Formation of Mono- and Dianions of Polycyclic Hydrocarbons through Deprotonation with the Alkyllithium-*N*,*N*,*N'*,*N'*-Tetramethylethylenediamine Complex. A Convenient General Method of Dehydrogenation

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Abstract: Interaction of 9,10-dihydroanthracene and its 9- and 10-methyl and ethyl derivatives (**1a–f**) with *n*-butyllithium in cyclohexane and excess *N*,*N*,*N'*,*N'*-tetramethylethylenediamine afforded the respective dianionic intermediates. The latter on treatment with cadmium(II) chloride or other metal salts underwent transformation to fully aromatic hydrocarbons in essentially quantitative yield. The presence of a secondary or tertiary alkyl group in the meso position inhibited deprotonation beyond the monoanion stage and altered the course of reaction to favor bimolecular dehydrogenation or methylene formation dependent upon whether or not a second alkyl group was present in the remaining meso position. The dimer obtained from 9-*tert*-butyl-9,10-dihydroanthracene was shown through detailed analysis of the 270-MHz nmr spectrum to exist in an unusual twisted conformation having the aromatic protons of one pair of rings oriented beneath the aromatic π cloud. Analogous reactions of 7,12-dihydrobenz[a]anthracene, acenaphthene, and bibenzyl proceeded similarly to afford benz[*a*]anthracene, acenaphthylene, and stilbene, respectively. In contrast, 9,10-dihydrophenanthrene underwent dehydrogenation to afford phenanthrene essentially quantitatively without added metal salt. 4,5,9,10-Tetrahydropyrene exhibited intermediate behavior, undergoing transformation directly to pyrene more efficiently in the presence of copper(II) iodide than in its absence. Finally, tetralin on treatment with even a large excess of the reagent for prolonged periods underwent only modest conversion to naphthalene. Evidence concerning the mechanism, the nature of the intermediates, and the stereochemistry of the foregoing reactions is presented and discussed.

Traditional methods of dehydrogenation of polycyclic hydrocarbons[1] include catalyzed reaction over platinum, palladium, or other metallic catalysts, treatment with sulfur or selenium at elevated temperatures, and interaction with a Lewis acid, usually aluminum chloride. More recently, reagents such as chloranil[2] and triphenylmethyl perchlorate[3] have also been employed for this purpose. These methods, however, are seldom completely satisfactory due to the numerous side reactions encountered and the relatively drastic conditions often required. These problems become acute in multistep syntheses involving rare or expensive compounds or affording products, *e.g.*, carcinogens, required to be of high purity for subsequent testing of biological activity.

We recently reported in a preliminary communication[4] a new general method of dehydrogenation utilizing the alkyllithium-*N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) complex.[5] The rationale for this research was the concept that if dianionic intermediates could be generated *via* double deprotonation, aromatization might be achieved through electron transfer to a suitable acceptor. Survey of the literature revealed, surprisingly, no precedent for formation of dianions of polycyclic hydrocarbons through proton abstraction, with the exception of formation of the acenaphthylene dianion through treatment of acenaphthene with *n*-butyllithium in tetrahydrofuran.[6] In our own experience, other dihydroaromatic compounds (*e.g.*, 9,10-dihydrophenanthrene) failed to undergo appreciable transformation beyond the monoanion stage with alkyllithium reagents under comparable conditions. Charge repulsion is undoubtedly a major factor contributing to the difficulty of removal of a second proton, and tight ion pair association or complex formation would be anticipated to counter this effect. As shown herein, the alkyllithium–TMEDA complex effectively deprotonates hydroaromatic molecules to dianionic intermediates[7] which upon treatment with a metal salt, such as cadmium(II) chloride, afford dehydrogenated products in generally high yield. Unexpectedly, 9,10-dihydrophenanthrene undergoes aromatization smoothly even in the absence of added metal salt.

The present report describes the use of this new method in the dehydrogenation of representative ring systems, the effect of alkyl substituent size on the course of reaction, and evidence concerning the mechanism and the nature of the intermediates.

Results

Although 1,4-dihydroaromatic molecules, such as 9,10-dihydroanthracene (**1a**), undergo facile dehydro-

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[1] E. Clar, "Polycyclic Hydrocarbons," Vol. 1, Academic Press, New York, N. Y., 1964, p 169.

[2] L. M. Jackman, *Advan. Org. Chem.*, **2**, 329 (1960).

[3] W. Bonthrone and D. Reid, *J. Chem. Soc.*, 2773 (1959); D. F. Lindow and R. G. Harvey, *J. Amer. Chem. Soc.*, **93**, 3786 (1971).

[4] Part I: R. G. Harvey, L. Nazareno, and H. Cho, *J. Amer. Chem. Soc.*, **95**, 2376 (1973).

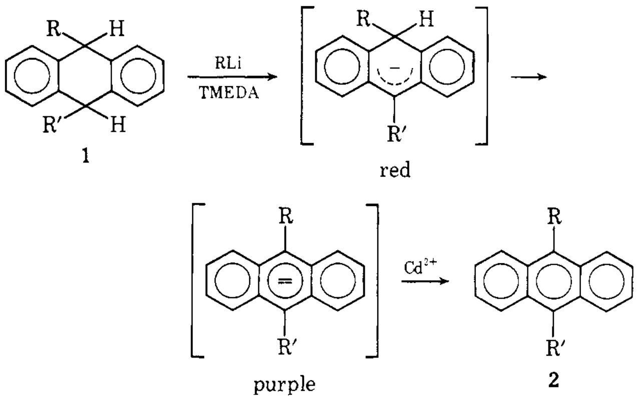
[5] G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, **29**, 2928 (1964); A. W. Langer, Jr., *Trans. N. Y. Acad. Sci.*, **27**, 741 (1965); C. G. Screttas and J. F. Eastham, *J. Amer. Chem. Soc.*, **87**, 3276 (1965).

[6] L. D. Kershner, J. M. Gaidis, and H. H. Freedman, *J. Amer. Chem. Soc.*, **94**, 985 (1972); the facility of acenaphthylene dianion formation by this means has been confirmed in our laboratory.

[7] During the course of this investigation the α,α'-dimetalation of xylene with *n*-amylsodium in the presence of TMEDA[8] and generation of the naphthalene dianion through treatment of 1,4-dihydronaphthalene with alkyllithium–TMEDA[9] were described.

[8] G. B. Trimitsis, A. Tuncay, and R. D. Beyer, *J. Amer. Chem. Soc.*, **94**, 2152 (1972).

[9] J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Amer. Chem. Soc.*, **94**, 7346 (1972), and references therein.



