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REACTIONS OF ANTHRACENE ANIONS WITH BERYLLIUM CHLORIDE

CARL M. BERKE and ANDREW STREITWIESER, JR

Department of Chemistry, University of California, Berkeley, CA 94720 (U.S.A.)

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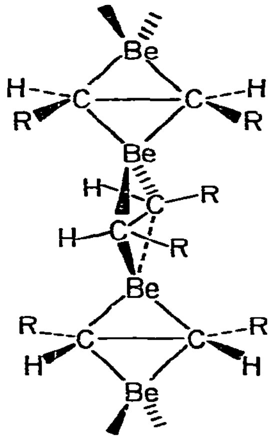
Summary

Reaction of anthracene radical anion with $BeCl_2$ in THF gives a crystalline polymeric organometallic compound that yields 9,9′,10,10′-tetrahydro-9,9′-bianthryl (THBA) on hydrolysis. Hydrolysis with D_2O gives exclusively *trans*-10-*d*, *trans*-10′-*d* hydrocarbon. Reaction of anthracene dianion with $BeCl_2$ in THF leads to cleavage of the solvent and formation of *cis*-9,10-dihydro-9,10-bis(4-hydroxybutyl)anthracene. Comparable reactions of cyclooctatetraene dianion are also discussed. The results point up the covalence of the carbon—beryllium bond.

Introduction

Beryllium chemistry provides a potentially rich lode of new chemistry since the area is relatively unexplored compared to its less toxic counterparts in the alkaline earth series. Most of what is known about organoberyllium compounds comes from the laboratories of Coates who has concentrated on the preparation and properties of the σ-complexes such as alkoxy, alkyl, amido, and mixed halide species [1]. Since the original preparation of beryllocene (dicyclopentadienylberyllium) [2], there has been an ongoing controversy concerning the structure of the complex [2]. The dual character of the metal coordination suggested interesting possibilities for extended arrays of carbon—beryllium π-bonding as in the polymer structure I. However, aside from beryllocene, the only other evidence for beryllium π-bond character comes from the X-ray structure of bis(di-t-butylmethyleneamido)beryllium dimer, which shows the shortest Be—N bond length yet reported [4].

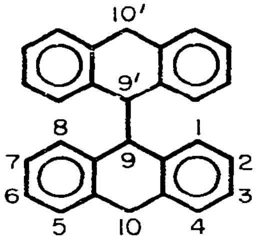
Anthracene was chosen as a prospective π ligand for bonding with the metal at the 9,10 positions. The symmetry of the dianion HOMO allows for stabilizing interaction of the low-lying in-plane *p*-orbitals of beryllium with the 9,10 positions of anthracene.in a manner similar to the bonding schemes proposed for beryllocene [5]. The dianion is a strong reducing agent that tends to reduce transition metal ions rather than form π-complex compounds with them. However, as an alkaline earth metal, Be^{2+} is expected to be more resistent to reduction. The experimental results were interesting and unexpected.



I

Reaction of anthracene radical anion with beryllium chloride

When lithium anthracene (radical anion) was allowed to react with solid beryllium chloride in THF, a yellow, non-volatile, insoluble, air-sensitive solid precipitated after several hours of stirring in the glove box. Subsequent Soxhlet extraction with THF removed the lithium chloride to leave approximately 20% yield of a product whose physical properties made thorough characterization difficult. Even strongly chelating solvents such as TMEDA and HMPA did not dissolve the complex. An X-ray powder pattern of the complex showed it to be microcrystalline and to contain no lines that could be indexed to starting materials. Elemental analysis showed the presence of beryllium but the overall stoichiometry was unsatisfactory, even after prolonged heating in high vacuum to remove solvent and catalyzed combustion with vanadium pentoxide.



II

Fig. 1. 9,9′-10,10′-Tetrahydro-9,9′-bianthryl (II). ^1H NMR, δ (TMS) ($CDCl_3$): 7.2—6.7 (16H, m, aromatic), 4.40 (2H, s, H(9,9′)), 3.36, 2.34 ppm (4H, dd, AB, *J* 19 Hz, H(10, eq), H(10, ax)). ^{13}C NMR: δ (TMS) ($CDCl_3$, ^1H, decoupled): 137.9 (q), 136.6 (q), 128.9, 127.2, 126.3, 125.5, 55.7 (C(9), C(9′)), 34.5 ppm (C(10) C(10′)).

