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(26) According to the Cahn–Ingold–Prelog rules, and to the official numbering system, the absolute configurations of the isolated chiral stereoisomers follow: TTT = 4a*S*,8a*S*,9a*S*,10a*S*,11*S*,12*S*; TTC = 4a*S*,8a*R*,9a*S*,10a*S*,11*S*,12*S*; TCC = 4a*S*,8a*R*,9a*R*,10a*S*,11*S*,12*S*;TC'C = 4a*R*,8a*R*,9a*R*,10a*S*,11*S*,12*S*.
(27) As for the olefinic compounds, the indicated symmetry corresponds to the apparent symmetry or the maximum allowed symmetry, related to the fast averaging of the conformation of the cyclohexene ring.

Synthesis and Rearrangement of *tert*-Butylanthracenes

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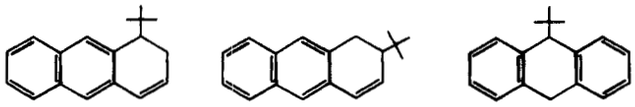
Dehydrogenation of a series of mono- and di-*tert*-butyldihydroanthracenes is investigated as a potential synthetic route to the corresponding *tert*-butylanthracenes. Synthesis of 1- and 2-*tert*-butylanthracene is accomplished through dehydrogenation with DDQ and *o*-chloranil, respectively. Dehydrogenations with the reagent trityl trifluoroacetate generated in situ from trityl alcohol in trifluoroacetic acid lead to rearrangement and disproportionation to afford anthracene, 2-*tert*-butylanthracene, and 2,6-di-*tert*-butylanthracene. Similar rearrangements of the fully aromatic *tert*-butylanthracenes occur in trifluoroacetic acid neat. Reaction of anthracene with *tert*-butyltrifluoroacetate affords 2,6-di-*tert*-butylanthracene directly in high yield. The mechanism of these reactions and structural assignments of the *tert*-butylarenes by NMR analysis are discussed.

Despite the voluminous literature on polycyclic hydrocarbons, remarkably few *tert*-butylarenes have ever been synthesized.[1] At the inception of this research, 1-*tert*-butylanthracene and 9,10-di-*tert*-butylanthracene were unknown, and 2- and 9-*tert*-butylanthracene were obtainable only through multistep syntheses.[2,3] Since the related mono-*tert*-butyldihydroanthracene compounds **1–3** are obtainable through addition of *tert*-butyllithium to anthracene,[4,5] and the di-*tert*-butyldihydro compounds **4** and **5** can be synthesized through alkylation of **3**,[5] dehydrogenation of **1–5** appears



1 **2** **3**

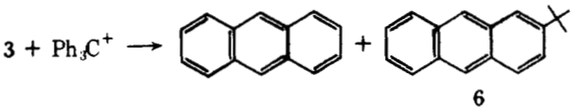
4 **5**

to offer a convenient route to the corresponding mono- and di-*tert*-butylanthracenes. In this study the synthetic utility of this and other approaches to *tert*-butyl substituted anthracenes is examined, and the products and mechanisms of rearrangements encountered are investigated.

Results

Dehydrogenation of 1-*tert*-butyl-1,2-dihydroanthracene (**1**) with DDQ gave 1-*tert*-butylanthracene, readily distinguished from its isomers by its NMR spectrum (cf. summary of NMR results presented later in this section). Similar reaction of 2-*tert*-butyl-1,2-dihydroanthracene (**2**) with DDQ afforded only tarry products, but when the milder reagent *o*-chloranil was employed, 84% of 2-*tert*-butylanthracene was obtained. Its NMR spectrum and other physical properties match those of an authentic sample.[2] In contrast, 9-*tert*-butyl-9,10-dihydroanthracene (**3**) resisted dehydrogenation by *o*-chloranil in refluxing benzene. Analogous reaction with DDQ gave a complex mixture of products containing less than 2% of the desired product, 9-*tert*-butylanthracene.