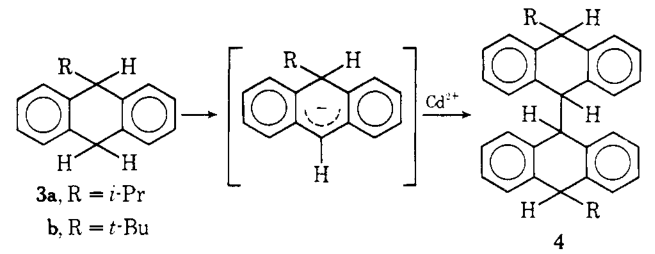
a, R = R′ = H
b, R = Me; R′ = Et
c, R = Me; R′ = H
d, R = Et; R′ = H
e, R = R′ = Me
f, R = R′ = Et

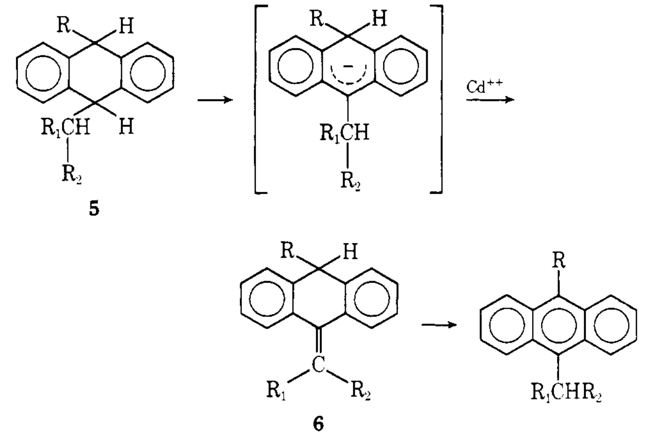
genation by various methods, related compounds substituted in the benzylic positions behave less satisfactorily. Thus, *cis*-9-ethyl-10-methyl-9,10-dihydroanthracene (**1b**) failed to afford crude yields of 9-ethyl-10-methylanthracene (**2b**) >50% by any of the conventional methods employed.[10] In contrast, treatment of a solution of **1b** in cyclohexane with *n*-butyllithium in the presence of TMEDA followed by addition of cadmium(II) chloride after 1 hr at reflux temperature afforded **2b** essentially quantitatively. Analogous reaction of dihydroanthracene and its methyl and ethyl derivatives (**1c–f**) proceeded similarly to afford the related methyl- and ethylanthracene derivatives **2a** and **2c–f** in essentially quantitative yield.

Formation of the monoanion was extremely rapid as evidenced by the essentially instantaneous appearance of its deep red color upon addition of the lithium reagent. Reflux temperature was required to change this to the intense purple hue characteristic of the dianion. This color persisted until discharged by the addition of the cadmium salt with concurrent precipitation of metallic cadmium. Other metal salts (*e.g.*, lead(II) chloride, copper(II) iodide or bromide, mercury(II) chloride, nickel(II) acetylacetonate) or other electron acceptors (*e.g.*, iodine) also serve, though none quite so effectively.

For optimum yields, excess quantities of both the lithium reagent and TMEDA are required. In the absence of severalfold excess of TMEDA over that calculated to complex the ionic intermediates, there were obtained a large proportion of insoluble polymeric products. For example, reaction of **1b** with *n*-butyllithium and cadmium chloride under standard conditions, except that only 3 ml rather than 15 ml of TMEDA was employed, gave as the major product a "polymer" which melted at 265–268°; the latter proved too insoluble for useful nmr spectral analysis.

The presence of a secondary or tertiary alkyl group in a meso position altered the course of reaction to favor either oxidative dimerization (*i.e.*, bimolecular dehydrogenation) or methylene formation (*i.e.*, 1,2-dehydrogenation), dependent upon whether or not a second alkyl group was present in the remaining meso position.





a, R = *i*-Pr; R$_1$ = R$_2$ = H
b, R = *i*-Pr; R$_1$ = CH$_3$; R$_2$ = H
c, R = *i*-Pr; R$_1$ = R$_2$ = CH$_3$

Thus, 9-*tert*-butyl-9,10-dihydroanthracene (**3b**) upon treatment with *n*-butyllithium–TMEDA and cadmium(II) chloride under the usual conditions provided a white, crystalline solid, mp 211–212°, as essentially the sole product. The integrated nmr spectrum[11] was consistent with the assigned dimeric structure **4b**, exhibiting methyl protons (18 H) as a singlet at δ 1.13, methine protons as a pair of singlets at 3.90 (2 H) and 5.53 (2 H), and aromatic protons (16 H) as a complex multiplet. Since the methine signal at higher field appears close to that of **3b** (δ 3.57),[12] it is assigned to the protons on carbon bearing *tert*-butyl, leaving the unusually low field signal at δ 5.53 to be assigned to the internal methine protons. Only one of the three possible stereoisomers appears to be formed in this reaction. Of the three, the cis,cis, the cis,trans, and the trans,trans, the latter appears most probable in view of the large steric demands of the *tert*-butyl group and its demonstrated[12] strong preference for the axial orientation in the monomer **3b**. The latter was previously shown by nmr spectroscopy to exist in a flattened boat structure.[12] Detailed analysis of the nmr spectrum of **4b** supports an unusual twisted conformation in which the dihydroanthracene rings are oriented approximately perpendicular to one another (*cf.* Discussion).

Analogous reaction of 9-isopropyl-9,10-dihydroanthracene (**3a**) proceeded less stereoselectively to afford a mixture of the three predicted stereoisomeric dimers, separated from one another through trituration and fractional crystallization. A small amount of 9-isopropylanthracene was also detected as a minor product (20%). Assignment of the cis,cis, cis,trans, and trans,trans dimeric structures was attempted

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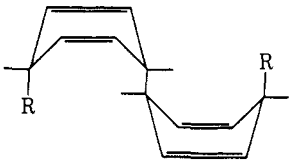
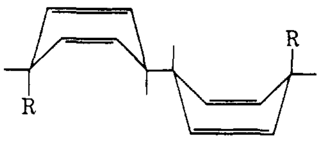
(10) Numerous attempts with other reagents [*e.g.*, sulfur, palladium on charcoal, AlCl$_3$, I$_2$, FeCl$_3$, SbCl$_5$, chloranil, DDQ, trityl perchlorate, Ce(NH$_4$)$_2$(NO$_3$)$_6$, and Pb(OAc)$_4$] led generally to relatively intractable mixtures from which only low yields of pure **2b** could be isolated.

(11) Nmr spectra are in deuteriochloroform with chemical shifts in ppm relative to TMS unless stated otherwise.

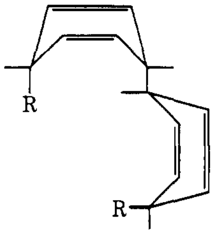
(12) A. W. Brinkmann, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **92**, 5912 (1970).



cis,cis



trans,trans

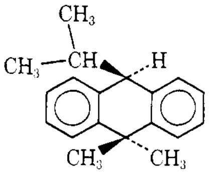


cis,trans

through analysis of the integrated proton nmr spectra in comparison with **3a** previously shown to exist preferentially in a flattened boat structure bearing the isopropyl group in the axial orientation.[13] On this basis, the isomer ratios were trans,trans (36%), cis,trans (22%), and cis,cis (12%). This accords reasonably well with expectation based on the probable influence of steric and conformational factors on the relative ease of formation and thermodynamic stability of the isomers. However, it must be emphasized that these assignments are only tentative, since they are based on extrapolation of the conformational preference of the monomer to the dimer, an assumption which may prove invalid.