Recourse was made to indirect characterization, principally through hydrolysis. Hydrolysis was performed by suspending a sample of the complex in an organic solvent and adding degassed water by syringe to the cold, stirred slurry. The reaction was over quickly, and the white insoluble beryllium hydroxide (or hydrated oxide) was filtered. Organic material was isolated as a white crystalline solid which was identified as 9,9',10,10'-tetrahydro-9,9'-bianthryl (II, THBA) (Fig. 1) by comparison with an authentic sample [6]. A significant feature of this hydrocarbon is that it gives no molecular ion in mass spectroscopy, even at low voltage and by chemical ionization mass spectroscopy, but does give a base peak for anthracene cation.

Conformation of THBA

The AB pattern in the proton NMR spectrum was checked by spin decoupling. The broadness of the AB signals is due to homoallylic and other unresolved long-range couplings, in accordance with the NMR data of Harvey and coworkers [7]. The benzylic positions of 9,10-dihydroanthracene contain two conformationally distinct types of bonds, designated as pseudoaxial and pseudoequatorial, which are interconvertible via "boat-to-boat" ring inversion [7f]. The expected non-equivalence in the pseudoaxial and pseudoequatorial orientation is evident by the significant difference in the chemical shift of the methylene doublets ($\Delta\delta = 1.0$ ppm; cf. 9-alkyl-9,10-dihydroanthracenes: $\Delta\delta = 0.2$—0.5 ppm) [7]. Absence of "time-averaging" of the resonance signals is interpreted as due to conformational rigidity. Harvey and co-workers have concluded that large 9-alkyl substituents in a series of 9-alkyl-9,10-dihydroanthracenes exist exclusively in the pseudoaxial position of the boat shaped central cyclohexadiene to minimize peri-interactions with the benzo rings. We assume by analogy that in II the rings are pseudoaxial with respect to each other. Several X-ray crystal structures of substituted dihydroanthracenes have confirmed the preference of 9 and 10 substituents for the pseudoaxial conformation [8].

Structure of the organoberyllium polymer

A deuterium labelling experiment was done to aid in the structure elucidation of the beryllium complex. Hydrolysis of the complex with D_2O yielded II-d_2 in which the downfield doublet of the AB set collapsed to a broad singlet in the ^1H NMR and the upfield doublet disappeared (Fig. 2). These changes are significant since they show that incorporation of deuterium has occurred and is stoichiometric as well as stereospecific. Harvey et al. [7a] have found that in 9-alkyl-9,10-dihydroanthracenes the pseudoequatorial protons generally resonate at higher field than their pseudoaxial partners; since the NMR spectrum of the deuterated II shows that the upfield methylene protons are replaced by deuterium, the deuteriums are assigned as pseudoequatorial. DDQ oxidation of the deuterated II yielded anthracene-9-d_1 indicating incorporation of one deuterium into each half of II. Although not by itself definitive, it is certainly consistent with this assignment that mass spectroscopy of II-d_2 shows a strong base peak for anthracene-d_1 cation. This result suggests a facile decom-

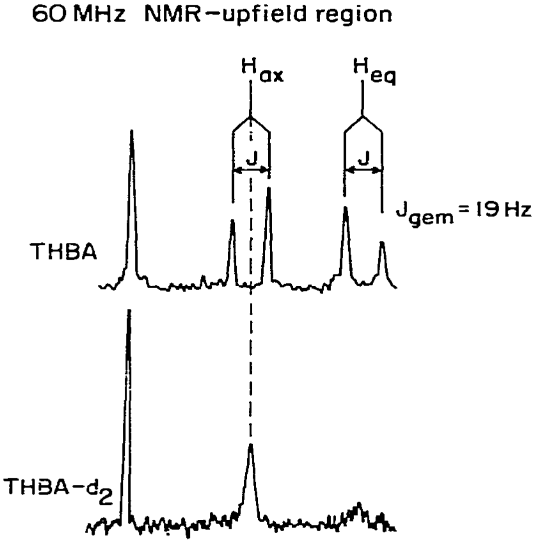


Fig. 2. A portion of the NMR spectrum of II (THBA) and its deuterated derivatives; H_{ax} and H_{eq} are δ 3.36 and 2.34 ppm, respectively.

position of the cation of II on electron impact in a Woodward—Hoffmann allowed manner to give anthracene cation and 9,10-dihydroanthracene. This interpretation also requires a trans orientation of the 9-substituent and 10-deuterium as in our assigned structure. With this assignment, the C(9) and C(10) peaks of the ^{13}C NMR spectrum can now also be assigned based on the observation that only the upfield sp^3 carbon is split by deuterium.