Attempted dehydrogenation of **3** with trityl trifluoroacetate generated from trityl alcohol in refluxing trifluoroacetic acid[6] furnished a mixture of anthracene, 2-*tert*-butylanthracene (**6**), and 2,6-di-*tert*-butylanthracene (**7**) in the approximate



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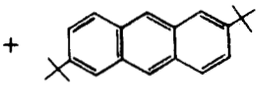
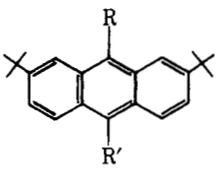
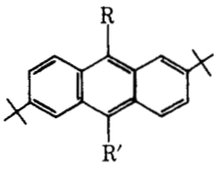


7

ratio of 2:1:1. All attempts to separate the components of this mixture by conventional chromatographic techniques on columns or thin layers of silica gel, alumina, or Florisil failed. Efficient separation was achieved, however, by chromatography on silica gel impregnated with 2% trinitrofluorenone.[7] The structural assignment of the 2,6-di-*tert*-butyl isomer **7** was made initially through analysis of its NMR spectrum in comparison with those of other *tert*-butylanthracene derivatives, as discussed later in this section. This assignment was confirmed and the alternative isomeric 2,7-di-*tert*-butylanthracene (**8a**) structure excluded through bromination to a monobromo derivative.[13] The NMR spectrum of the latter was entirely consistent with the structure **9a** anticipated to be formed from **7** and incompatible with either **8b** or **8c** expected to be formed from **8a**.



8a, R = R' = H
b, R = Br; R' = H
c, R = H; R' = Br



9a, R = Br; R' = H
b, R = R' = CH_3

Table I. Dehydrogenation and Rearrangement of Mono- and Di-*tert*-butyldihydroanthracene with Trityl Trifluoroacetate Generated in Situ[a]

Registry no.	Compd	Amount, mg	Time, h	Yield, %[b] Anthracene	6	7
62337-61-5	1	20	16	45	35	20
62337-62-6	2	15	20	35	50	15
13387-48-9	3	25	24	55	25	20
54974-11-7	*trans*-4	383	24	5	15	80
54974-12-8	5	82	20	20	25	55
54974-10-6	*cis*-4[c]	30	15	0	0	0

[a] Conditions are described in the Experimental Section. In all experiments, a 5% molar excess of trityl alcohol was employed. [b] Yields are based on the integrated NMR spectra and represent product percentage composition rather than isolated yields of pure products. The estimated error is in the range of ±5%. [c] Only TFAA (5 mL) without trityl alcohol was employed.

Analogous reaction of **1** or **2** with trityl trifluoroacetate in trifluoroacetic acid also afforded anthracene, **6**, and **7** as the principal products (Table I). Reaction of *trans*-9,10-di-*tert*-butyl-9,10-dihydroanthracene (**4**) with trityl trifluoroacetate under similar conditions led to formation of 2,6-di-*tert*-butylanthracene (80%) accompanied by lesser amounts of anthracene (5%) and **6** (15%). Similar reaction of the *cis*-1,4-di-*tert*-butyl compound **5** gave the same three products in somewhat different ratio (Table I).

The rearranged products apparently arise via an anthracenonium ion formed by initial hydride abstraction. Thus, the di-*tert*-butyl compounds **4** and **5** when refluxed in trifluoroacetic acid in the absence of trityl alcohol gave no reaction. Since dehydrogenation (i.e., loss of a proton from the intermediate) may conceivably precede rearrangement, reactions of the *tert*-butylanthracenes in trifluoroacetic acid were investigated. When 9-*tert*-butylanthracene was heated at reflux in trifluoroacetic acid for 24 h, a mixture of anthracene, **6**, and **7** was obtained in similar ratio to that isolated from dehydrogenation and rearrangement of **3** (Table I). Analogous reaction of 2-*tert*-butylanthracene in trifluoroacetic acid gave a mixture of the same three products (Table I). While this result apparently supports the idea that dehydrogenation precedes rearrangement, it is inconclusive since protonation of a *tert*-butylanthracene derivative in strong acid can afford the same carbonium ion intermediate as hydride abstraction from a *tert*-butyldihydroanthracene (cf. Discussion).

As discussed in greater detail in the following section, *tert*-butyl trifluoroacetate appears to be the active intermediate species which *tert*-butylates anthracene and its derivatives regiospecifically in the 2 position during these rearrangements. To test this hypothesis, reaction of anthracene with *tert*-butyl alcohol in trifluoroacetic acid was investigated and found to furnish the 2,6-di-*tert*-butyl isomer virtually quantitatively (Table II). Even with short reaction time and low ratios of the reagent, no more than traces of the mono-*tert*-butyl derivative **6** could be detected, indicating the second *tert*-butylation step to be much more rapid than the first.

