Stereochemistry of 9-Alkyl-9,10-dihydroanthracenes. Confirmation by Nuclear Overhauser Enhancements and Long-Range Coupling Constants[1,2]

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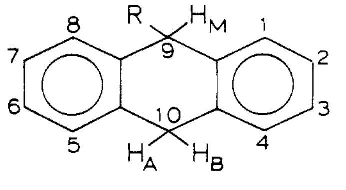
Abstract: The preferred orientation of 9-alkyl groups in a series of 9-alkyl-9,10-dihydroanthracenes is shown to be pseudoaxial; nuclear Overhauser enhancements (NOE) of the C-9 and C-10 proton signals provide unequivocal evidence for this conclusion. Results are presented to show that, contrary to earlier assignments, the 9-*t*-butyl, 9-isopropyl, and 9-ethyl groups exist virtually exclusively in the pseudoaxial orientation. The 9-methyl and 9-phenyl groups, although preferentially pseudoaxial, occupy the pseudoequatorial position to some extent. Long-range homoallylic couplings, $H—C_9—C{=}C—C_{10}—H$, exhibit the expected geometrical dependence consonant with conclusions drawn from the NOE results. Previous erroneous interpretations of the proton chemical-shift trends are discussed on the basis of the present data.

Controversy surrounds the question of preferred conformations of 1,4-cyclohexadiene and its derivatives. For the parent compound, results have been presented by various authors[6–11] indicating the planar form to be the most stable; these include Raman[6–8] and infrared[8,9] data as well as electron diffraction[10] and nmr[11] results. On the other hand, nmr data for several substituted 1,4-cyclohexadienes[12] indicate a preference for a nonplanar ring in agreement with semiempirical calculations based on angle and torsional strain.[13] Very recent electron-diffraction results[14] for the parent diene also agree with this conclusion; these authors discuss the conflicting interpretations in some detail. In contrast there is general agreement that the central ring of 9,10-dihydroanthracene, **1** (R = H), is nonplanar, as shown by X-ray diffraction,[15] but the preferred orientation of 9 substituents has been a matter of some dispute. Whereas **1**, R = H, undoubtedly inverts rapidly between equivalent conformers,[16,17] the presence of a 9 substituent can bias this equilibrium to favor one of the two forms: $\mathbf{2}_{a'}$ in which R is pseudoaxial or $\mathbf{2}_{e'}$ where R is pseudoequatorial. The earlier chemical studies[16] clearly pointed to an overwhelming preference for $\mathbf{2}_{a'}$. Unfortunately, later nmr results led some authors[18–20] to the opposite conclusion, although their rationalization rests on a tenuous analogy between the chemical-shift trends in cyclohexane in the chair form[21] with those "expected" for the central boat in **2**. The influence of the boat conformation of the central ring has been considered in the interpretation of the nmr results for other polysubstituted examples, however, and, in



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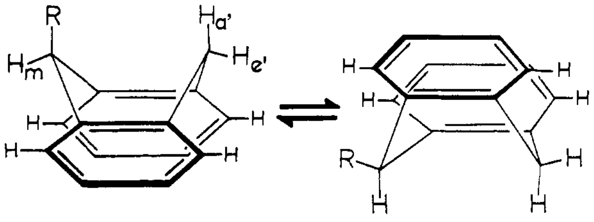

2a' **2e'**

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conjunction with chemical evidence, led the authors[22] to conclude that the larger group(s) preferentially exist in the *a′* orientation. In light of these results we wish to report the nmr results for several 9-alkyl(phenyl)-9,10-dihydroanthracenes which unequivocally establish the orientation of the 9 substituent by measurements of the nuclear Overhauser enhancements (NOE).[23] Furthermore, the NOE results confirm the geometrical dependence of the homoallylic coupling constants, H—C_9—C=C—C_{10}—H, permitting assignments of the orientation of 9 substituents for related systems in which the NOE technique is not applicable. In addition, the chemical shifts, some preliminary reports of which have appeared,[24] are shown to be entirely consistent with the other data.