The high stereospecificity of the protonation reaction of the complex strongly suggests a simple S_E2 hydrolysis with retention *. Nicholls and Szwarc [10] report that no deuterium is incorporated into the phenyl ring when alkyldihydroanthracyl anions are quenched with D_2O. There is evidence in the literature [11] that stereoselective protonation of 10-t-butyl-9-lithio-9,10-dihydroanthracene is governed by the solvation of the associated cation. Contact ion pairs appear generally to direct frontside attack to avoid excessive separation of oppositely charged ions. The NMR assignment of pseudoequatorial-deuterium in the structure of II-d_2 combined with the assumed hydrolysis stereochemistry provide a consistent structural hypothesis for the beryllium-anthracene polymer as illustrated in Fig. 3.

A monomeric structure such as shown in Fig. 4 is less probable because only the pseudoaxially deuterated species would result on deuterolysis. Most alkyl-

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* Hydrolysis of carbanions generally involves ion pair reactions with predominant net retention of configuration [9a]. Studies of hydrolysis stereochemistry of various organometallic compounds are not common but have invariably shown net retention of configuration [9b]. To these several examples of stereochemistry of protonolysis of organometallic compounds we can add that reaction of *endo*-norbornylmagnesium halide [9c] with D_2O gives norbornane-*endo*-2-*d* [9d]. The possibility that such retention actually results from two inversions of configuration is, of course, not rigorously excluded, but has no reasonable analogies and would appear to have exceedingly low probability.

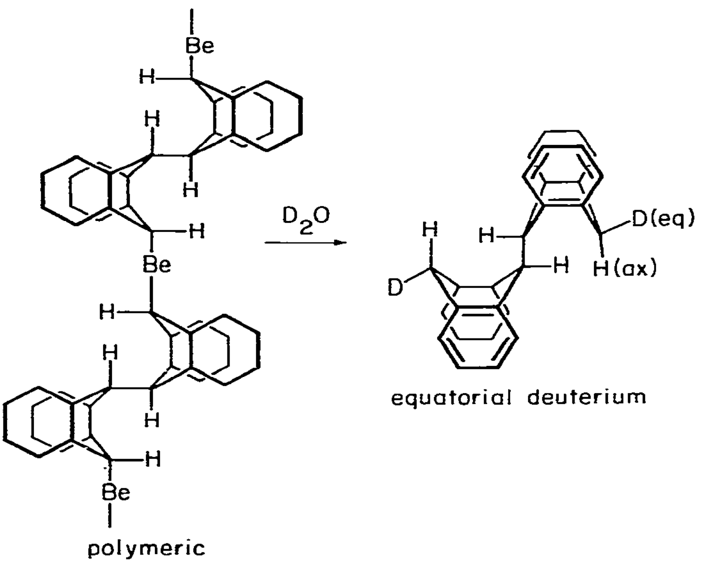


Fig. 3. Hypothesized structure of the beryllium polymer and its hydrolysis with D_2O.

beryllium compounds are oligomeric or highly polymeric with bridging ligands in order to satisfy the Lewis octet. Only sterically bulky groups such as t-butyl force the complex to adopt an unbridged linear 2-coordinate structure similar to Fig. 3 [12]. Additional coordination is probably satisfied by loosely bound THF and would account for non-stoichiometric elemental analysis.