In view of the efficiency of this synthesis, additional examples were examined to extend its generality. Analogous reactions of 2-methylanthracene and 9,10-dimethylanthracene furnished 2-methyl-6-*tert*-butylanthracene (**10**) and 9,10-dimethyl-2,6-di-*tert*-butylanthracene (**9b**), respectively, in good yields.

The NMR spectra of the *tert*-butylanthracene compounds exhibit characteristic chemical shift patterns in the aromatic region which are consistent with the assigned structures. The meso (γ) protons of anthracene appear as a singlet at lowest field (δ 8.38), and the α and β protons appear as multiplets at δ 8.02 and 7.43, respectively.[8] The NMR spectrum of 1-*tert*-butylanthracene shows one less α proton, and the meso proton adjacent to the *tert*-butyl group appears downfield at δ 8.98 ($\Delta\delta$ = 0.60 ppm). This relatively large deshielding effect of the *tert*-butyl group in the adjacent peri proton is consistent with values found previously for other *tert*-butyl substituted arenes.[8,9] The spectrum of 9-*tert*-butylanthracene shows a single proton at δ 8.22 shifted upfield ($\Delta\delta$ = 0.16) from the meso protons of anthracene. One pair of α protons (H_4, H_5) appears in the anthracene region, while the remaining pair (H_1, H_8) is found ~0.60 ppm downfield, consonant with their location in the positions peri to the *tert*-butyl group. The chemical shift pattern of 2-*tert*-butylanthracene differs little from that of the parent hydrocarbon except for the absence of one β proton. Although a shift of the ortho protons of *tert*-butylbenzene[10] and 2,7-di-*tert*-butylpyrene[11] to lower field has been noted, this effect appears relatively insignificant in 1- and 2-*tert*-butylanthracene.

Table II. *tert*-Butylation of Anthracene with *tert*-Butyl Alcohol in TFAA[a]

Molar ratio $(CH_3)_3COH/C_{14}H_{10}$	Time, h	Product composition, %[b] Anthracene	6	7
1	0.25	>99	Tr	0
1	24	50	0	50
2	24	0	0	100
3	24	0	0	100

[a] Experimental details are described in the Experimental Section. [b] Product compositions are determined from the integrated NMR spectra of the products isolated according to the procedure described.

The NMR spectrum of 2,6-di-*tert*-butylanthracene exhibits a relatively simple pattern consonant with the symmetry of the assigned structure. The β protons (H_3, H_7) appear as a doublet at δ 7.48 (J_{ortho} = 9.0, J_{meta} = 2.0 Hz), while the α protons ortho to the *tert*-butyl groups (H_1, H_5) appear as a singlet at δ 7.84, and the remaining pair of α protons (H_4, H_8) occur as a doublet at δ 7.90 (J_{ortho} = 9.0 Hz); the meso protons appear as a singlet at δ 8.29. This spectral pattern, while consistent with structure **7**, does not rule out the alternative 2,7-di-*tert*-butyl structure **8a**. However, the spectrum of the monobromo derivative obtained through reaction with cupric bromide[12] is consistent only with structure **9a**, proof of its origin from **7**. Most significant are the markedly different chemical shifts of the two α protons at H_1 and H_5. The peak at δ 8.21 assigned to H_1 is strongly displaced downfield ($\Delta\delta$ = 0.37) relative to that of the parent hydrocarbon **7**, while the H_5 signal (δ 7.75) is only slightly shifted, clear evidence for the location of the bromine at C-9 adjacent to H_1. Similarly, the remaining two α protons (H_4 and H_8) appear as doublets (J = 9 Hz), one of which exhibits a major downfield shift ($\Delta\delta$ = 0.42) relative to **7**, while the other signal (δ 7.90) is only slightly shifted. Therefore, the former can be assigned to H_8 which must also be located adjacent to the bromine atom. All four α protons are, therefore, different, a structural feature characteristic of the unsymmetrical structure **9a** and inconsistent with the symmetrical isomers **8b** and **8c**. Thus, structures **9a** and **7** can be assigned unequivocally to the monobromo compound and the parent hydrocarbon, respectively.