In contrast, analogous reaction of the 10-methyl derivative of **3a**, *i.e.*, 9-isopropyl-10-methyl-9,10-dihydroanthracene (**5a**), afforded the 10-methylene compound **6a** as the principal product. It was accompanied by a minor amount of the aromatized product 9-isopropyl-10-methylanthracene and recovered **5a**; no dimeric products were detected. In support of the structure assigned to **6a** the nmr spectrum exhibited a pair of vinylic protons as a singlet at δ 5.58, a benzylic proton as a doublet at 3.59 (J = 6 Hz), and six methyl protons as a doublet at 0.75 ppm (J = 6 Hz). The chemical shift of the vinylic protons (δ 5.58) corresponds to that reported for the closely related 10,10-dimethyl-9-methylene-9,10-dihydroanthracene[13] (δ 5.60), and differs by only 0.12 ppm from that of the analogous 6,8,12-trimethyl-7-methylene-7,12-dihydrobenz[*a*]anthracene[14] (δ 5.70). Acid-catalyzed isomerization of the 10-methylene compound in refluxing toluene converted it to the fully aromatic 9-isopropyl-10-methylanthracene, thus attaining in two steps the initial goal of aromatization. In similar manner, the 9-ethyl-10-isopropyl and the 9,10-diisopropyl derivatives (**5b,c**) of 9,10-dihydroanthracene underwent transformation to the corresponding methylene compounds (**6b,c**). Also, acid-catalyzed isomerization of **6b** proceeded smoothly to afford 9-ethyl-10-isopropylanthracene. However, **6c** failed to undergo analogous transformation. Evidence will be presented in a subsequent paper that **6c** is the thermodynamically stable form.

In all of the foregoing reactions of the isopropyl or *tert*-butyl derivatives of **1a** with RLi–TMEDA (twofold excess over that calculated to generate the dianion), the solutions retained the deep red coloration of the monoanion until discharged by the metal salt. The monoanionic nature of these intermediates was further confirmed by trapping experiments. Thus, treatment of the intermediate from **5a** with methyl iodide afforded 9,9-dimethyl-10-isopropyl-9,10-dihydroanthracene (**7**) as the sole product, while reaction of the same intermediate with deuterium oxide furnished **5a** incorporating a single deuterium atom in the 10 position (*i.e.*, carbon bearing methyl). Similar experiments with the intermediate from 9-isopropyl-9,10-dihydroanthracene gave as the principal product the monomethyl derivative (**5a**, 83%) accompanied by 9-isopropylanthracene[15] (14%). Deuteration of the same intermediate gave the 10-deuterio and 9,10-dideuterio derivatives of **3a** in approximately similar ratio (4:1) by nmr analysis (mass spectra proved unreliable due to the facility of cracking). These results indicate a marked steric inhibition of proton abstraction from the monoanion bearing a bulky group (*i.e.*, isopropyl or *tert*-butyl) in the benzylic position concerned. This effect may be due to (a) steric interference with approach of the attacking reagent, (b) the tendency of bulky groups to favor the axial orientation[16] thereby forcing proton abstraction to occur from the less favored equatorial direction,[17] or (c) steric interference with formation of a tight Li–TMEDA complex. Such complexes on the basis of the elegant investigations of Stucky[9] would be expected to adopt a boat-like structure with the metal cation above the central ring on the same side as alkyl substituent. A dissociated monoanion would be expected to be considerably less susceptible to abstraction of a second proton.



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The stereochemistry of the starting compound, whether cis or trans, had no observable effect on either the rate or the course of reaction in those cases where comparison was made. This would be anticipated on the assumption that the structure of the intermediate monoanion is independent of its origin. Although stable cis and trans Li–TMEDA complexes of the monoanion which could restrict conformational interconversion are conceivable, this does not appear to be an important factor in determining the overall course of the present reactions. Generally, the cis isomers were employed, since these were readily available through alkylation of dihydroanthracene with *n*-butyllithium and the appropriate alkyl halide in tetrahydrofuran at low temperature.[18,19] The overall sequence which con-

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(13) S. Dickman, J. Berg, J. Haase, and R. Varma, *J. Amer. Chem. Soc.*, **89**, 5457 (1967).

(14) J. Pataki, C. Duguid, P. W. Rabideau, H. Huisman, and R. G. Harvey, *J. Med. Chem.*, **14**, 940 (1971).

(15) 9-Isopropylanthracene is believed to arise from the corresponding dianion through electron transfer to methyl iodide. This is supported by the results of deuteration which affords 9,10-dideuterio-**3a** in its stead.

(16) Previous nmr investigation[12] of the 9-alkyl-9,10-dihydroanthracene system demonstrated an increasing preference for the axial orientation in the series Me < Et < *i*-Pr < *t*-Bu.

(17) (a) R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *J. Amer. Chem. Soc.*, **91**, 4535 (1969); (b) R. G. Harvey and L. Arzadon, *Tetrahedron*, **25**, 4887 (1969).

(18) R. G. Harvey and C. C. Davis, *J. Org. Chem.*, **34**, 3607 (1969).

(19) High yields of alkyldihydroanthracenes can generally be obtained by conducting reactions of dihydroanthracene with the lithium reagent (1 or 2 equiv, depending upon the number of alkyl groups desired to introduce) in THF at −30°, and subsequent alkylation at −78°.

stitutes a net synthesis of the 9-mono- and 9,10-dialkylanthracenes from dihydroanthracene is, by all criteria (*i.e.*, yield, conversion, speed, purity of products) the method of choice for preparation of these compounds.

Epimerization of the cis,trans isomers was observed on protonation of the monoanionic intermediates. Thus, *trans*-9,10-diisopropyl-9,10-dihydroanthracene (**5c**) on treatment with *n*-butyllithium–TMEDA under the usual conditions with omission of the metal salt afforded a crude product containing >95% of the cis isomer by nmr analysis. Recrystallization from petroleum ether gave *cis*-**5c**, mp 114.5–115.5° (lit.[20,21] 116.5–117.0°, 109–110°). The nmr spectrum was in agreement with this assignment; in particular, the benzylic protons appeared as a doublet with chemical shift (δ 3.30) and coupling constant (J = 9.5 Hz) characteristic of the cis isomer.[20,21] Analogous reaction of the 9-ethyl and 9-methyl analogs of **5c** (*i.e.*, **5b,a**) gave decreasing cis preference, 75 and 55%, respectively.

Predominance of the cis isomers is quite surprising and significant, since metal–ammonia reduction of 9,10-diisopropylanthracene has been shown to furnish the trans isomer;[17a] thus protonation of the same monoanionic intermediate, the monoanion of **5c**, affords opposite stereoisomers in these two reactions! Although some type of complexation or association would appear to be involved, its exact nature remains uncertain. A reasonable hypothesis is that in ammonia the carbanion is less strongly associated (probably solvent separated) and is thus free to undergo protonation from the preferred axial direction (cis to the other isopropyl group) to furnish the trans isomer,[17] while the tightly Li–TMEDA complexed carbanion in cyclohexane is restricted to backside attack to form the cis isomer. Alternatively, it is conceivable that the bulk of the Li–TMEDA group forces it, rather than the isopropyl group, to adopt the equatorial position; protonation from this direction would afford the cis isomer. In any case, further experiments will be required to resolve these questions.