Experimental Section

Nmr Spectra. All measurements were carried out on sealed, vacuum-degassed solutions (30–40 mg/ml) of the compounds in carbon disulfide. No attempt was made to ensure identical concentrations since, in several cases (9-methyl, 9-phenyl, and 1,4,9-trimethyl), spectra run at several concentrations showed no changes other than in intensity. The spectra were determined on either a Varian HA-100 spectrometer, probe temperature *ca.* 37°, or a HA-60-IL spectrometer operating at *ca.* 27°. Some spectra were obtained at −37° using a V-4341 variable temperature accessory. The low temperatures were measured using a degassed sample of methanol containing some TMS.

Spectra were calibrated with a HP 5245L counter and the precision of the measurements is judged to be ±0.15 Hz for the coupling constants (from 50-Hz width spectra) and ±0.02 ppm for the shifts. The nuclear Overhauser enhancements are the differences in the integrated intensities of a specific signal caused by double irradiation at the proton signals noted and at a blank region of the spectrum (*i.e.*, off-resonance) consecutively, using the same irradiating power (10–20 mV). These enhancements are the average of at least ten comparisons and have a precision of ±2%.

Materials. The 9-methyl- and 9-ethyl-9,10-dihydroanthracene derivatives were synthesized by reduction of the corresponding 9-alkylanthracene with lithium in liquid ammonia as previously described.[22c]

9-Phenyl-9,10-dihydroanthracene. 9-Phenylanthracene (760 mg, 3 mmol) in THF (100 ml), followed by lithium wire (52 mg, 2.5 equiv), was added to refluxing ammonia (150 ml). The color was discharged after 1 hr by the addition of water. Evaporation of the ammonia followed by partition of the residue between ether and water led to recovery of a pale yellow oil which crystallized on standing. Recrystallization from 95% ethanol (20 ml) gave white needles (520 mg, 68%) melting at 89–90° (lit.[25] 87°).

9-Isopropyl- and 9-*t*-Butyl-9,10-dihydroanthracene. These were synthesized[26] by addition of the appropriate organolithium reagent (54 mmol) in pentane to a solution of anthracene (4.44 g, 25 mmol) in THF (125 ml). Reaction of the isopropyl compound was conducted at 0° and quenched after 2 hr with water. The crude product, an oil, on glpc on a 6-ft column of 10% SE-30 on Chromosorb W at 175° showed only one peak. It was further purified by passage through a column of alumina. Reaction of the *t*-butyl compound was conducted at ambient temperature and quenched after 40 min with ethanol. Three recrystallizations of the crude product (5.34 g) afforded 9-*t*-butyl-9,10-dihydroanthracene (460 mg, 8%) melting at 125.5° (lit.[18] 126°). Preparative glpc of the remainder on an 8-ft column of 20% SE-30 on Chromosorb W at 250° afforded, after recrystallization from ethanol, 1.22 g of the 9-*t*-butyl compound, and three additional products: (a) 250 mg, (b) 440 mg, and (c) 210 mg. To component a was tentatively assigned the structure 1-*t*-butyl-1,2-dihydroanthracene: mp 102.3–103.3°; uv max (EtOH) 247 nm (ε 42,700); nmr ($CDCl_3$) δ 7.17–7.83 (m, 6, aryl), 6.55, 6.13 (m, 2, vinyl), 3.37 (m, 1, CH), 2.67 (m, 2, CH_2) and 1.07 (s, 9, CH_3).

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.57; H, 8.36.

Component b was assigned the isomeric 2-*t*-butyl-1,2-dihydroanthracene structure: mp 108–109°; uv max (EtOH) 252 nm (ε 35,600); nmr ($CDCl_3$) δ 7.13–8.03 (m, 6, aryl), 6.65, 6.07 (AB system, *J* = 10 Hz, in which the low-field and high-field protons at C-4 and C-5, respectively, are further split by the allylic proton, *J* = 2 and 3 Hz, respectively), 2.92 (d (?), 2, *J* = 8 Hz, CH_2), 2.30 (broad multiplet, 1, CH), and 0.93 (s, 9, CH_3).

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.66; H, 8.27.