The chemical shifts of the *tert*-butyl protons of the mono-*tert*-butylanthracenes exhibit marked dependence on the site of substitution. The *tert*-butyl protons of 2-, 1-, and 9-*tert*-butylanthracene appear as singlets at δ 1.42, 1.73, and 1.85, respectively. The observed order $\beta < \alpha < \gamma$ corresponds to the known relationship of the chemical shifts of protons or methyl

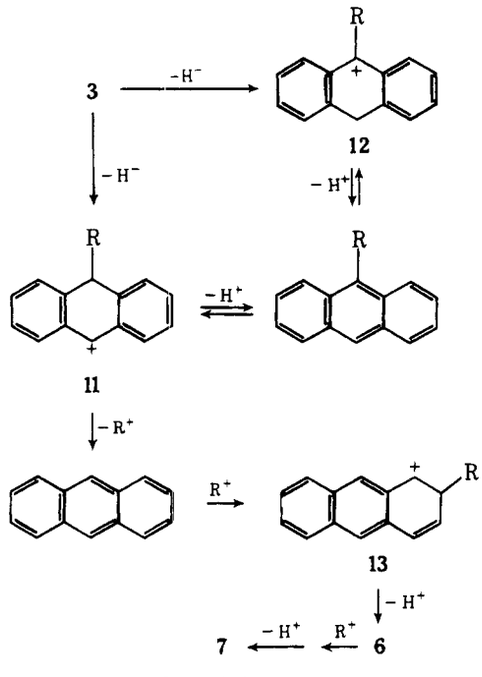
groups in these positions[9] which is considered primarily a consequence of the aromatic ring current effect. The chemical shifts of the *tert*-butyl protons of compounds **7, 9a, 9b,** and **10** corresponded closely to that of the 2-*tert*-butyl isomer, confirming the assigned location of this group in β positions in all cases. The two *tert*-butyl groups of **9a** exhibited slightly different chemical shifts (δ 1.47, 1.50), further evidence for the unsymmetrical isomeric structure assigned.

Discussion

Synthesis of 1- and 2-*tert*-butylanthracene through addition of *tert*-butyllithium to anthracene followed by dehydrogenation of the resulting 1,2-dihydroanthracene adducts with DDQ and *o*-chloranil, respectively, provides a relatively convenient route to these difficulty accessible compounds. Attempted analogous synthesis of 9-*tert*-butyl- and 9,10-di-*tert*-butylanthracene proved unsatisfactory. Alternative approaches involving either dehydrogenation with trityl trifluoroacetate or direct *tert*-butylation of anthracene with *tert*-butyl alcohol in trifluoroacetic acid also failed to furnish the desired 9-*tert*-butylanthracene derivatives. Instead, the rearranged products of **6** and/or **7** were obtained. From a purely synthetic viewpoint, direct *tert*-butylation with *tert*-butyl alcohol in trifluoroacetic acid provides a convenient and efficient synthesis of 2,6-di-*tert*-butylanthracene and related compounds such as **9b** and **10.** This reagent, first reported by Svanholm and Parker,[13] holds considerable promise as a generally useful reagent for the direct *tert*-butylation of other polycyclic hydrocarbons in ring positions of minimum steric hindrance.

All the reactions described in this report, despite their superficial differences, may be interrelated through a common mechanistic scheme (Chart I). This may be illustrated for **3,**

Chart I



R = $(CH_3)_3C$

the conformation of which has been shown to be a flattened boat structure with the bulky *tert*-butyl group oriented axially as a consequence of the steric interaction with the peri hydrogens in the 1 and 8 positions.[4] Hydride abstraction from the 10 position of **3** by trityl cation, DDQ, or chloranil affords the carbonium ion **11.** Although hydride abstraction could conceivably also take place at the 9 position of **3** to afford **12,** attack in this region is less probable since the hydrogen atom at C-9 is equatorial and highly hindered. In any case, it is known that **12** undergoes facile conversion to **11** in the presence of acid.[3] The intermediate **11** can undergo loss of either a proton or a *tert*-butyl ion. The latter is favored due to the strong steric resistance to formation of 9-*tert*-butylanthracene. The *tert*-butyl carbonium ion produced can recombine with anthracene, possibly without prior dissociation, to provide the new intermediate **13.** Aromatization of the latter is energetically favorable, since the peri steric interaction present in **11** is lacking. Dehydrogenation of **2** under similar conditions is expected to provide directly the intermediate **13** which collapses to 2-*tert*-butylanthracene (**6**) without involvement of rearrangement. Subsequent reaction of **6** with a second *tert*-butyl cation, probably as *tert*-butyl trifluoroacetate, takes place at the equivalent position on the other side of the molecule, i.e., the 6 position, to furnish **7.** Reaction stops at this stage, since there remain no positions unhindered by either peri hydrogen or a *tert*-butyl group.