Analogous reactions of other partially saturated aromatic ring systems proceeded similarly. Thus, 7,12-dihydrobenz[*a*]anthracene, acenaphthene, and bibenzyl on treatment with *n*-butyllithium and TMEDA and cadmium(II) chloride under the usual conditions underwent smooth conversion to benz[*a*]anthracene (97%), acenaphthylene (98%), and stilbene (67%), respectively. Dianionic intermediates are probable, at least for benz[*a*]anthracene and acenaphthylene; however, no attempt was made to trap these by deuteration or alkylation.

In contrast, 9,10-dihydrophenanthrene underwent smooth dehydrogenation to phenanthrene without the necessity for added metal salt. Two equivalents of the lithium reagent were required for quantitative conversion; with 1 molar equiv of *n*-butyllithium, dihydrophenanthrene was recovered unchanged. 4,5,9,10-Tetrahydropyrene exhibited intermediate behavior, undergoing transformation directly to pyrene moderately well (72%) in the absence of added metal salt, but more efficiently (94%) in the presence of copper(II) iodide.

The nature of the intermediate and the mechanism of hydrogen loss from these 1,2-dihydro ring systems is more difficult to interpret. Although aromatization *via* hydride expulsion from a monoanion would appear unlikely on the basis of the stoichiometry and the fact that the reaction mixture retains its intense dark reddish brown color until it is discharged with water, these observations are compatible with metalation of phenanthrene assumed to be the initial product. Indeed, reaction of phenanthrene with *n*-butyllithium under similar conditions furnished a similar dark brown solution. Attempted methylation of this product afforded only recovered phenanthrene. Other observations would appear to rule out a dianion. Thus attempted methylation of the intermediate (3 molar equiv of RLi employed) with methyl bromide at 0° provided phenanthrene (94%) as the sole major product. Failure to undergo methylation is by itself inconclusive, since reduction of alkyl halides *via* electron transfer from radical–anions or dianions is consistent with the known properties of these entities. However, attempted deuteration with D_2O also failed, again affording only phenanthrene (99%). Moreover, reagents capable of readily oxidizing other aromatic dianions, such as copper(II) iodide and sodium benzoate, failed to discharge the color of the intermediate. It was also observed that attempted methylation of the monoanion generated from dihydrophenanthrene and a single equivalent of the lithium reagent, despite rapid discharge of the anion color, afforded only unmethylated dihydrophenanthrene. Thus, the exact nature of the intermediate remains uncertain, and further studies are required.

Finally, tetralin on treatment with even relatively large excess of the lithium reagent for more prolonged periods (3 hr) and cadmium(II) chloride underwent only moderate conversion to naphthalene (12–20%). Here also, the nature of the intermediate is uncertain, although consecutive metalation and hydride loss is more probable than polymetalation to afford a tetraanion.

Discussion

The foregoing results clearly demonstrate the utility of the alkyllithium–TMEDA complex in generating mono- and dianions of polycyclic hydrocarbons *via* metalation. Previously, aromatic dianions have been formed through electron addition to fully aromatic ring systems by alkali metals either in ethereal solvents[22,23] or in liquid ammonia.[25] These methods are in many

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Yields and stereoselectivity were generally superior to those obtained from alkylation in liquid ammonia (at −33°) which in turn were found to provide cleaner products than reactions in ethereal solvents at 0° or above.[18] The lower stereoselectivity and yields reported by some investigators[21] appear to be a consequence principally of the higher temperatures employed, although other differences in experimental conditions may also be involved.

(20) D. A. Redford, Ph.D. Thesis, The University of Saskatchewan, 1967; *Diss. Abstr. B*, **28**, 4074 (1968).

(21) H. E. Zieger, D. J. Schaeffer, and R. M. Padronnagio, *Tetrahedron Lett.*, 5027 (1969).

(22) P. Balk, G. J. Hoijtink, and J. W. Schreurs, *Recl. Trav. Chim. Pays-Bas*, **76**, 813 (1957); E. DeBoer and S. I. Weissman, *ibid.*, **76**, 824 (1957); R. G. Lawler and C. V. Ristagno, *J. Amer. Chem. Soc.*, **91**, 1534 (1969).

(23) Some of the claims in the literature regarding formation of dianions by this means are based solely on spectral measurements and should be regarded with caution in the absence of evidence to rule out other species (*e.g.*, radical anions) or competing reaction pathways (*e.g.*, disproportionation[24]).

(24) N. H. Velthorst and G. J. Hoijtink, *J. Amer. Chem. Soc.*, **89**, 209 (1967).

(25) R. G. Harvey, *Synthesis*, **2**, 161 (1970); D. F. Lindow, C. N. Cortez, and R. G. Harvey, *J. Amer. Chem. Soc.*, **94**, 5406 (1972); R. G. Harvey, D. F. Lindow, and P. W. Rabideau, *ibid.*, **94**, 5412 (1972); *Tetrahedron*, **28**, 2909 (1972).

respects complementary. Metalation allows preparation of both mono- and dianions as complexes, which are often isolable in crystalline state,[9] whereas electron addition affords radical anions and dianions in solution. Aromatic dianions are formed more readily through electron addition in liquid ammonia[26] than in organic solvents; however, solutions in ammonia (bp −33°) are inconvenient for some experimental studies (*e.g.*, spectroscopic measurement).

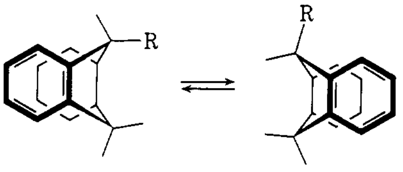
The mechanistic details of the foregoing transformations have not been fully probed, since it is the objective of these initial studies to determine the scope and limitations of the method with particular application to the synthesis of carcinogenic molecules required in other investigations. However, a number of interesting features have been uncovered. Thus, relatively large excess of TMEDA over that calculated for a stoichiometric 1:1 complex with the lithium reagent is required for optimum yield. The role of TMEDA in enhancing metalation is generally considered to involve activation of the lithium reagent through complexation of the metal ion with consequent weakening of the carbon–lithium bond and disruption of aggregation.

Since initial proton abstraction is facile even in the absence of TMEDA, this factor would appear to be of minor significance in this step, although it probably does play an important role in facilitating abstraction of the second proton. With minimum TMEDA (Li/TMEDA = 1:1), dianion formation appears normal (*i.e.*, deep purple solution). Therefore, the excess TMEDA is apparently involved in the final step, the electron transfer to the metal ion. A reasonable explanation is that TMEDA enhances solubilization of Cd^{2+} through association; low concentration of the metal ion would be expected to diminish the rate of electron transfer, permitting the accumulation of radical–anion intermediates which would then dimerize or polymerize.