1,4,9-Trimethyl-9,10-dihydroanthracene. In a typical experiment, 0.51 g (0.0023 mol) of 1,4,9-trimethylanthracene was dissolved in a benzene–ether mixture (1:1, v/v) and treated with 0.10 g (0.014 g-atom) of metallic lithium at 30° for 22 hr. The resulting mixture was cooled (0–5°) and diluted with *ca.* 20 ml of 95% ethanol. After the addition of *ca.* 40 ml of water, the organic layer was separated and dried (sodium sulfate). Removal of the solvent under reduced pressure afforded 0.51 g of the desired product. Glpc (20% SE-30 on Chromosorb W) indicated that the product consisted of one major (89%) component.

Column chromatography (silica gel, hexane eluent), followed by recrystallization of the resulting solid from 95% ethanol afforded the desired compound, purity >99.5% (glpc), mp 73–75°. Several reactions indicated an average isolated yield of *ca.* 20%.

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.72; H, 8.10.

Results

All spectra in this series are similar consisting of a low-field aryl multiplet, an AB pattern for the C-10 methylene protons, and the expected pattern for the R–C_9–H grouping (R = Me, Et, *i*-Pr, *t*-Bu, Ph). In each case further splitting of the AB pattern is apparent arising from long-range, spin–spin interactions, *i.e.*, homoallylic coupling with the C-9 proton and allylic coupling with the *peri*-aryl protons. The origins of these couplings were readily confirmed by spin decoupling. For the AB patterns of the monosubstituted derivatives, δ_{AB} is 0.2–0.5 ppm and, with the aryl protons decoupled, the lower field A portion consistently exhibits a homoallylic coupling larger than that found for the B portion. Although at room temperature these two homoallylic couplings are the same for the 9-phenyl derivative, at −37° the A proton is the more strongly coupled. With the aid of spin decoupling to simplify the spectra for those cases in which the C-9 methine absorption overlaps the AB pattern, the parameters for the benzylic protons were readily determined and are collected in Table I. With the exception of the 9-phenyl derivative these data were found to be essentially independent of temperature over the range −37 to +37°. Thus, it appears that these compounds are nearly conformationally homogeneous in either of the two possible conformers, $2_{a'}$ or $2_{e'}$. The fact that in one case the homoallylic coupling constant, J_{BM}, exhibits a temperature dependence is consistent with the presence of an equilibrium mixture of two forms. It may be noted that there appears to be a small decrease, 0.05 Hz, in J_{BM} over this temperature range for the 9-methyl system, but the change is too small to confirm the presence of an equilibrium mixture. On the basis of the relative magnitudes of the homoallylic coupling constants, the assignments for "H_A" and "H_B" are reversed for the 1,4,9-trimethyl derivative, *i.e.*, H_A, exhibiting the

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Table I. Proton Parameters for **1** in CS_2 Solutions[a]

R	δ_{CH_3}	δ_{CH}	δ_A	δ_B	δ_M	J_{AB}	J_{AM}	J_{BM}
CH_3	1.16		3.98	3.73	3.90	18.1_0	1.0_0	0.7_0
CH_3CH_2	0.78	1.50	3.96	3.67	3.67	18.3_5	1.1_0	0.4_5
$(CH_3)_2CH$	0.79	1.77	4.03	3.67	3.49	18.3_0	1.1_0	0.4_0
$(CH_3)_3C$	0.83		4.11	3.65	3.57	18.8_0	1.3_0	0.4_0
C_6H_5			3.88	3.70	5.04	18.1_0	1.2_0 $(1.1_5)^b$	1.2_0 $(1.0_5)^b$
1,4,9-$(CH_3)_3$[c]	1.32		3.75	3.87	4.12	18.8	0.9_5	0.6_0

[a] δ parts per million from TMS; *J* in hertz. [b] At −37°. [c] Aryl methyls at δ 2.29 and 2.34.

larger homoallylic interaction, is upfield from H_B; this reversal is discussed below.

