[6a,7,33] Examination of the homoallylic coupling constant data also provides evidence for such steric interactions. In the case of *cis*-9-*tert*-butyl-10-methyl-DHA and *cis*-9-*tert*-butyl-10-ethyl-DHA, the homoallylic coupling constants ($J_{9,10}$) are significantly larger (1.3 Hz) than expected for diequatorial coupling (~0.5 Hz). This is consistent with increased axial character and suggests that steric repulsions between the *tert*-butyl group and a 10-alkyl group are causing a "flattening" of the central ring.

Finally, 1,4-di-*tert*-butyl-1,4-dihydroanthracene was also examined by these same nmr techniques, but the isomer assignment can only be tentative (particularly since only one isomer is available). The observed NOE from the 9,10-aryl protons to H_1H_4 would seem to suggest a cis isomer, but we are concerned about the rather small vicinal coupling constant, $J_{1,2}$ = 1.95 Hz. Possibly the ring is somewhat flattened, or alternatively we are in error in interpreting the spacings of the $H_{1,4}$ and $H_{2,3}$ doublets to be the coupling constant. However, even if there are significant contributions from allylic couplings leading to a deceptive AA′XX′ pattern, one would still expect J_{AX} to be similar to the separation of the two major lines found in each of the apparent doublets.[34] Our data do not rule out a planar trans structure.

Some general conclusions about the stereochemistry of *cis*- and *trans*-9,10-dialkyl-9,10-dihydroanthracenes can also be drawn from the nuclear Overhauser and spin decoupling experiments. An empirical rule has been suggested for the distinction of cis and trans isomers on the basis of a more complex aromatic region for the nmr spectra of the trans compounds.[7] We can now show conclusively that this is due to deshielding of the peri protons by an adjacent alkyl group in a pseudo-equatorial position. For example, the aromatic region of the nmr spectrum of 9-*tert*-butyl-10-ethyl-9,10-dihydroanthracene is shown in Figure 1. The downfield multiplet (approximately two protons) is shown to sharpen considerably when H_{10} is irradiated, indicating substantial coupling.[35] In addition, a small (~2%) nuclear Overhauser enhancement for H_{10} was observed when this multiplet was irradiated. Hence, these aromatic protons must represent H_4 and H_5. Conversely, the maximum enhancement at H_9 was observed by irradiating the larger, upfield aromatic multiplet, and it can be concluded that aromatic protons H_1 and H_8 are contained in this multiplet. Thus, alkyl groups in the pseudo-axial position do not lead to any appreciable change in the chemical shift of adjacent

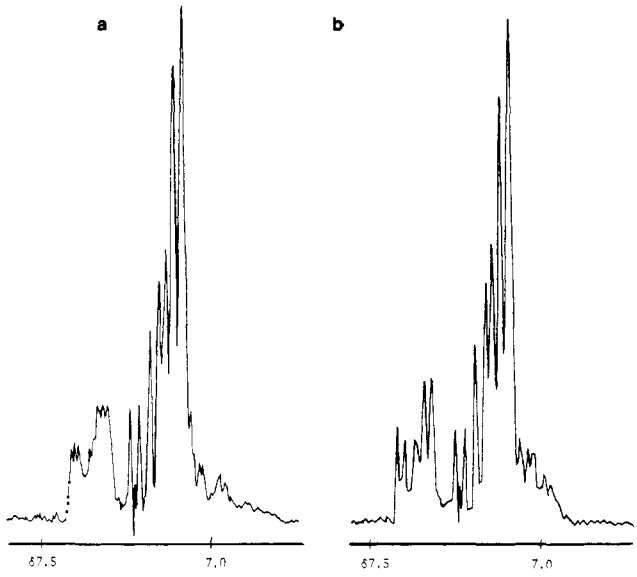


Figure 1. Aromatic region of 100-MHz nmr spectrum of *trans*-9-*tert*-butyl-10-ethyl-9,10-dihydroanthracene in CS_2: (a) without decoupling; (b) with decoupling of H_{10}.

peri aromatic protons. Thus, the appearance of the aromatic signals of most *cis*-9,10-dialkyl-9,10-dihydroanthracenes[7] as a singlet indicates that these compounds exist in a boat conformation with the alkyl groups preferentially in a pseudo-axial position. For the trans isomer, ring inversion results in all peri protons being adjacent to an alkyl group at least 50% of the time. As we have shown above, this results in deshielding and leads to a more complex aromatic signal.