THF cleavage reactions

When lithium anthracenide is allowed to react with $BeCl_2$, but in the absence of excess anthracene, the product obtained is similar in appearance and physical properties to the bianthryl complex. However, the hydrolysis product of the resulting insoluble beryllium polymer is a crude oil. Kugelrohr distillation followed by crystallization from chloroform/hexane yielded white platelets. Mass spectroscopy of this hydrolysis product showed a small parent ion for a dialkylated species, 9,10-bis(4-hydroxybutyl)-9,10-dihydroanthracene (III), which readily cleaves both benzylic side chains to result in a base peak corresponding to the molecular weight of anthracene. The NMR, IR, and elemental analysis all support this structural assignment.

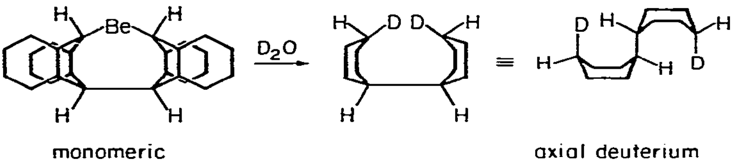
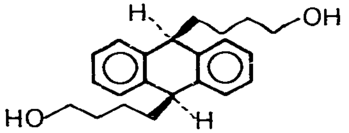


Fig. 4. Hydrolysis of a cyclic monomeric beryllium structure leads to a different II-d_2. Some benzo rings have been omitted for clarity.



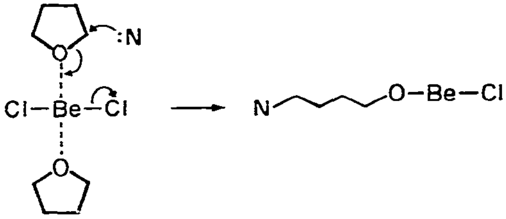


Fig. 5. 9,10-Bis(4-hydroxybutyl)-9,10-dihydroanthracene (III). ^{1}H NMR, δ(TMS) ($CDCl_3$): 7.22 (s, phenyl, 8H), 3.86 (t, benzylic, 2H), 3.58 (t, CH_2OH, 4H), 2.1 (s, OH, 2H), 1.62 ppm (m, methylene, 12H). ^{13}C NMR, δ(TMS) ($CDCl_3$): 139.9 (q), 128.7, 126.0, 62.7, 46.6, 42.2, 32.8, 24.7 ppm.

Fig. 6. Ether cleavage assisted by $BeCl_2$.

The structure was verified by conversion of the diol to 9,10-di-n-butyl-9,10-dihydroanthracene by hydride reduction of the dimesylate derivative. Comparison with NMR data of Harvey et al. [7b] shows the key feature of the singlet aromatic peak characteristic of *cis* substitution (Fig. 5). We note that alkylation of anthracene dianion with primary alkyl halides is also reported to yield the *cis* stereochemistry [7b].

Naphthalene, anthracene, and acenaphthalene dianions have all been shown to slowly attack THF by an ether cleavage reaction. For example, Burgess et al. [13] have reported the formation of 9-(4-hydroxybutyl)-9,10-dihydroanthracene when excess alkali metal is added to a solution of anthracene in THF at room temperature. Beryllium chloride is a strong Lewis acid and apparently complexes to the THF to facilitate ring opening even by such relatively delocalized anion nucleophiles as anthracene dianion, to yield a beryllium alkoxide (Fig. 6). The possible synthetic utility of this hydroxybutylation reaction has not yet been exploited. In agreement with our observations for the THF adduct, most of the beryllium alkoxides are known as amorphous solids which neither melt nor sublime and are practically insoluble in all organic solvents [14].

Attempts to prepare the beryllium anthracene complex in other solvents or with the potassium salt yielded primarily this beryllium alkoxide. The high yield of this dialkylated material, III, at room temperature is rather surprising. In order to account for this, we note that Szwarc et al. [15] discovered that even though the disproportionation constant for anthracene radical anion is of the order of 10^{-9}, the dianion is actually the reactive species in protonation reactions. In our case, in order to obtain the bianthryl polymer, the cleavage reaction must the thwarted by the use of excess anthracene or even naphthalene to act as an "electron diluent" and shift the disproportionation equilibrium even more towards monoanion:

$$2A^{-\cdot} \rightleftharpoons A + A^{2-}$$

Conditions which favor ion pairing also promote dianion stabilization. The metal gegenion probably helps to overcome the extra electron repulsion of the dianion by Coulomb attraction and to shift the equilibrium accordingly *. The

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* The second ion pair acidily constant for dihydroanthracene is less than 4 pK units smaller than the first [16].

net reaction is undoubtedly driven towards alkoxide because the product is removed from equilibrium by precipitation. Diethyl ether is a relatively poor coordinating solvent, favoring contact ion pairs, and only alkoxide is produced when the reaction is run in this solvent. When glyme, a solvent of intermediate coordinating ability, was substituted for THF, a mixture of bianthryl complex and alkoxide was obtained.