The mechanism of interaction of Cd(II) and other metal salts with the anthracene dianion involves overall transfer of two electrons. Conceivably, this may be preceded by transient existence of an organocadmium intermediate, although evidence regarding this point is lacking. Similarly, oxidative dimerization of 9-*tert*-butyl- and 9-isopropyl-9,10-dihydroanthracene may proceed *via* an organocadmium intermediate. Indeed, the essentially quantitative formation of the 9-*tert*-butyl dimer renders this course more likely than dimerization of radical intermediates initially formed through one-electron transfer. In like manner, 1,2-dehydrogenation of the 9,10-dialkyl derivatives of dihydroanthracene, *i.e.*, **5**, may involve intermediacy of an organocadmium compound, decomposition of which with β elimination of hydrogen would furnish the methylene compounds **6**. These questions have not been pursued, since they lie outside the scope of our research objectives.

$$A^{2-} + Cd^{II} \longrightarrow [A\ Cd] \longrightarrow A + Cd^{0}$$

The structure of the dimeric products **4a** and **4b** appears to be unusual and of interest in view of the controversy surrounding the conformation of 1,4-cyclohexadiene ring systems. The conformational preference of the parent hydrocarbon (planar *vs.* flattened boat), despite numerous investigations,[27] remains unsettled. On the other hand, 9,10-dihydroanthracene is thought to be nonplanar and to undergo rapid ring inversion (nmr time scale) even at very low temperatures.[28] The 9-alkyl-9,10-dihydroanthracenes (**8**) have been shown in a recent nmr study[12] involving long range coupling constants and nuclear Overhauser effects to exist preferentially in a boat conformation (**8a**) with the substituent group in the axial orientation.[29] This conformational preference appears largely a consequence of steric interaction with the adjacent hydrogen atoms in the peri positions.[17] The *cis*-9,10-dialkyl-9,10-dihydroanthracenes, though less thoroughly studied, also appear to exist in a preferred diaxial conformation;[17] on the other hand, the trans isomers apparently either undergo rapid ring inversion, or the central ring is essentially flat, since distinct benzylic coupling constants for axial and equatorial protons are not detected over a wide temperature range.[17,31] These preferred conformations may, however, be altered in response to steric effects. Thus steric interaction between bulky 9,10-diaxial groups or between groups in the 9,10 and 1,4 positions leads to restricted rotation[21,33] and possible flattening of the ring system and/or distortion of ring geometry.



8a **8b**

The 9-*tert*-butyl-9,10-dihydroanthracene dimer **4b** is tentatively assigned the trans,trans structure on the following basis. The monomer **8a** (R = *tert*-Bu) is known to exist in the boat conformation bearing the *tert*-butyl substituent in the axial orientation.[12] Combination of two such monomeric units in the unsubstituted positions can take place in three possible ways to form cis,cis, cis,trans, or trans,trans structures. The cis,cis isomer contains in both rings a 9-*tert*-butyl-9,10-dihydroanthracenyl group in one axial position and a *tert*-butyl group in the other, the bulky nature of which would be expected to prevent free rotation of either group. As a consequence, a difference in chemical shift between methyl groups above the rings and the other methyl groups might, therefore, be expected. However, the nmr spectrum (Figure 1) of **4b** exhibited

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(26) Facility of addition of electrons in ammonia is a consequence of factors which include: (1) ease of formation of solvated electrons in this medium; (2) stabilization of intermediates through ion pairing; and (3) shift of equilibria through protonation by ammonia.[25]

(27) E. W. Garbisch, Jr., and M. G. Griffith, *J. Amer. Chem. Soc.*, **90**, 3590 (1968); D. J. Atkinson and M. J. Perkins, *Tetrahedron Lett.*, 2335 (1969); J. L. Marshall, K. C. Erickson, and T. K. Folsom, *J. Org. Chem.*, **35**, 2038 (1970), and references therein.

(28) W. B. Smith and B. A. Shoulders, *J. Phys. Chem.*, **69**, 2022 (1965).

(29) Earlier nmr studies using the cyclohexane (chair form) as a model for the central ring led some authors[30] to assign erroneously the alternative structure (**8b**; R = equatorial) to the favored conformation. The designations axial and equatorial are used in this paper in preference to the terms pseudoaxial and pseudoequatorial, since the simpler terminology appears to offer no disadvantage.

(30) W. Carruthers and G. Hall, *J. Chem. Soc. B*, 861 (1966); D. Nicholls and M. Szwarc, *J. Amer. Chem. Soc.*, **88**, 5757 (1966); *Proc. Roy. Soc., Ser. A*, **301**, 231 (1967).

(31) P. W. Rabideau and R. G. Harvey, unpublished results.

(32) R. H. Williams and H. R. Snyder, *J. Org. Chem.*, **36**, 2327 (1971).

(33) P. W. Rabideau and J. W. Paschal, *J. Amer. Chem. Soc.*, **94**, 5801 (1972).

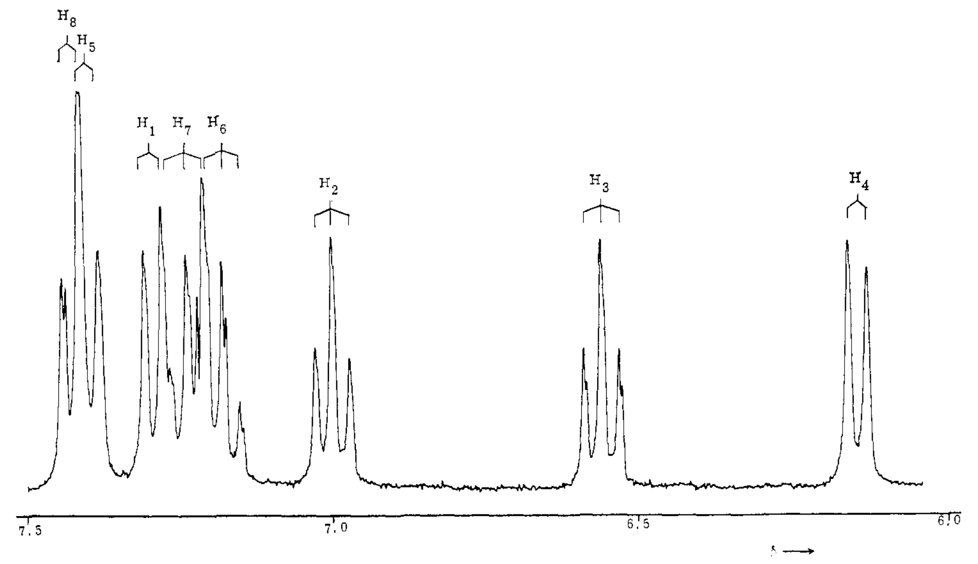
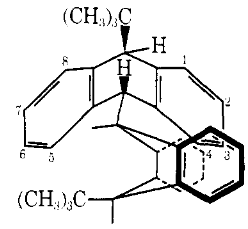


Figure 1. Aromatic region of 270-MHz nmr spectrum of dimer **4b** in $CDCl_3$.

only a single sharp singlet at δ 1.13 for the methyl protons making the cis,cis structure improbable. Also, the nmr spectrum of **4b** shows two pairs of aromatic protons at usually high field (δ 6.16, d, J = 7.5 Hz; δ 6.57, t, J = 7.5 Hz) which cannot be accounted for by the highly symmetrical cis,cis structure. The cis,trans structure may also be excluded on the basis of the similar restricted rotation of the *tert*-butyl group; also, the inner α-hydrogen atoms are subject to extreme steric crowding, rendering this structure highly improbable. On the other hand, the trans,trans structure offers relative freedom of rotation of both *tert*-butyl groups and minimum steric crowding in a unique twisted conformation in which one ring system is in an approximately vertical plane with respect to the other. If, as anticipated, both ring systems are nonplanar, the inner α-hydrogen atoms on each ring should be of two types, the one under and close to the aromatic rings of the other component, the other held above and further away from the aromatic π electrons. The observation of two pairs of aromatic protons at high field is in accord with this structure, the higher field signal corresponding to the α protons under the aromatic rings (H_4, H_4); the observed coupling constant J_{34} = 7.5 Hz is in the normal range for ortho coupling.[34]