Similar reaction of **1** presumably involves initial formation of an intermediate analogous to **13** bearing the positive charge in the 2 position. Aromatization of this intermediate, since there is a peri hydrogen on only one side of the carbon atom bearing the *tert*-butyl group, is expected to occur with greater facility than **11** and slower than **13.**

Reactions of the disubstituted compounds **4** and **5** are presumed to proceed via analogous pathways.

Prolonged heating of any of the isomeric mono- or di-*tert*-butylanthracenes in TFAA may be expected, according to this mechanism, to result in eventual conversion to anthracene and **7.** It is likely also that loss of the *tert*-butyl group as isobutylene could become seriously competitive under such conditions.

Finally, the technique of "charge-transfer chromatography" on silica gel impregnated with 2,4,7-trinitrofluorenone[7] is deserving of further comment. A mixture of anthracene, the three isomeric mono-*tert*-butylanthracenes, and 2,6-di-*tert*-butylanthracene which migrated together as a single spot on silica gel, Florisil, and alumina was clearly separated into its individual components on a TNF–silica gel plate. Moreover, each compound exhibited a distinctive color characteristic of its charge-transfer complex. These follow in order of R_f value: 9-*tert*-butyl- (brown) > 2,6-di-*tert*-butyl (blue-gray) > 1-*tert*-butyl- (red-violet) > 2-*tert*-butyl- (violet-red) > anthracene (maroon). This powerful technique is routinely employed in our laboratory to effect many difficult separations of hydrocarbon isomers and derivatives. It is highly recommended for general use.

Experimental Section

Physical Data. ^1H NMR spectra were obtained on Varian T-60 and Bruker 270 MHz spectrometers; chemical shifts are reported relative to Me_4Si in CCl_4. Integration was consistent with all assignments. Gas chromatographic analyses were performed on a Varian 2700 chromatograph employing a 5.5 ft × 0.25 in. 10% SE-30 60–80 mesh Chromosorb WA column, with 21 psig helium pressure. Thin layer plates of silica gel impregnated uniformly with 2,4,7-trinitrofluorenone (TNF) were prepared as described previously[7] and developed with benzene in hexane (1:2).

Materials. Benzene was dried over lithium aluminum hydride and redistilled from this reagent. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and *o*-chloranil were purchased from Araphahoe and Upjohn, respectively. Anthracene, 2-methylanthracene, and 9,10-dimethylanthracene were crystallized before use. The dihydroanthracene derivatives **1–5** were prepared as described previously.[4,5] Trityl alcohol, *tert*-butyl alcohol, and trifluoroacetic acid (TFAA) were obtained from commercial sources and used without purification.

Dehydrogenation of 1-*tert*-Butyl-1,2-dihydroanthracene (1) with DDQ. A solution of **1** (54 mg, 0.23 mmol) and DDQ (120 mg, 0.53 mmol) in benzene (10 mL) was refluxed for 1 h. After removal of benzene, the residue was chromatographed over silica gel. Elution with

hexane–benzene (4:1) gave 1-*tert*-butylanthracene (10 mg, 19%) as a colorless oil: NMR (CCl_4) δ 1.73 (s, 9, CH_3), 7.42 (m, 4, H_2, H_3, H_6, and H_7), 7.92 (m, 3, H_4, H_5, and H_8), 8.40 (s, 1 H_{10}), and 8.98 ppm (s, 1, H_9); GLC retention time 12 min.