In accord with these facts, one would expect that minimizing the ambident $BeCl_2$ concentration would also inhibit ether cleavage. This was conveniently accomplished by using commercial anhydrous $BeCl_2$, a calcined material of very low kinetic solubility, that allows reaction to proceed slowly. As mentioned above, this procedure leads to the polymer. On the other hand, a highly soluble source of $BeCl_2$ is the solvate, $BeCl_2 \cdot 2$ THF. Reaction with it occurred instantaneously with anthracenide to form the alkoxide; the salt complex itself decomposed spontaneously after several months in an inert atmosphere.

In an attempt to make the beryllium-bianthryl polymer more soluble and tractable, t-butylberyllium chloride was considered as a means to "cap" the polymer. Also, the alkyl group should reduce the Lewis acidity of the beryllium. Di-t-butylberyllium was made successfully by reaction of two equivalents of t-butyllithium with $BeCl_2$ in ether; the product distills as a pure viscous liquid with some coordinated THF. When stirred with an equimolar quantity of $BeCl_2$ in THF, t-butylberyllium chloride is formed instantaneously by disproportionation [17]. When 0.5 equivalents of lithium anthracenide was added to t-butylberyllium chloride, only alkoxide precipitated. This result is rationalized by recalling that alkylberyllium halides can equilibrate back to dialkylberyllium plus $BeCl_2$ by disproportionation. Only a catalytic amount of $BeCl_2$ is apparently necessary to convert all of the available anthracenide to alkoxide.

The foregoing results provide a background for understanding the behavior of cyclooctatetraene dianion with $BeCl_2$. Reaction of the potassium salt with $BeCl_2$ in THF at room temperature produced a yellow insoluble, non-volatile precipitate *. Exposure to air produced little change in the IR spectrum of the solid. The IR, however, showed a strong band for hydroxy stretch. Hydrolysis yielded a colorless oil which appeared to be a mixture of alcohols as indicated by mass spectrum (m/e 178) and the change in the NMR spectrum on addition of D_2O. Chromatography gave poor resolution. The oil was unstable to polymerization and was not studied further. It seems clear that the reaction again involves attack at THF to give a mixture of 4-hydroxybutylated cycloocta-polyenes.

Conclusions

The formation of a beryllium compound of tetrahydrobianthryl is a remarkable result that leads to important conclusions concerning the nature of carbon—beryllium bonding. A magnesium—anthracene complex has been described from the direct reaction of metal with hydrocarbon in THF [18]. Hydrolysis of this sparingly soluble complex yielded only 9,10-dihydroanthra-