4b

Detailed analysis of the aromatic region of the 270-MHz nmr spectrum of **4b** aided by spin decoupling permitted essentially complete assignment of all peaks (Table I). Saturation of the high field doublet at δ 6.16 (H_4, $H_{4'}$) resulted in collapse of the triplet (J = 7.5 Hz) at δ 6.57 (H_3, $H_{3'}$) into a doublet, while irradiation of the latter led to collapse of the high field doublet to a singlet and the triplet (J = 7.5 Hz) at δ 7.00 (H_2, $H_{2'}$) to a doublet. In further agreement with these assignments, saturation of the triplet at δ 7.00 (H_2, $H_{2'}$) simplified the triplet at δ 6.57 to a doublet and the doublet at δ 7.29 to a singlet (not sharp), indicative of the expected loss of coupling with the H_3, $H_{3'}$ and H_1, $H_{1'}$ protons (J_{12} = J_{23} = 7.5 Hz), respectively. While further decoupling experiments were complicated by the closeness of the peaks concerned, the results were also consistent with the assigned structure.

Table I. Nmr Spectral Data of Dimer **4b**

Proton[a]	δ[b]	Multiplicity	J
1	7.29	d	7.5
2	7.00	t	7.5
3	6.57	t	7.5
4	6.16	d	7.5
5[c]	7.38	d	7.5
6[c]	7.17	t	7.5
7[c]	7.23	t	7.5
8[c]	7.42	d	7.5
9	3.90	s	
10	5.52	s	

[a] Since the two halves of the dimer molecule are identical, the corresponding protons (H_1, H_1, etc.) are chemically equivalent. [b] Chemical shifts are in ppm relative to TMS in deuteriochloroform. [c] The higher field component of the pair of overlapping doublets derived from H_5 and H_8 is tentatively assigned to H_5 on the basis of the shielding expected due to its position over the aromatic ring system. The H_6 and H_7 protons are tentatively assigned on similar grounds.

The major dimeric product obtained from analogous reaction of 9-isopropyl-9,10-dihydroanthracene (**3a**) is assigned the *trans,trans*-10,10′-diisopropyl-9,9′,10,10′-tetrahydro-9,9′-bianthracenyl structure (**4a**) on similar grounds.

Experimental Section

Physical Data. Proton nmr spectra were obtained on Varian T-60 and Brucker 270-MHz spectrometers; chemical shifts are reported relative to TMS in $CDCl_3$ or CCl_4. Integration was consistent with all assignments. Mass spectra were determined on a Finnigan 1015 mass spectrometer at 70 eV, except the deuterium analyses for which 8–10 eV were employed. Gas chromatographic analyses were performed on a F&M Model 500 chromatograph employing a 6 ft × 0.25 in. 10% SE-30 60–80 mesh Chromosorb W column.

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(34) K. D. Bartle and D. W. Jones, *Advan. Org. Chem.*, **8**, 317 (1972).

Materials. Cyclohexane, tetrahydrofuran, and TMEDA were dried over lithium aluminum hydride and redistilled. *n*-Butyllithium (15% in hexane) was obtained from Apache Chemicals. Cadmium chloride was dried *in vacuo* at 100° overnight and stored in air-tight vials.

9-Alkyl-9,10-dihydroanthracene (1c, 1d, 3a,b). The method to be described provides cleaner products than the procedure reported earlier[19] and is, we suggest, the method of choice for synthesis of analogous compounds. In a typical reaction a solution of *n*-butyllithium (52.5 mmol) in hexane was added to a stirred solution of 9,10-dihydroanthracene (9 g, 50 mmol) in dry THF (200 ml) at −33° under a helium atmosphere. The resulting solution was maintained at this temperature for 30 min, then cooled to −78° and stirred an additional 30 min. A stream of gaseous methyl bromide was then introduced rapidly (through a tube of Ascarite) into the solution over a 3-min period and then the reaction quenched by addition of solid NH_4Cl (20 g). Addition of water and ether and followed by conventional work-up afforded **1c** (9.55 g), shown by glpc (150°) and nmr analysis in comparison with authentic compound[17] to be essentially pure.

Analogous alkylation of **1a** at 0° furnished **1c** (74%) contaminated with both unreacted **1a** and the 9,10-dimethyl homolog **1e**. Alkylation of **1a** in THF–ammonia at −33° afforded a higher proportion of **1c** (84%), while similar reaction at −78° provided virtually pure **1c** (98%). Thus, temperature appears to be a major factor determining the extent of alkylation, with lower temperature inhibiting reaction beyond the desired stage.

Similar reaction of the 9,10-dihydro-9-anthracenyl carbanion generated in THF at −33° with ethyl and isopropyl bromide (25 mmol diluted to 25 ml in THF) at −78° provided **1d** (98%), and **3a** (98%), respectively.

9,10-Dialkyl-9,10-dihydroanthracene (1b,e,f, 5a–c). The 9-ethyl-10-methyl and *cis*-9,10-diethyl compounds (**1b**,**f**) were synthesized through addition of ethyllithium to anthracene in THF at 0° followed by alkylation of the resulting anion with the appropriate alkyl halide.[18,19]

The 9-methyl-10-isopropyl-, 9-ethyl-10-isopropyl-, and 9,10-diisopropyl-9,10-dihydroanthracenes (**5a–c**) were obtained through alkylation of **3a** with *n*-butyllithium and the appropriate alkyl bromide under the conditions described above for monoalkylation of **1a**. Analogous methylation of **1c** afforded the dimethyl compound **1e**. Yields in all cases exceeded 80%. The crude products were recrystallized from ethanol, and purity established by glpc and nmr in comparison with the authentic compounds before use in subsequent reactions.

Dehydrogenation of 9-Alkyl- and 9,10-Dialkyl-9,10-dihydroanthracenes (1a–f). In a typical experiment, a solution of *n*-butyllithium (20 mmol) in hexane was introduced by syringe into a solution of **1b** (5 mmol) in dry cyclohexane (30 ml) and TMEDA (15 ml) and the resulting deep red solution of the monoanion brought to reflux, whereupon the color changed to the intense purple characteristic of the dianion. After 1 hr at reflux, the mixture was allowed to cool (5 min) and the color discharged by the addition of anhydrous cadmium(II) chloride (10 mmol). The product, isolated by conventional extraction procedures, was 9-ethyl-10-methylanthracene (**2b**) (99%). Analogous reaction of 9,10-dihydroanthracene or its 9-methyl, 9-ethyl, 9,10-dimethyl, or 9,10-diethyl derivatives proceeded similarly to afford the related anthracenes **2a**,**c–f** in similar high yield. The structures of all the foregoing compounds were confirmed by nmr and glpc analysis in comparison with the authentic compounds.[17]

Dehydrogenation of 9-*tert*-Butyl-9,10-dihydroanthracene (3b). To a solution of **3b** (0.59 g, 2.5 mmol) in cyclohexane (15 ml) and TMEDA (7.5 ml) was added a solution of *n*-butyllithium (10 mmol) in hexane. The resulting solution retained the reddish brown color of the monoanion during heating under reflux for 1 hr. The heat was removed, the solution allowed to cool for 5 min, and then $CdCl_2$ (0.91 g, 5 mmol) was added. The mixture was stirred for an additional 30 min, then water added and the product extracted with ether. The ethereal solution was washed with water, dried over $MgSO_4$, and evaporated to provide the trans,trans dimer **4b** of 9-*tert*-butyl-9,10-dihydroanthracene (0.53 g). Recrystallization twice from benzene provided the analytical sample (0.47 g), mp 211–212°, nmr described in the main body of the paper.