Dehydrogenation of 2-*tert*-Butyl-1,2-dihydroanthracene (2) with *o*-Chloranil. A solution of **2** (70 mg, 0.3 mmol) and *o*-chloranil (75 mg, 0.3 mmol) in benzene (10 mL) was refluxed for 50 min. After removal of benzene by rotatory evaporator, the dark brown-black residue was extracted with 20 mL of hot hexane. The filtrate was then chromatographed on silica gel. Elution with hexane–benzene (9:1) gave a colorless solid (63 mg) which was identified as 2-*tert*-butylanthracene (**6**) containing a trace of anthracene by TLC on silica gel impregnated with TNF. Recrystallization from methylene chloride–petroleum ether (bp 30–60 °C) gave pure **6** as a colorless solid, 58 mg (84%), mp 146–147 °C (lit.[2] 145.5–146.5 °C). The NMR spectrum, TLC, and GLC retention time (13.2 min) were identical with those of an authentic sample, provided by Dr. L. H. Klemm.

Dehydrogenation and Rearrangement of Mono- and Di-*tert*-butyldihydroanthracene with Trityl Alcohol in TFAA. A mixture of *trans*-9,10-di-*tert*-butyl-9,10-dihydroanthracene (**4**, 383 mg, 1.31 mmol), trityl alcohol (360 mg, 1.38 mmol), and TFAA (6 mL) was heated at reflux for 1 day. The solution was cooled, quenched with water, neutralized with sodium bicarbonate, and partitioned between ethyl ether and water. The ethereal layer was separated, dried over magnesium sulfate, and evaporated to dryness to yield 719 mg of a brown solid. Analyses by NMR and TLC on TNF–silica gel revealed the presence of anthracene, **6**, and **7** in the ratio 5:15:80, together with triphenylmethane, and a trace of recovered **4**. Chromatography on a column of silica gel (2.5 × 25 cm) eluted with hexane gave pure **7** as a colorless solid, 278 mg, mp 150–152 °C.

Analogous reactions with **1**, **2**, **3**, and **5** furnished the products summarized in Table I.

Rearrangement of 9-*tert*-Butylanthracene. 9-*tert*-Butylanthracene (100 mg, 0.43 mmol) in 7 mL of TFAA was refluxed for 22 h. TFAA was removed under vacuum to afford a light brown solid (89 mg). Analysis of the NMR spectrum confirmed by TLC on TNF–silica gel indicated the product to contain anthracene, **6**, and **7** in the ratio 55:20:25.

In a separate experiment, 20 mg of 9-*tert*-butylanthracene in 5 mL of TFAA heated at reflux for 20 min gave a product containing anthracene, **6**, and **7** in the ratio of 85:10:5.

Rearrangement of 2-*tert*-Butylanthracene (6). A solution of **6** (30 mg, 0.13 mmol) in 5 mL of TFAA was heated at reflux for 30 min. Analysis of the product obtained following the usual workup revealed unchanged **6** containing only trace amounts of anthracene and **7**. A similar reaction for 4 h gave 85% recovered **6** accompanied by equal amounts of anthracene and **7**.

Nonrearrangement of 2,6-Di-*tert*-butylanthracene (7). A solution of **7** (100 mg) refluxed in 10 mL of TFAA for 4 h gave no reaction.

***tert*-Butylation of Anthracene.** A mixture of anthracene (1.78 g, 10 mmol), *tert*-butyl alcohol (2.22 g, 30 mmol), and TFAA (10 mL) was heated at reflux for 24 h. The resulting dark brown solution was allowed to cool to room temperature, and water (50 mL) was added. The solution was neutralized with sodium bicarbonate and extracted with ethyl ether. The ethereal layer was separated and dried over magnesium sulfate, and ether was removed, giving a brownish solid (3.18 g). NMR analysis confirmed by TLC showed the presence of only **7**. Chromatography on a silica gel column eluted with hexane gave **7** which was recrystallized twice from methanol to afford the analytical sample of **7** as light yellow plates, 2.09 g (72%): mp 151–152.5 °C; NMR (CCl_4) δ 1.42 (s, 18, CH_3), 7.48 (d, 2, J = 9.0 Hz, H_3 and H_7), 7.84 (s, 2, H_1 and H_5), 7.90 (d, 2, J = 9.0 Hz, H_4 and H_8), and 8.29 ppm (s, 2, H_9 and H_{10}).