If these compounds preferentially exist in conformer $\mathbf{2}_{a'}$ it can be seen that the pseudoequatorial proton, $H_{e'}$, at C-10 and the *meso* proton, H_M, are appreciably closer to the *peri* protons than is $H_{a'}$; in $\mathbf{2}_{e'}$, of course, the situation is reversed. Thus a measurement of the nuclear Overhauser enhancement of the benzylic protons upon irradiation of the aryl absorption should permit one to decide which of $\mathbf{2}_{a'}$ and $\mathbf{2}_{e'}$ predominates. The results of these experiments are collected in Table II. Additional NOE results were obtained for the *t*-butyl and trimethyl derivatives. For the former, irradiation of the *t*-butyl methyl protons causes a 14% enhancement of the lowfield pattern, H_A, without measurably affecting the H_B absorption. In 1,4,9-trimethyl-9,10-dihydroanthracene, irradiation of the 9-methyl doublet enhances the upfield methylene absorption, H_A, by +5% while H_B is virtually unaffected. Furthermore, irradiation of the aryl methyl signals enhances the H_M signal by +15%, H_B by +6%, and the H_A absorption remains essentially unchanged (−1%).

Table II. NOE Results[a] for the Benzylic Protons in **1**

R	H_A	H_B	H_M
CH_3	*b*	*b*	+15
$(CH_3)_2CH$	−1	+5	+13
$(CH_3)_3C$	−1	+5	+16
C_6H_5	+1	+10	+15
1,4,9-$(CH_3)_3$	0	0	+7

[a] Given as per cent (intensity with aryl irradiation − intensity with off-resonance irradiation). [b] The complexity of the spectrum precludes precise intensity measurements.

Discussion

Nuclear Overhauser Enhancements. From the NOE results for the 9-alkyl derivatives in Table II it is apparent that an interaction between the methine *meso* proton H_M, and the aryl protons provides an important relaxation pathway for the former, indicating that these protons are pseudoequatorial as in $\mathbf{2}_{a'}$. If the preferred form were $\mathbf{2}_{e'}$, H_M would be pseudoaxial and much further separated from the *peri* protons. Since the vicinal protons of the R groups are also close to H_M it is reasonable that the observed NOE is only *ca.* 15%. From Table II it can be seen that the methylene protons are unequally affected by saturation of the aryl absorption, H_B is enhanced while -H_A is little changed. Although less conclusive, this indicates that H_B is in the *e'* orientation. The dominant factor governing the relaxations of neighboring protons has been shown to be the dipolar interaction which depends on the internuclear separation as r^{-6}; thus, each methylene proton is efficiently relaxed by its geminal neighbor and the contribution of other neighboring protons is much smaller.[27] It is this feature that undoubtedly leads to the relatively small enhancements found for H_B. The same explanation accounts for the different effects observed for the benzylic protons in 1,4,9-trimethyl-**1**; saturation of the aryl methyl signals produces about twice the enhancement for H_M as for H_B. Clearly the *meso* proton is relaxed by interactions with both the *peri*-methyl and the *peri* proton at C-8. It may be noted that the latter contribution is *ca.* 50% that found for the monoalkyl derivatives as one would predict since there is only one *peri* proton.

Thus a consistent trend emerges for the alkyl substituted systems. In each monosubstituted case the higher field methylene proton, H_B, and the methine proton, H_M, must be near neighbors of the *peri* positions; furthermore H_A is close to the *t*-butyl group in 9-*t*-butyl-**1** and to the 9-methyl group in the trimethyl derivative. These results are only consistent with the predominance of conformer $\mathbf{2}_{a'}$. It may be noted that analogous observations in the 7,12-dihydropleiadene series were employed by Colson, Lansbury, and Saeva for their stereochemical assignments.[28]

Coupling Constants. From Table I it is apparent that the geminal couplings are the same, within experimental error, except for the *t*-butyl and trimethyl derivatives. The latter, presumably more negative, values appear to be a natural consequence of increased steric interaction between $H_{a'}$ and the R group in $\mathbf{2}_{a'}$. In 9-*t*-butyl-**1**, the separation between $H_{a'}$ and the closest methyl protons is less than the sum of their van der Waals radii unless the boat is somewhat flattened but this tendency will be opposed by the nonbonded interactions between the methyl and *peri* protons. In 1,4,9-trimethyl-**1**, nonbonded interactions between the 1- and 9-methyl protons presumably alter the geometry of the central ring somewhat from that for 9-methyl-**1** since the geminal couplings differ. Twisting the C-10 methylene group in a direction to reduce steric interaction with an *a'*-R grouping, however, alters the dihedral angle between the C–$H_{a'}$ and the aryl ring plane in the direction which is known to increase J_{gem} values for sp^3-hybridized methylene groups.[29] Thus the observed geminal couplings indicate a slight flattening of the central ring for these

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two derivatives relative to the monosubstituted systems.