Thus, from the data presented in this paper, together with previous findings, the following generalities can be made concerning the stereochemistry of 9,10-dialkyl-9,10-dihydroanthracenes. Symmetrical trans isomers consist of equal populations of conformations as a result of rapid "boat-to-boat" inversion of the central ring. For unsymmetrical trans isomers, the larger group assumes the pseudo-axial position preferentially, and this can also cause preferential rotational positions of the smaller group as a result of steric interactions from the adjacent "peri" positions of the aromatic rings. The cis isomers exist with both alkyl groups preferentially in the pseudo-axial positions, and steric interactions between the two groups can result in preferential rotational requirements of the substituent groups as well as some degree of "flattening" of the central ring.

Experimental Section

Physical Data. Proton nmr spectra were obtained on Varian T60, A60-A, HA 100 and Brucker 270-MHz spectrometers; chemical shifts are reported relative to TMS in $CDCl_3$, CCl_4, or CS_2 as indicated. Integration was consistent with all assignments. Gas chromatographic analyses were performed on an F&M Model 500 chromatograph employing a 6 ft × 0.25 in. 10% SE 30 60–80 mesh Chromosorb W column at 150° or on a Varian Aerograph Series 2400 chromatograph employing a 5 ft × 0.125 in. 1.5% OV-101 on 100–120 mesh Chromosorb G column at 180°. The NOE data were determined on dilute, deoxygenated samples in CS_2, as an average of repeated integrations of the signal in question with the external oscillator on and off resonance.

Materials. Tetrahydrofuran, cyclohexane, ether, and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were dried over lithium aluminum hydride and redistilled from this reagent. *n*-Butyllithium (15% in hexane) and *tert*-butyllithium (8% in pentane) were obtained from Apache Chemicals and Foote Mineral Co., respectively. 9,10-Dihydroanthracene (Aldrich) was recrystallized from ethanol and dried carefully in a vacuum oven to remove all traces of alcohol. 9-Isopropyl-10-ethylanthracene was prepared as described previously.[14] Gaseous methyl bromide (Matheson) was purified by passage through a tube containing Ascarite. Silica gel employed for chromatography was Davison grade 950, 60–200 mesh; other commercial grades supplied by laboratory supply houses proved much less satisfactory.

9-Isopropyl-9,10-dihydroanthracene. The method employed, which is based on the general procedure described in the preceding paper,[14] provides the compound essentially pure and is recommended as the method of choice. A solution of *n*-butyllithium (52.5 mmol) in hexane was added to a stirred solution of DHA (9.0 g, 50 mmol) in THF (200 ml) at −30° for 30 min, then at −78° for an additional 30 min. A solution of isopropyl bromide (70 mmol) in THF (25 ml) was then added and the reaction mixture quenched after 5 min by solid NH_4Cl (30 g). Addition of water and ether followed by conventional work-up gave crude 9-isopropyl-9,10-dihydroanthracene (11.28 g) in 98% yield by glpc analysis; the nmr spectrum matched that of the authentic compound.[13] Before use in subsequent reactions, the compound was purified by chromatography on silica gel.

Alkylation of 9-Isopropyl-DHA. The procedure was essentially that employed for isopropylation of DHA described in the preceding paragraph, except that reactions were conducted on a 10-mmol scale in 100 ml of THF. Products were analyzed by glpc and nmr. The products of methylation and isopropylation were identified in comparison with samples of the authentic compounds previously prepared.[3,5,8] Results are summarized in Table I.

Ethylation provided a pale yellow oil (2.50 g) shown by nmr and glpc to contain 9-isopropyl-10-ethyl-DHA (93%, cis/trans, 72/28) along with recovered **1** (R = *i*-Pr) (4%). Careful chromatography on silica gel gave pure *cis*-9-isopropyl-10-ethyl-DHA eluted with hexane as a colorless oil: nmr (CCl_4) δ 0.97 (d, 6, J = 7 Hz, $(CH_3)_2CH$), 1.08 (t, 3, J = 7.5 Hz, CH_3CH_2), 1.60 (m, 1, methine), 1.70 (m, 2, CH_3CH_2), 3.33 (d, 1, J = 9.2 Hz, H_9), 3.67 (t, 1, J = 8 Hz, H_{10}), and 7.09 ppm (m, 8, aromatic).

Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.16; H, 8.77.

Further elution with hexane gave a mixture of cis and trans isomers from which the pure trans isomer could not be separated. Attempted rechromatography on neutral alumina gave in the initial fractions the trans isomer contaminated with a trace amount of an unidentified impurity which could not be removed through rechromatography. Therefore, the pure trans isomer was prepared *via* the following alternate method.

Reduction of 9-Isopropyl-10-ethylanthracene. 9-Isopropyl-10-ethylanthracene (1.17 g, 4.7 mmol) was reduced with lithium in liquid ammonia following the general procedure adopted recently[4] in our laboratory as the *recommended standard method* for reduction of polycyclic aromatic hydrocarbons. It differs from the procedure utilized earlier for reduction of dialkylanthracene compounds[2] in that reaction times are shorter, reactions are quenched with NH_4Cl rather than water, and products are isolated rapidly by extraction. Glpc analysis of the crude product (1.17 g) showed 9-isopropyl-10-ethyl-DHA in 97% yield. The nmr spectrum indicated the presence of 74% of the trans isomer; this result is unexpected since analogous reactions of both 9,10-diethyl- and 9,10-diisopropylanthracene were found previously to afford the trans isomer regiospecifically within the limit of experimental detection. Chromatography on neutral alumina gave the pure analytical sample of *trans*-9-isopropyl-10-ethyl-DHA as a colorless oil: nmr (CCl_4) δ 0.80 (d, 6, J = 6.9 Hz, $(CH_3)_2CH$), 0.82 (t, 3, J = 7.8 Hz, CH_3CH_2), 1.62–2.12 (m, 1, methine), 2.25–2.72 (m, 2, CH_3CH_2), 3.58 (d, 1, J = 7.8 Hz, H_9), 4.04 (t, 1, J = 4.5 Hz, H_{10}), and 7.03–7.60 ppm (m, 8, aromatic).

Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.04; H, 8.91.

9-*tert*-Butyl-DHA. Since *tert*-butylation of 9,10-dihydroanthracene by the general procedure afforded a low yield of **1** (R = *t*-Bu), this compound was synthesized through addition of *tert*-butyllithium to anthracene.[8,13] A solution of *tert*-butyllithium (108 mmol) in pentane was added to a solution of anthracene (8.91 g, 50 mmol) in dry THF (200 ml) at −30 to −40° over a period of 1 hr under a helium atmosphere. The resulting dark green solution was stirred for an additional hour and reaction mixture quenched with NH_4Cl (30 g), followed by conventional work-up. The crude product (11.32 g) was shown by glpc to contain anthracene (7%), **1** (R = *t*-Bu) (45%), 1-*tert*-butyl-1,2-dihydroanthracene (27%), and

2-*tert*-butyl-1,2-dihydroanthracene (21%).

The mixture was refluxed with maleic anhydride (1.23 g, 12.5 mmol) in xylene (150 ml) for 4 hr. Xylene was then removed under vacuum and the residue extracted with hot hexane, evaporation of which gave the mixed *tert*-butyl-DHA isomers (9.8 g) free of anthracene. Careful chromatography on silica gel afforded initially on elution with hexane a mixture of the 1- and 2-*tert*-butyl isomers. Further elution with hexane gave 9-*tert*-butyl-DHA (4.88 g, 41% yield) as a colorless solid, mp 122–125°, recrystallization of which gave pure **1** (R = *t*-Bu) (4.43 g), mp 125.5–126° (lit.[13,20] 125.5–126°). The nmr spectrum was identical with that previously reported.[13] Characterization of the 1- and 2-*tert*-butyl-1,2-dihydroanthracene isomers was previously described.[13]

Alkylation of 9-*tert*-Butyl-DHA. Reactions were conducted at 0° since yields were markedly higher than at lower temperatures.