Anal. Calcd for $C_{36}H_{38}$: C, 91.86; H, 8.14. Found: C, 91.91; H, 8.06.

Analogous reaction employing a 1:1 molar ratio of the hydrocarbon **3b** to the lithium reagent resulted in only 30% conversion to the dimer **4b**. Attempted further dehydrogenation of the dimer by the same method was unsuccessful.

Dehydrogenation of 9-Isopropyl-9,10-dihydroanthracene (3a). Analogous dehydrogenation of **3a** (2.22 g, 10 mmol) under the standard conditions gave a pale brown crystalline powder, trituration of which with ether (20 ml) provided an insoluble solid (0.63 g) and an ether-soluble fraction. Evaporation of the latter furnished an oil (1.6 g), shown by nmr to consist principally of 9-isopropylanthracene and the trans,trans and cis,trans dimers, **4a**. Crystallization of the oil from petroleum ether gave two kinds of crystals which were separated mechanically. The slightly yellow crystals were recrystallized from chloroform–ethanol to give flower-like bundles of colorless needles of *trans,trans*-**4a** (0.56 g): mp 287–288°, nmr (CCl_4) δ 1.09 (d, 12, J = 6.5 Hz, CH_3), 1.7–2.5 (m, 2, $(CH_3)_2CH$), 3.63 (d, 2, J = 9 Hz, CH-9, 9′), 5.31 (s, 2, CH-10, 10′), and 6.3–7.4 ppm (m, 16, aromatic). *Anal.* Calcd for $C_{34}H_{34}$: C, 92.29; H, 7.71. Found: C, 92.11; H, 7.86. The other crystals, white clumps, were recrystallized from benzene to yield the *cis,trans*-**4a** (60 mg): mp 285–292° (disappeared on heating); nmr (CCl_4) δ 1.15 (d, 6, J = 6.5 Hz, CH_3), 1.51 (d, 6, J = 7 Hz, CH_3), 1.4–2.2 (m, 1, $(CH_3)_2CH$), 2.9–3.6 (m, 1, $(CH_3)_2CH$), 3.37 (d, 1, J = 9 Hz, CH-9), 4.0–4.2 (broad base with a singlet at 4.07, 3, CH-10, 10′ and CH-9), 6.05 (d, 2, J = 7 Hz, α aromatic), 6.3–7.3 (m, 12, aromatic), and 7.52 (d, 2, J = 7 Hz, α aromatic). *Anal.* Calcd for $C_{34}H_{34}$: C, 92.29; H, 7.71. Found: C, 92.07; H, 7.89. The ether-insoluble portion (0.63 g) a slightly yellow crystalline powder, which consisted of *cis,trans*-**4a** and *cis,cis*-**4a** in a molar ratio of 1.3:1 as indicated by nmr integration, was treated with warm ether (100 ml). The insoluble pale yellow crystalline powder (0.38 g) which was rich in *cis,cis*-**4a** was recrystallized three times from benzene to give shining colorless plates of pure *cis,cis*-**4a** (50 mg): mp 290–293° (fast heating); nmr ($CDCl_3$) δ 1.25 (d, 12, J = 6.5 Hz, CH_3), 1.9–2.6 (m, 2, $(CH_3)_2CH$), 1.53 (d, 2, J = 11 Hz, CH-9, 9′), 4.11 (s, 2, CH-10, 10′), 6.23 (d, 4, J = 7.5 Hz, α aromatic), and 6.7–7.4 ppm (m, 12, aromatic other than α protons). *Anal.* Calcd for $C_{34}H_{34}$: C, 92.29; H, 7.71. Found: C, 92.24; H, 7.70. The overall yields of the products based on nmr integration at the various stages of the separation procedure were estimated to be 9-isopropylanthracene (20%), *trans,trans*-**4a** (36%), *cis,trans*-**4a** (22%), *cis,cis*-**4a** (12%), and unidentified products (10%).

Dehydrogenation of *cis*-9-Isopropyl-10-methyl-9,10-dihydroanthracene (5a). Analogous reaction of **5a** (0.59 g, 2.5 mmol) under the standard conditions provided an oil (0.59 g). Glpc (150 and 180°) and nmr analysis indicated, in addition to recovered **5a** (8% plus a trace of the trans isomer) and 9-isopropyl-10-methylanthracene (5%), a major product (63%) assigned the structure 9-isopropyl-10-methylidene-9,10-dihydroanthracene (**6a**). The latter, collected off the glpc (slightly contaminated with *trans*-**5a**), exhibited characteristic nmr peaks (CCl_4) δ 0.75 (d, 6, J = 7 Hz, CH_3), 3.59 (d, 1, J = 6 Hz, CH-9), 5.58 (s, 2, $=CH_2$), and 7.0–7.7 ppm (m, 8, aromatic).

Isomerization of the above crude reaction product was accomplished in refluxing toluene (100 ml) in the presence of *p*-toluenesulfonic acid (1 g) for 2 hr. Conventional work-up provided a brown solid (0.57 g) shown by glpc analysis, cross-checked by nmr to contain 9-isopropyl-10-methylanthracene (70%). Chromatography on neutral alumina (5 g) and elution with petroleum ether, followed by crystallization from petroleum ether, provided pure 9-isopropyl-10-methylanthracene: mp 98–99°; nmr (CCl_4) δ 1.74 (d, 6, J = 7.5 Hz, $(CH_3)_2CH$), 3.03 (s, 3, CH_3), 4.54 (heptet, 1, J = 7.5 Hz, CH), 7.20–7.50 (m, 4, aromatic), and 8.1–8.5 ppm (m, 4, aromatic).

Anal. Calcd for $C_{18}H_{18}$: C, 92.96; H, 7.74. Found: C, 92.30; H, 7.60.

Methylation of the 5a Anionic Intermediate. Similar reaction of **5a** with substitution of methyl iodide (5 ml) for the cadmium salt afforded an oily product, glpc (180°) and nmr analysis of which showed 9,9-dimethyl-10-isopropyl-9,10-dihydroanthracene **7** (97%). Chromatography on silica gel eluted with hexane gave pure **7** as a colorless oil: nmr (CCl_4) δ 0.78 (d, 6, J = 7 Hz, $(CH_3)_2CH$), 1.65 (s, 3, CH_3 cis to isopropyl), 1.69 (s, 3, CH_3 trans), 1.40–2.20 (m, 1, $(CH_3)_2CH$), 3.72 (d, 1, J = 5.5 Hz, benzylic), and 7.00–7.60 ppm (m, 8, aromatic).

Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.25; H, 8.70.