Anal. Calcd for $C_{22}H_{26}$: C, 90.76; H. 9.24. Found: C, 90.95; H, 9.03.

***tert*-Butylation of 2-Methylanthracene.** Analogous reaction of 2-methylanthracene (960 mg, 5 mmol) in *tert*-butyl alcohol (2.22 g, 30 mmol) and TFAA (10 mL) for 16 h, followed by conventional workup, gave a brown solid (1.67 g). Chromatography on a column of Florisil (2.5 × 20 cm) eluted with hexane, followed by recrystallization from methylene chloride–petroleum ether (bp 30–60 °C), gave pure 2-methyl-6-*tert*-butylanthracene (**10**) as a yellow solid (843 mg, 68%): mp 173–175 °C; NMR (CCl_4) δ 1.44 (s, 9, *tert*-butyl), 2.57 (s, 3, CH_3), 7.08–7.44 (m, 2, H_3 and H_7), 7.50–7.98 (m, 4, H_1, H_4, H_5, and H_8), 8.20 (apparent s, 1, H_9), and 8.23 ppm (apparent s, 1, H_{10}).

Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.73; H, 8.15.

***tert*-Butylation of 9,10-Dimethylanthracene.** Analogous reaction of 9,10-dimethylanthracene (515 mg, 2.5 mmol) in *tert*-butyl alcohol (0.74 g, 10 mmol) and TFAA (8 mL) for 16 h, followed by similar workup and recrystallization from methylene chloride–petroleum ether, gave pure 2,6-di-*tert*-butyl-9,10-dimethylanthracene (**9b**) as yellow-green plates (5.72 mg, 72%): mp 245–247 °C; NMR (CCl_4) δ 1.46 (s, 18, *tert*-butyl), 3.03 (s, 6, CH_3), 7.48 (d of d, 2, J_{ortho} = 9.0, J_{meta} = 2.0 Hz, H_3 and H_7), 8.08 (s, 2, H_1 and H_5), and 8.17 ppm (d, 2, J = 9.0 Hz, H_4 and H_8).

Anal. Calcd for $C_{24}C_{30}$: C, 90.51; H, 9.49: Found: C, 90.42; H, 9.50.

9-Bromo-2,6-di-*tert*-butylanthracene (9a). A solution of **7** (320 mg, 1.1 mmol) and cupric bromide (507 mg, 2.27 mmol) in distilled carbon tetrachloride (20 mL) was refluxed for 20 h under N_2. After cooling to room temperature, the solution was filtered to remove an insoluble residue and washed with carbon tetrachloride. The filtrate was then chromatographed on a column of Florisil (2 × 20 cm). Elution with hexane–benzene (3:1) gave a yellow oil (393 mg). HPLC on a Li-Chromosorb silica gel column (10 μm, 1.5 × 35 cm) at 125 psig eluted with hexane cleanly separated the product into two components, both of which were collected and identified. The starting material **7** (retention time 20 min) was not detected. The minor component (retention time 10 min) was identified as 9,10-dibromo-2,6-di-*tert*-butylanthracene mainly by mass spectral analysis [m/e (70 eV) 448]. The major component (retention time 14.5 min) was **9a**: mp 148–150 °C; NMR (CCl_4) δ 1.47 (s, 9, 6-*tert*-butyl), 1.50 (s, 9, 2-*tert*-butyl), 7.49 (d of d, 1, J_o = 9, J_m = 2 Hz, H_3), 7.59 (d of d, 1, J_o = 9, J_m = 2 Hz, H_7), 7.75 (s, 1, H_5), 7.80 (d, 1, J = 9 Hz, H_4), 8.21 (s, 1, H_1), 8.32 (s, 1, H_{10}), and 8.32 ppm (d, 1, J = 9 Hz, H_8).

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Registry No.—**6**, 18801-00-8; **7**, 62375-58-0; **9a**, 62337-63-7; **9b**, 62337-64-8; **10**, 62375-59-1; 1-*tert*-butylanthracene, 62337-65-9; anthracene, 120-12-7; 2-methylanthracene, 613-12-7; *tert*-butyl alcohol, 75-65-0; 9,10-dimethyanthracene, 781-43-1; 9-*tert*-butylanthracene, 13719-97-6.

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