(1) Methylation. To a solution of **1** (R = *t*-Bu) (0.83 g, 3.46 mmol) in THF (25 ml) at 0° was added a solution of *n*-butyllithium (3.8 mmol) in hexane. The resulting deep red solution was stirred at 0° for 1 hr, then decolorized by passage of methyl bromide into the solution. NH_4Cl (20 g) was added, and the reaction was worked up in the usual manner. Glpc and nmr analyses of the crude product (0.83 g) showed *cis*- and *trans*-9-*tert*-butyl-10-methyl-DHA (72%), along with recovered **1** (R = *t*-Bu) (27%) and anthracene (1%). Chromatography on silica gel gave pure *trans*-9-*tert*-butyl-10-methyl-DHA: mp 115.5–117° (lit.[8] 115.5–117°); nmr (CCl_4) δ 0.93 (s, 9, *tert*-butyl), 1.75 (d, 3, J = 7 Hz, CH_3), 3.67 (s, 1, H_9), 4.06 (q, 1, J = 7 Hz, H_{10}), and 7.00–7.50 ppm (m, 8, aromatic). This isomer was erroneously assigned the cis structure in an earlier study.[8] Similar reaction with methyl iodide gave the result indicated in Table II.

(2) Ethylation. Analogous reaction of **1** (R = *t*-Bu) (0.71 g, 3 mmol) with ethyl bromide gave a product (0.75 g) shown by glpc and nmr analyses to contain *cis*- and *trans*-9-*tert*-butyl-10-ethyl-DHA (14 and 66%, respectively), 9-*tert*-butyl-DHA (19%), and anthracene (1%). Chromatography on neutral alumina followed by recrystallization from methanol gave pure *trans*-9-*tert*-butyl-10-ethyl-DHA as colorless needles: mp 120.5–122°; nmr (CCl_4) δ 0.67 (t, 3, J = 7 Hz, CH_3), 0.82 (s, 9, *tert*-butyl), 2.32–2.77 (m, 2, methylene), 3.66 (s, 1, H_9), 4.17 (t, 1, J = 4 Hz, H_{10}), and 7.02–7.58 ppm (m, 8, aromatic).

Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.82; H, 9.13.

Similar reaction with ethyl iodide gave the result indicated in Table II.

(3) Isopropylation. Analogous reaction with isopropyl bromide on the same scale gave a yellow oil (0.82 g) shown by glpc and nmr analyses to contain *cis*- and *trans*-9-*tert*-butyl-10-isopropyl-DHA (3% and 88%, respectively), 9-*tert*-butyl-DHA (8%), and anthracene (1%). Chromatography on silica gel eluted with hexane gave pure *trans*-9-*tert*-butyl-10-isopropyl-DHA as a colorless oil: nmr (CCl_4) δ 0.89 (s, 9, *tert*-butyl), 1.25 (d, 6, J = 7 Hz, CH_3), 2.72–3.20 (m, 1, methine), 3.63 (s, 1, H_9), 4.08 (apparent s, 1, H_{10}), and 7.01–7.62 ppm (m, 8, aromatic).

Anal. Calcd for $C_{21}H_{26}$: C, 90.59; H, 9.41. Found: C, 90.48; H, 9.46.

Similar reaction with isopropyl iodide gave the result indicated in Table II.

(4) *tert*-Butylation. Analogous reaction with *tert*-butyl bromide gave *trans*-9,10-di-*tert*-butyl-DHA (18%), 9-*tert*-butyl-DHA (75%), and anthracene (5%). Chromatography on silica gel followed by recrystallization from acetone gave pure *trans*-9,10-di-*tert*-butyl-DHA as white needles: mp 176–177.5° (lit.[20] 176°); nmr (CCl_4) δ 1.14 (s, 18, *tert*-butyl), 3.85 (s, 2, benzylic), and 6.92–7.42 ppm (m, 8, aromatic).

Epimerization of *trans*-9-*tert*-Butyl-10-alkyl-DHA. To a solution of 9-*tert*-butyl-10-alkyl-DHA (1–3 mmol) in dry cyclohexane (10 ml) and TMEDA (fourfold molar ratio) was added a solution of *n*-butyllithium (fourfold molar ratio) in hexane. The resulting deep red solution of the monoanion[14] was maintained at reflux for 1 hr (5 and 21 hr also employed for di-*tert*-butyl), cooled (5 min), and the color discharged by addition of water. Conventional work-up procedures afforded essentially quantitative recovery of products shown by glpc and nmr to consist of only *cis*- and *trans*-**3**. The results are summarized in Table IV. All the cis isomers were isolated by chromatography on alumina eluted with hexane.