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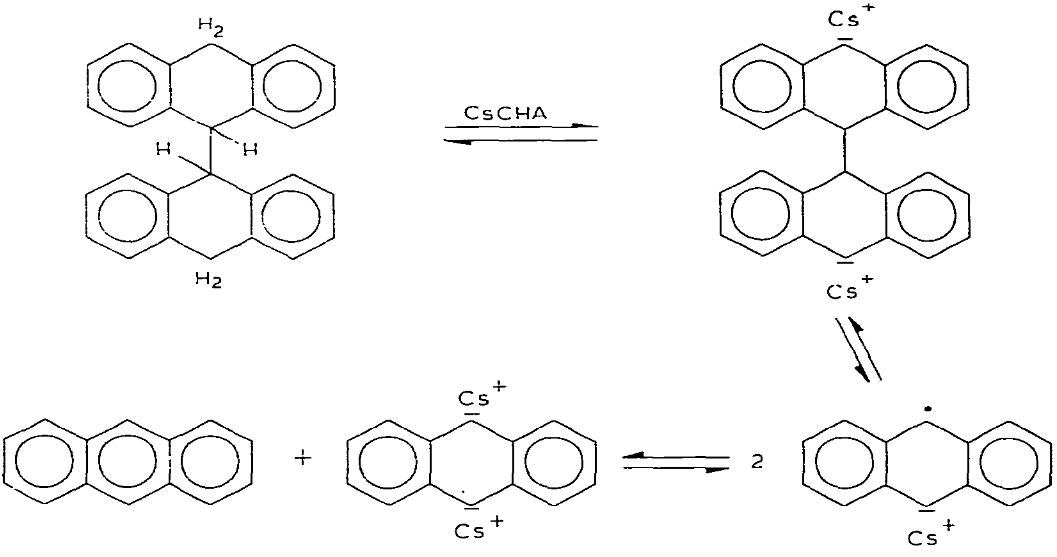
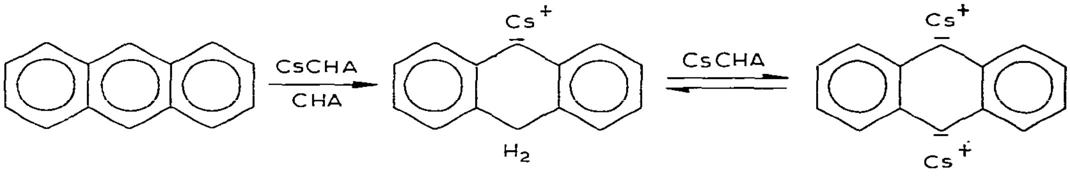
* Preliminary experiments were carried out by David F. Starks, Dissertation, University of California, Berkeley, CA 1974.

cene and THF. Thus, the reaction with anthracene does not stop at the bianthryl stage. Moreover, treatment of II with cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA) gives anthracene dianion rapidly. We expect II to give significant amounts of the dicesium salt in cyclohexylamine [16]. This salt apparently dissociates completely to the cesium salt of anthracene radical anion, which, in turn, is in equilibrium with anthracene and its dianion (Scheme 1) *. We found independently that anthracene is rapidly converted to salts of dihydroanthracene with CsCHA in CHA. This reduction is not without analogies. A similar reaction occurs with lithium cyclohexylamide but more slowly [20]. Potassium hydride appears to add to anthracene in the presence of crown ether [21]. Finally, alkyllithium reagents add to anthracene [8].





The intermediate produced by reaction of anthracene radical anion with beryllium chloride clearly cannot be regarded as a beryllium anthracenide ion pair. The analogies discussed above do not suggest dimerization. Instead, such an intermediate must have substantial C—Be covalent character such that the organic moiety is less an ion pair and has more of the character of a free radical which dimerizes **.

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[*] These reactions are probably related to the recently reported cleavage of II by reduction [19].

[**] A recent theoretical comparison shows that the CH_3—Be bond is substantially less ionic than CH_3—Li [22].

Experimental

THF and ether were dried by distillation from sodium/benzophenone followed by vacuum transfer from $LiAlH_4$. Hydrocarbons were purified by sublimation and recrystallization. Melting points are uncorrected. Beryllium chloride was used as obtained commercially from ROC/RIC. Lithium metal was used as wire containing 2% sodium as obtained from Alfa/Ventron. Manipulation of air-sensitive materials was done under argon atmosphere using high vacuum line techniques and specially adapted glassware [23]. All beryllium compounds were treated as extremely toxic thus imposing many experimental constraints. A Vacuum-Atmosphere Corp. Drilab (continuously recirculating glovebox) with helium atmosphere was used for most of the air-sensitive beryllium reactions. Di-t-butylberyllium was prepared using Schlenck-type equipment in a high velocity hood. Chemical ionization mass spectra were obtained through the Dept. of Pharmaceutical Chemistry, UCSF.

Preparation of the beryllium-bianthryl polymer

In the glove box, anthracene (3.85 g, 21.6 mmol) was stirred with Li wire (0.1 g) for 2 h or until all the metal was consumed. Solid anhydrous $BeCl_2$ (0.57 g, 7.2 mmol) was added and the mixture was stirred for 36 h at room temperature. The precipitate was filtered and Soxhlet extracted for 18 h with THF to yield 0.84 g of pale yellow, insoluble powder. X-ray powder pattern, Cu radiation 1.5418 Å, d spacings (intensity): 9.34vs, 7.67vs, 6.35w, 5.52w, 5.33s, 5.11w, 4.84w, 4.57w, 4.18s, 3.96w, 3.89s, 3.69s, 3.51w, 3.38w, 2.52m, 2.40m, 1.99m.