Dehydrogenation of 9-Isopropyl-10-ethyl-9,10-dihydroanthracene (5b). Analogous reaction of a mixture of *cis*- and *trans*-**5b** (0.63 g, 2.5 mmol) under the standard conditions provided an oil (0.64 g). Glpc (150 and 180°) and nmr analysis indicated, in addition to recovered **5b** (48% as cis isomer) and 9-isopropyl-10-ethylanthracene (10%), a major product assigned the structure 9-isopropyl-10-ethylidene-9,10-dihydroanthracene (**6b**) (42%). The latter structure was based on the nmr spectrum of the crude reaction product which showed a quartet at δ 6.09 (J = 7.5 Hz, vinylic) and a doublet at δ 2.12 ppm (J = 7.5 Hz, $CH_3CH{=}$) and formation of 9-isopropyl-10-ethylanthracene from acid-catalyzed rearrangement of the crude product. Isomerization took place under the conditions employed in the preceding example to afford a crude product (0.61 g) shown by glpc and nmr to contain 9-isopropyl-10-ethylanthracene (40%). Chromatography on alumina followed by crystallization from petroleum ether gave pure 9-isopropyl-10-ethylanthracene: mp 110–111°; nmr (CCl_4) δ 1.45 (t, 3, J = 7.5 Hz, CH_3CH_2), 1.75 (d, 6, J = 7.5 Hz, $(CH_3)_2CH$), 3.59 (q, 2, J = 7.5 Hz, CH_3CH_2), 4.53 (heptet, 1, J = 7.5 Hz, $(CH_3)_2CH$), 7.1–7.5 (m, 4, aromatic), and 8.1–8.5 ppm (m, 4, aromatic).

Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.81; H, 8.23.

Dehydrogenation of *trans*-9,10-Diisopropyl-9,10-dihydroanthracene (*trans*-5c). Similar reaction of *trans*-**5c** (0.66 g, 2.5 mmol) gave a crystalline product (0.65 g) shown to contain two components, *cis*-**5c** and 9-isopropyl-10-isopropylidene-9,10-dihydroanthracene (**6c**), in the ratio of 2:1 by nmr analysis in comparison with the authentic compounds.[35]

Epimerization of *trans*-5c to *cis*-5c. Similar reaction of *trans*-**5c** with the substitution of water (5 ml) for the cadmium salt afforded a product shown by nmr analysis to contain >95% *cis*-**5c**. Recrystallization from petroleum ether gave colorless crystals (0.55 g) of pure *cis*-**5c**: mp 114.5–115.5° (lit.[20,21] 116.5–117° and 109–110°); nmr (CCl_4) δ 0.99 (d, 12, J = 6 Hz, $(CH_3)_2CH$), 1.40–2.10 (m, 2, $(CH_3)_2CH$), 3.30 (d, 2, J = 9.5 Hz, benzylic), and 7.06 ppm (apparent s, 8, aromatic).

Acknowledgment. This research was supported by U. S. Public Health Service Grant CA 11968. The technical assistance of Mrs. Leticia Nazareno in the early part of this work is also gratefully acknowledged.

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(35) In an earlier report[17b] from this laboratory the *cis*-**5c** structure was assigned to the product of reductive diisopropylation of anthracene with lithium and isopropyl chloride in liquid ammonia in analogy with the cis product shown to be obtained from reductive diethylation. However, it is now clear that the *trans*-**5c** structure is correct on the basis of the comparative nmr spectral analysis of both isomers by Zieger, *et al.*,[21] and by Redford.[20] The *trans*-**5c** isomer is also furnished in high yield from reduction of 9,10-diisopropylanthracene with lithium in ammonia by the procedure reported earlier.[17a]

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XIII. Di-*tert*-butylmethyl and Related Radicals[1]

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Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada, and Department of Chemistry, University of Toronto, Scarborough College, West Hill, Ontario. Received September 20, 1973

Abstract: Di-*tert*-butylmethyl, $B_2\dot{C}H$, and a wide variety of related radicals, *e.g.*, $B_3\dot{C}$, $B_2\dot{C}CH_2C_6H_5$, $B_2\dot{C}CH_2P(O)(OEt)_2$, etc., are extremely long lived when compared with less highly substituted alkyl radicals. They show no sign of dimerizing even at low temperatures. At ambient temperatures these radicals decay with first-order kinetics and Arrhenius parameters for these reactions are reported. The decay mechanism could not be unequivocally established but it is believed to be either a β scission (*e.g.*, $B_2\dot{C}H \rightarrow B(H)C{=}CMe_2 + Me\cdot$) or a 1,3-intramolecular hydrogen atom transfer (*e.g.*, $B_2\dot{C}H \rightarrow BCH_2CMe_2\dot{C}H_2$). At low temperatures most $B_2\dot{C}CH_2R$ radicals decay with second-order kinetics, presumably yielding the disproportionation products, B_2CHCH_2R and $B_2C{=}CHR$.

It has recently been shown that nonconjugated carbon-centered radicals having bulky alkyl groups attached to the radical center possess remarkably long lives.[4] For example,[4] a 10^{-5} *M* solution of di-*tert*-butylmethyl prepared by hydrogen abstraction, by *tert*-butoxy, from the parent hydrocarbon has a half-life of about a minute at room temperature.[5] We now report in more detail on the decay kinetics of this radical and on the decay of a number of structurally related radicals containing the di-*tert*-butylmethyl moiety.

In this paper B is used to represent the *tert*-butyl group.

Experimental Section

The general experimental technique has been adequately described in previous papers from this laboratory.[1,4,6]

Radical Generation. With one exception (*vide infra*), kinetic studies were carried out on radicals (R·) generated photolytically, directly in the cavity of a Varian E-3 epr spectrometer. The following methods were used.

A. Photolysis of a di-*tert*-butyl peroxide (BOOB) solution of RH.

$$\mathrm{BOOB} \xrightarrow{h\nu} 2\mathrm{BO}\cdot$$

$$\mathrm{BO}\cdot + \mathrm{RH} \longrightarrow \mathrm{BOH} + \mathrm{R}\cdot$$

B. Photolysis of a mixture of hexamethylditin and RCl.

$$\mathrm{Me_3SnSnMe_3} \xrightarrow{h\nu} 2\mathrm{Me_3Sn}\cdot$$

$$\mathrm{Me_3Sn}\cdot + \mathrm{RCl} \longrightarrow \mathrm{Me_3SnCl} + \mathrm{R}\cdot$$

C. Photolysis of a mixture of BOOB, a trialkylsilane (generally Me_3SiH), and RCl.

$$\mathrm{BO}\cdot + \mathrm{Me_3SiH} \longrightarrow \mathrm{BOH} + \mathrm{Me_3Si}\cdot$$

$$\mathrm{Me_3Si}\cdot + \mathrm{RCl} \longrightarrow \mathrm{Me_3SiCl} + \mathrm{R}\cdot$$

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[1] Issued as N.R.C.C. No. 13,899. Part XII: D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 554 (1973).

[2] (a) N.R.C.C. Postdoctoral Fellow, 1971–1973. (b) N.R.C.C. Postdoctoral Fellow, 1973–1974.

[3] University of Toronto.

[4] G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 3422 (1973).

[5] In contrast, similar concentrations of less hindered carbon-centered radicals decay completely in a few milliseconds.[6]

[6] See, *e.g.*, G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 491 (1972).

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