(1) *cis*-9-*tert*-Butyl-10-methyl-DHA. Recrystallization from petroleum ether gave pure *cis*-9-*tert*-butyl-10-methyl-DHA: mp 124–126° (lit.[22] 125–126°); nmr (CCl_4) δ 0.91 (s, 9, *tert*-butyl), 1.77 (d, 3, J = 7.2 Hz, CH_3), 3.73 (s, 1, H_9), 4.08 (q, 1, J = 7.2 Hz, H_{10}), and 6.90–7.37 ppm (m, 8, aromatic).

(2) *cis*-9-*tert*-Butyl-10-ethyl-DHA. Recrystallization from methanol provided the analytical sample as white needles: mp 55–56°; nmr (CCl_4) δ 0.91 (s, 9, *tert*-butyl), 1.29 (t, 3, J = 7 Hz, CH_3), 1.98 (q, 2, J = 7 Hz, CH_2), 3.77 (s, 1, H_9), 3.77 (t, 1, J = 7 Hz, H_{10}), and 6.93–7.35 ppm (m, 8, aromatic).

Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.64; H, 9.22.

(3) *cis*-9-*tert*-Butyl-10-isopropyl-DHA. Recrystallization from methanol provided the analytical sample as white needles: mp 114.5–116°; nmr (CCl_4) δ 1.0 (s, 9, *tert*-butyl), 1.10 (d, 6, J = 5 Hz, $(CH_3)_2CH$), 1.72–2.25 (m, 1, methine), 3.37 (d, 1, J = 10 Hz, H_{10}), 3.88 (s, 1, H_9), and 7.08 ppm (apparent s, 8, aromatic).

Anal. Calcd for $C_{21}H_{26}$: C, 90.59; H, 9.41. Found: C, 90.36; H, 9.52.

(4) *cis*-9-10-Di-*tert*-butyl-DHA. Recrystallization from methanol afforded white needles: mp 138.5–139.5° (lit.[7] 139–140°); nmr (CCl_4) δ 1.10 (s, 18, *tert*-butyl), 4.05 (s, 2, benzylic), and 6.95–7.35 ppm (m, 8, aromatic), identical with that reported.[7]

Reaction of 9,10-Dihydroanthracene with *n*-Butyllithium and *tert*-Butyl Bromide. A solution of *n*-butyllithium (0.2 mol) in hexane was added to a stirred solution of DHA (16.79 g, 93 mmol) in THF (150 ml) at 0° over a period of 20 min. The resulting dark purple solution was maintained at 0° for 1 hr, then *tert*-butyl bromide (54.8 g, 0.4 mol) in THF (30 ml) was added. The reaction mixture was then quenched by addition of NH_4Cl (30 g) and worked up in the usual manner. Glpc analysis showed 9-*tert*-butyl-DHA (10%), anthracene (13%), *trans*-9,10-di-*tert*-butyl-DHA (2%), along with recovered DHA (70%).

Repetition of the foregoing reaction procedure on the initial product mixture gave according to glpc analysis 9-*tert*-butyl-DHA (15%), *cis*- and *trans*-9,10-di-*tert*-butyl-DHA (13 and 21%, respectively), 1,4-di-*tert*-butyl-1,4-DHA (23%), and anthracene (5%). Crystallization of the crude oily product from ethyl ether gave *trans*-9,10-di-*tert*-butyl-DHA (2.19 g); recrystallization from methylene chloride–petroleum ether furnished the pure compound as colorless needles, mp 176–177.5° (lit.[20] 176°). A second crystallization of the main body of the product from acetone provided 1,4-di-*tert*-butyl-1,4-dihydroanthracene (1.58 g), further purification of which through chromatography on silica gel furnished the pure compound as colorless needles, mp 145–147° (lit.[20] 148°).