Preparation of cis-9,10-dihydro-bis(4-alkoxybutylberyllium)anthracene

In the glove box, 2 g of anthracene was stirred with 78 mg of Li wire (1 eq) in THF overnight. Solid anhydrous $BeCl_2$ (0.44 g, 0.5 eq) was added and the mixture was stirred for 36 h at room temperature. The precipitate was filtered and Soxhlet extracted with THF to yield 1.2 g of yellow, insoluble, non-volatile powder. Substitution of etherate complexes for anhydrous $BeCl_2$ resulted in instantaneous reaction to form the same product.

Hydrolysis (deuterolysis) of beryllium-bianthryl

A sample of polymer (80 mg) was stirred in 10 ml of THF under inert atmosphere. To the cooled suspension was added 2 ml of cold water (or D_2O) by syringe. After 5 min, the mixture was filtered and the precipitate was washed wih benzene. The combined filtrate and washings were extracted successively with 2 *N* HCl, water, and brine. The organic layer was dried over $MgSO_4$ and evaporated to yield 45 mg of white crystalline II. Molecular weight was determined to be 356 ± 10 by osmometry in benzene. NMR, UV, and IR spectra were all identical with an authentic sample of II and the mixed melting point was undepressed. Both electron impact and chemical ionization mass spectra of the deuterolysis product show no parent and a base peak at m/e 179 (anthacene-d_1).

DDQ oxidation of II-d_2

To a stirred solution of II-d_2 (100 mg, obtained by deuterolysis of the beryllium polymer) in benzene was added 15 mg of DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) and the solution was stirred for 3 h. The mixture was then filtered and the hydroquinone residue was washed with benzene. The filtrate was then extracted with basic sodium hyposulfite ($Na_2S_2O_3$) to remove unreacted oxidant. The organic layer was washed with water, dried over $MgSO_4$, and evaporated in vacuo to yield anthracene-9-d_1; deuterium content was determined by ^1H NMR integration (3 peaks, 1/4/4) and mass spectroscopy: *m/e* 180 (15.7), 179 (100), 178 (47.5), 177 (18.7), 176 (13.6), 175 (3.9).

Preparation of 9,9',10,10'-tetrahydro-9,9'-bianthryl

Commercial anthrone (25 g) was heated to reflux in 125 ml of glacial acetic acid with 30 mesh granulated zinc (15 g) in a 3-neck round bottom flask equipped with condenser and mechanical stirrer. Concentrated HCl (15 ml) was added dropwise over a period of 10 min. The mixture was stirred for another hour, and washed successively with acetic acid, dilute HCl, and water. The crude product was recrystallized with hot filtration from toluene. Successive recrystallization from pyridine, CCl_4 and benzene yielded 5.6 g (25%) of pure bianthryl, m.p. 360°C.

Bianthryl (0.5 g) was refluxed in 30 ml of pentyl alcohol while reagent grade sodium (2.0 g) was added in small pieces during 2 h. The solution was diluted with MeOH and poured onto ice. The precipitate was filtered and washed with water and ether. Recrystallization twice from benzene yielded 0.22 g of white crystals. Anal.: Found: C, 93.63; H, 6.25. $C_{28}H_{20}$ calcd.: C, 93.81; H, 6.19%. UV (THF): 274 nm ($\epsilon = 3050$), 255 (3100), 261 (sh, 2240), 254 (2810). Yield 43%; m.p. 249—250°C (lit. m.p. [6b] 248—249°C) NMR: see text.

Isolation of cis-9,10-dihydro-bis(4-hydroxybutyl)anthracene (III)

Hydrolysis of the previously described beryllium alkoxide yielded a crude oil. Kugelrohr distillation (160°C, 1 mmHg) followed by crystallization from chloroform/hexane yielded white platelets, m.p. 109—110°C. NMR: see text. Anal.: Found: C, 81.18; H, 9.87. $C_{22}H_{20}O$ calcd.: C, 81.44; H, 9.80%. Low voltage electron impact mass spectrum: *m/e* 324.