The long-range homoallylic coupling constants were expected to provide confirmatory evidence for the stereochemical assignments in these systems since it was known that these interactions depend on the relative orientation of the coupled protons.[30] The three possible interactions have been found to follow the order $J_{a'a'} > J_{a'e'} > J_{e'e'}$ with typical values of 2.5, 1.5, and 0.5 Hz, respectively, in systems in which the π bond is aromatic. The observed couplings in Table I, therefore, indicate that H_A is pseudoaxial and H_B pseudoequatorial since H_M is shown by its NOE to be pseudoequatorial. The fact that the homoallylic couplings in 9-isopropyl-**1** were found to be independent of temperature down to $-37°$ strongly indicates that this system is almost entirely in that form having the alkyl group pseudoaxial. On this basis, 0.4 and 1.1 Hz can be taken as the values for $J_{e'e'}$ and $J_{a'e'}$, respectively. The somewhat larger J_{BM} values for the methyl derivatives, however, suggest that these materials undergo inversion $\mathbf{2}_{a'} \rightleftarrows \mathbf{2}_{e'}$, although $\mathbf{2}_{a'}$ predominates. If the homoallylic couplings for isopropyl-**1** are taken as characteristic of a system essentially "frozen" in $\mathbf{2}_{a'}$, the J_{BM} values indicate that *ca.* 75% of the 9a'-methyl form is present at equilibrium.

It may be noted that the homoallylic couplings in 3(6)-substituted 1,4-cyclohexadienes are appreciably larger; the J_{cis} and J_{trans} values lie in the range 7–11 Hz.[11,12] While reasons for these enhanced values relative to those in the dihydroanthracenes are not immediately obvious, two differences between these skeletons may contribute. Electron-diffraction results indicate that the cyclohexadiene ring is flatter having a dihedral angle viewed along the C-3,6 axis of *ca.* 160°[14] whereas the corresponding dihedral angle in 9,10-dihydroanthracene is *ca.* 145°;[15] thus the dihedral angles between the sp^3-hybridized C–H bonds and the plane of the adjacent π bonds differ. In addition, electron delocalization of the aryl bond in **1** may serve to reduce the magnitude of the homoallylic interaction relative to that in the system having a simple π bond.

In contrast to the alkyl derivatives, 9-phenyl-**1** exhibits equal homoallylic coupling at room temperature. As the temperature is lowered, however, J_{BM} decreases indicating that $\mathbf{2}_{a'}$ (R = Ph) is the more stable form. It may be noted that the coupling between $H_{a'}$ and H_m in $\mathbf{2}_{a'}$ is expected to be temperature independent even if there is a substantial concentration of $\mathbf{2}_{e'}$, since in both forms the interaction is $J_{a'e'}$. On the other hand, $J_{e'm}$ ($\mathbf{2}_{a'}$) should increase with increasing concentration of $\mathbf{2}_{e'}$ since this coupling is $J_{a'a'}$ in $\mathbf{2}_{e'}$. Thus, the fact that only J_{BM} is temperature dependent is further evidence in favor of the present assignments. Lacking an experimental value for $J_{a'a'}$ in these systems, one cannot deduce the relative amounts of $\mathbf{2}_{a'}$ and $\mathbf{2}_{e'}$ (R = Ph); however, it would appear that the equatorial form $\mathbf{2}_{e'}$ makes a substantial contribution. Presumably the barrier to conformational interconversion is smallest in this compound because the phenyl group can lie parallel to the C-9,10 axis as the system passes through the transition state thereby reducing the steric interactions with the *peri* protons relative to those in the case of a methyl (or larger) group; the van der Waals radius of the methyl group is 0.2 nm whereas the half-thickness of the aryl ring is 0.185 nm. It should be noted that the methylene protons of the parent compound, **1**, R = H, are equivalent at $-60°$, indicating rapid inversion at that temperature.[17] In view of these results for 9-phenyl-**1** it is not surprising that the homoallylic couplings reported for 1,4-dihydrobiphenyl are equal;[12] undoubtedly the latter compound readily undergoes conformational interconversion at room temperature which would average the $J_{1,4}$ interactions to the same value.