Epimerization of *trans*-9,10-Di-*tert*-butyl-DHA in the Presence of HMPA. To a solution of *trans*-9,10-di-*tert*-butyl-DHA (140 mg, 0.48 mmol) in dry cyclohexane (10 ml) and TMEDA (1.4 ml) was added a solution of *n*-butyllithium (1.5 ml, 1.92 mmol) in hexane. The resulting deep red solution was maintained at reflux for 21 hr, then cooled (5 min), and HMPA (6 ml) was added. The solution was stirred at 35° for an additional 30 min, then quenched with absolute ethanol (5 ml). Conventional work-up afforded 138 mg of a brown oil. Glpc and nmr analyses showed *cis*-9,10-di-*tert*-butyl-DHA (87%) together with an unidentified product (13%). No *trans*-9,10-di-*tert*-butyl-DHA was detected in the product mixture. A similar reaction mixture quenched with NH_4Cl (5 g) followed by water (5 ml) gave 139 mg of a crude product shown by nmr and glpc to contain the same products in virtually identical proportion (88 and 12%).

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(12) 9-*tert*-Butyl-9,10-dihydroanthracene was obtained by addition of *tert*-butyllithium to anthracene and chromatographic separation from the two *tert*-butyldihydroanthracene isomers also formed.[8,13]
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(24) Efficient epimerization of *trans*- to *cis*-9,10-diisopropyl-DHA with the *n*-butyllithium–TMEDA reagent was previously noted.[14]
(25) Although only contact and solvent-separated ion pairs are represented in Scheme I, completely dissociated ions may also be present, particularly in solvents such as HMPA.
(26) Association with a cation may be expected to influence charge localization within the anion distorting electron-density distribution into the region of the cation with consequent effects on ring geometry. The lithium–TMEDA complexes of aromatic dianions have been shown to exist with the metal cation located above or below the face of a puckered aromatic ring system; *cf.* J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Amer. Chem. Soc.*, **94**, 7346 (1972), and references therein. It is conceivable, however, that in certain cases, ion-pair association may occur preferentially with the equatorial anion.
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(30) The facile isomerization of 9,10-diisopropylanthracene to the thermodynamically more stable 9-isopropylidene-9,10-dihydroanthracene reported in the accompanying paper[31] may conceivably occur prior to reduction.
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Retention of Configuration at the Migrating Atom in the Photochemical 1,3-Allylic Shift of a Benzyl Group[1]

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Abstract: 3-Phenylcyclohexylidenemalononitrile was synthesized and rearranged photochemically to the nonconjugated isomer, 2,2-dicyano-1-methylene-3-phenylcyclohexane. The investigation concentrated mainly on stereochemical aspects in order to confirm the mechanism detected previously for such allylic and diallylic rearrangements. With the help of a methyl marker at C-5 of the cyclohexyl moiety, both stereoisomers of 5-methyl-3-phenylcyclohexylidenemalononitrile were isolated. Both the cis and the trans isomers were photolyzed separately under identical conditions. The photoproducts, isolated by column chromatography, were confirmed by spectroscopic evidence as cis and trans isomers of 2,2-dicyano-1-methylene-5-methyl-3-phenylcyclohexane, respectively. The degradation of the trans photoproduct and the *trans*-3-methyl-5-phenylcyclohexanone gave *trans*-3-methyl-5-phenylpimelic acid. Condensation of 3-phenylcyclohexanone with methyl cyanoacetate gave a mixture of cis and trans products. One pure geometrical isomer was isolated and photolyzed. The photoproduct was identified as a mixture of two stereoisomers of 2-carbomethoxy-2-cyano-1-methylene-3-phenylcyclohexane. The recovered starting material from incomplete rearrangement also lost its geometrical purity. Synthesis and condensation of 2-methyl-3-phenylcyclohexanone with malononitrile afforded only the cis isomer. The photoproducts of the pure cis isomer was confirmed by nmr as one isomer with the methyl at the exocyclic double bond being trans to the nitrile groups. 3-Phenylcyclohexylidenemalononitrile was found to be quite stable to sensitized photolysis; thermal treatment of the photoproduct failed to reverse the photochemical rearrangement.

Cookson and coworkers have discovered that during the photochemical rearrangement of the diallyl derivatives of the 1,5-hexadiene system only one allyl group undergoes 1,3 shift.[2a] This simple fact draws attention to the possibility of a concerted 1,3 shift in the excited state rather than dissociation into a pair of radicals followed by recombination. The complete lack of inversion of the migrating allyl group has also been demonstrated by the photolytic reaction **1** → **2**, **1** being a stereospecifically deuterated diallyl derivative.[2b] The cis–trans equilibration in the product seems to be an integral part of the rearrangement. This photochemical rearrangement is thermally reversible, however, with the in-