Conversion to cis-9,10-dihydro-9,10-di-n-butylanthracene

The following procedures were adapted from ref. 24. A solution of *cis*-9,10-bis(4-hydroxybutyl)-9,10-dihydroanthracene (100 mg, 0.308 mmol) and freshly distilled methanesulfonyl chloride (50 μl, 1.05 eq) was cooled in an ice bath. To the stirred solution was added by syringe 86 μl of distilled triethylamine. After 20 min at room temperature, the ammonium chloride was filtered and washed with benzene. The filtrate and washings were evaporated under reduced pressure to an oil that crystallized to a white solid in ether. IR showed no residual hydroxy band and the characteristic mesylate bands were present at 1348s cm^{-1} and 1172s cm^{-1}. NMR showed a mesylate peak at δ 2.93 ppm. The mesylate was used immediately without purification in the next step.

Under an argon atmosphere, $LiAlH_4$ (110 mg, 10 eq) was added to a solution of the previously prepared mesylate in 15 ml of dry THF. The mixture was stirred at reflux for 30 min, then cooled and the excess hydride was quenched with ice. Dilution with benzene, followed by washing with 2 *N* HCl, water, brine, drying over $MgSO_4$, and evaporation under reduced pressure yielded 80 mg of yellow oil (85%). Filtration on a short column of silica gel yielded a clear colorless viscous liquid. The ^1H NMR spectrum is identical to that reported previously [7b].

Preparation of di-t-butylberyllium *

To a 2-neck flask fitted with a gas adapter and addition funnel, commercial $BeCl_2$ (6.48 g) was dissolved in 200 ml of dry ether by stirring for several days. t-Butyllithium (81 ml of 2.3 *M*, 2.0 eq) in pentane was added over 2 min to the ice-cooled $BeCl_2$ solution; vigorous reaction occurred immediately. Finely divided LiCl precipitated and the suspension was allowed to settle overnight. The mixture was concentrated by evaporation in vacuo using two low-temperature traps to prevent contamination of the pump. The remaining solution was transferred by syringe to a short-path all-glass high-vacuum distillation apparatus equipped with a two-neck pot for pumping off the residual ether directly. The solidified product mixture was heated to 90° C and the distillate was collected from 60—80° C with the receiver cooled in Dry Ice. It is important that the distillation be carried out as quickly as possible and at minimum pressure to prevent decomposition. All fractions proved to be pure di-t-butylberyllium which is extremely sensitive; the compound smokes in air. ^1H NMR (benzene-d_6) δ(TMS): 2.85 (q, CH_2, 5.4H), 0.88 (s, t-butyl, 18H), 0.53 (t, CH_3, 3.6H). Integration shows that 0.9 equivalents of ether are complexed.

Reaction of $BeCl_2$ with dipotassium cyclooctatetraenediide

Under an inert atmosphere, 3.0 g of distilled COT was stirred with 1.13 g (2 eq) of potassium in THF at —40° C until all of the metal was dissolved (3 h). The solution was transferred to a glove box and 2.30 g anhydrous of $BeCl_2$ was added. The mixture was stirred overnight and solvent was removed in vacuo. The residue was Soxhlet extracted with THF for 48 h to yield 1.2 g of yellow, insoluble, non-volatile powder.

Isolation of hydroxybutylcyclooctatrienes

A sample of product from the reaction of $BeCl_2$ and K_2COT was hydrolysed as described above for the beryllium-bianthryl polymer. Column chromatography of the crude hydrolysis product (silica gel, hexane/ethyl acetate) yielded no significant quantity of non-polar components. Kugelrohr distillation (130° C, 3 mmHg) of the combined polar fractions yielded a clear colorless oil; ^1H NMR, δ(TMS) ($CDCl_3$): 6.09—5.39 (m, 5H), 3.75—3.36 (m, CH_2OH, OH), 3.15—2.19 (m, allyl), 1.75—1.40 (m, alkyl) total olefin/alkyl integration: calcd. 2.6; found 2.4. Electron impact mass spectrum: *m/e* 178.

Acknowledgement

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* After this work was completed another preparation of di-t-butylberyllium was published [25].

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