Chemical Shifts. In 9-ethyl-, 9-isopropyl-, and 9-*t*-butyl-9,10-dihydroanthracene, the upfield methylene proton, H_B, absorbs at the same position, 3.65 ± 0.01 ppm, while the shielding of H_A depends on the substituent, decreasing with increasing bulk of R. Furthermore H_B in the methyl derivatives is deshielded relative to the above. These results are completely consistent with the foregoing stereochemical assignments for these protons and the R groups, since it is well known that the close approach of neighboring protons tends to deshield these nuclei.[31] Since the first three examples cited exist almost entirely as $\mathbf{2}_{a'}$, H_B must be the pseudoequatorial methylene proton while H_A is pseudoaxial. The finding that the pseudoaxial protons absorb at lower field than their pseudoequatorial counterparts is consistent with the results found for the dihydropleiadenes.[32]

In 9-methyl-**1**, the presence of some $\mathbf{2}_{e'}$ (R = Me), would be expected to alter the environment of H_B slightly since this proton is pseudoaxial in the minor form $\mathbf{2}_{e'}$. An estimate of the H_B shielding in a mixture of $\mathbf{2}_{a'}$ and $\mathbf{2}_{e'}$ (R = Me) can be made from the methylene shift for 9,10-dihydroanthracene, δ 3.80, and that for the pseudoequatorial C-10 proton in the "fixed" systems, δ 3.65. These values lead to a predicted shift of 3.95 ppm for the pseudoaxial orientation in the parent system. Since in $\mathbf{2}_{e'}$ (R = Me) the pseudoaxial C-10 proton should not be affected by the 9-methyl group, the observed shielding for H_B will be the weighted average of the two shifts: 3.65 and 3.95 ppm. Thus an estimated H_B shielding for a mixture of 75% $\mathbf{2}_{a'}$–25% $\mathbf{2}_{e'}$, R = Me, (the composition given by the homoallylic couplings) is 3.73 ppm in remarkable agreement with the observed value, indicating that the equilibrium mixture indeed contains *ca.* 75% $\mathbf{2}_{a'}$ (R = Me).

The low-field shifts exhibited by the *meso* proton, H_M, and H_B in the 1,4,9-trimethyl derivative are probably due to interactions with the nearby *peri*-methyl protons of the 1- and 4-methyl groups, rerespectively, but it is difficult to account for the apparent upfield shift of H_A. The reversal in the relative shifts of H_A and H_B in this case, however, clearly illustrates the potential dangers associated with extrapolation of shift trends in related systems. In view of the uncertainty regarding the composition of the equilibrium mixture for 9-phenyl-**1** and the orientation

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of the phenyl group it is not possible to comment on the chemical shifts found for this system other than to note that H_B absorbs at nearly the same field as the corresponding proton in the monoalkyl systems.

The shielding trend exhibited by the methine proton at C-9 is interesting, but puzzling. On the basis of the anisotropic shielding effect of the aryl rings one might expect this proton to be increasingly deshielded as its e' population increases; the observed tendency, however, is in the opposite direction. Furthermore, the e' populations of the 9-isopropyl and 9-*t*-butyl derivatives appear to be very similar but their H_M shieldings are not. Similar trends are found for the C-9 proton in the corresponding 9-alkylthioxanthene (Me, δ 3.97; Et, δ 3.81; *i*-Pr, δ 3.50; *t*-Bu, δ 3.79)[33] and 9-alkylacridine series,[34] as well as for the C-7 proton in the corresponding series of 1-*t*-butyl-7-alkyl-1,3,5-cycloheptatrienes (δ 3.26, 3.06, 2.82, and 3.23).[35] It seems reasonable to suggest that the effect is principally due to the alkyl groups.

Conclusions

These results, taken together, provide conclusive evidence that the alkyl groups in 9-ethyl- and 9-*t*-butyl-9,10-dihydroanthracene preferentially, if not exclusively, exist in the pseudoaxial orientation, contrary to the earlier claims of Nicholls and Szwarc[19] and Carruthers and Hall,[18] respectively. The same situation holds for the 9-isopropyl derivative while the 9-methyl and 9-phenyl substituted systems appear to exist as equilibrium mixtures of the two conformers but with predominantly pseudoaxial 9 substituents. Clearly, analogies between the chemical-shift differences in chair and boat forms of the six-membered ring are unwarranted especially if one contains unsaturated centers.

Also, these results support the proposed mechanism for the observed stereospecific *trans* reduction of 9,10-dialkylanthracenes, an essential feature of which was the concept that ethyl and larger groups would preferentially assume the pseudoaxial orientation.[22c]

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Free-Radical Chlorination of Methyl Cyclohexanecarboxylates.
I. Stereochemistry of the Chlorination Step

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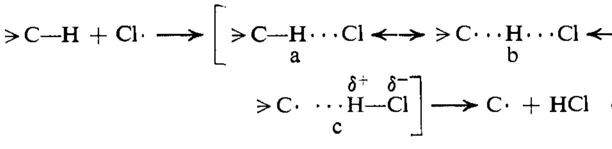
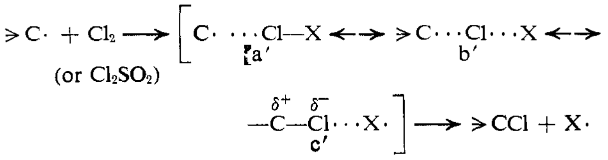
Abstract: The free-radical chlorination of methyl cyclohexanecarboxylate and its 4-methyl and 4-*t*-butyl derivatives by sulfuryl chloride shows a preference for *trans* attack at positions remote from the ester group. Even for the *trans*-4-*t*-butyl deriative, 3-chloro prefers to enter *trans* to the ester in spite of this position being *cis* to *t*-butyl as well as axial. It is proposed that this preferred *trans* orientation in the chlorination step results from polar interactions between the ester dipoles and the incipient dipole generated at the forming carbon chlorine bond in the transition state.

The investigations reported in this and the following paper were designed to add to knowledge of the two steps involved in free-radical chlorination. While a great deal of data is available,[2] while there is some



$$>C{-}H + Cl\cdot \longrightarrow \left[\underset{a}{>C{-}H\cdots Cl} \longleftrightarrow \underset{b}{>C\cdots H\cdots Cl} \longleftrightarrow \underset{c}{>C\cdot\cdots \overset{\delta^+}{H}{-}\overset{\delta^-}{Cl}} \right] \longrightarrow C\cdot + HCl \qquad (A)$$



$$\underset{(\text{or } Cl_2SO_2)}{>C\cdot + Cl_2} \longrightarrow \left[\underset{a'}{C\cdot\cdots Cl{-}X} \longleftrightarrow \underset{b'}{>C\cdots Cl\cdots X} \longleftrightarrow \underset{c'}{-\overset{\delta^+}{C}{-}\overset{\delta^-}{Cl}\cdots X\cdot}\right] \longrightarrow >CCl + X\cdot \qquad (B)$$

considerable agreement that transition states for both reactions are reactant-like (a and a′), while electrical effects from contributions of c have been proposed to explain orienting effects of chlorination away from electronegative substituents,[3–6] the relative importance of steric factors in the two steps has not been clearly established.

A notable preference for *trans* or "anti" products (hereafter denoted "*trans* effect") has been observed in chlorinations of cyclic or acyclic systems suitable for observation of this phenomenon.[5c,d,7] This "*trans* effect" has alternately been explained either by steric interaction between the electronegative substituent and

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