Halogenations of Anthracenes and Dibenz[*a,c*]anthracene with *N*-Bromosuccinimide and *N*-Chlorosuccinimide[1]

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Halogenation of dibenz[*a,c*]anthracene (**1**) by NBS in CCl_4 affords the products of 9- and 10-monobromination in the ratio of 9:1. The reaction is accelerated by iodine, and HBr effects rearrangement of 9-bromo product to the sterically less crowded 10-bromo isomer. The mechanism is proposed to involve reversible addition of Br_2, followed by elimination of HBr. Reaction of NCS with **1** in CCl_4 requires addition of HCl and affords exclusively 9-chlorination. The different reactivities of NBS and NCS are ascribed to the relative amounts of free halogen produced (due to differences in N−X bond strengths involving Br and Cl), and the different sizes of the halogens. Under similar conditions, NCS chlorinates 9-bromoanthracene (**2a**) to afford 9,10-dichloroanthracene and 9-bromo-10-chloroanthracene in the ratio of 65:35. This reaction ostensibly occurs by addition of Cl_2 to **2a**, followed by preferential loss of HBr rather than HCl. 9-Methylanthracene (**3**) affords exclusively 9-(bromomethyl)anthracene with NBS in the absence of iodine, but mainly (67%) 9-bromo-10-methylanthracene in the presence of iodine. Chlorination of **3** with NCS in the presence of HCl also affords mostly (65%) nuclear halogenation. Nuclear bromination of anthracene, 9-methylanthracene, and dibenz[*a,c*]anthracene by NBS in the absence of added HBr is accelerated by iodine. This effect is probably due to an increase in the amount of bromine produced from NBS in the presence of iodine.

Introduction

N-bromosuccinimide (NBS) and *N*-chlorosuccinimide (NCS) commonly are used to effect allylic and aromatic halogenations.[2] Despite the wide usage of these halogenating agents, many aspects of the mechanism of halogenation remain controversial. Allylic bromination by NBS generally is described as a free radical chain reaction. This process originally was proposed to involve succinimidyl radicals,[3,4] but more recently studies have implicated bromine atoms,[5] or an equilibrium between both radicals,[6] as chain carriers. A similar mechanism for allylic chlorination by NCS may be presumed.

Nuclear halogenations of aromatic compounds with NBS and NCS to form haloarenes also are known. In polar solvents, the mechanisms probably are electrophilic aromatic substitutions[7] and involve molecular halogen.[8] The mechanism for nuclear halogenation of aromatic compounds in nonpolar solvents is less clear. For example, nuclear bromination of methylanisoles with NBS in CCl_4 has been proposed to occur by electrophilic aromatic substitution,[9] whereas bromination of anthracene was proposed to involve a radical chain with bromine atom carriers.[10]

Recently, we desired the regiospecifically defined nitrile of dibenz[*a,c*]anthracene (**1**), 9-cyanodibenz[*a,c*]anthracene (**1g**), for which no synthesis has been reported. Chlorosulfonyl isocyanate has been used effectively for cyanations of related aromatic hydrocarbons.[11] However, chlorosulfonyl isocyanate failed to react with **1** under a variety of conditions. Steric effects likely are responsible for the unreactivity of **1** toward CSI. An alternative convenient, efficient, and general synthetic route for cyanation of arenes involves halogenation followed by reaction of the aryl halide with cuprous cyanide.[12,13] Use of NBS to halogenate **1**[14] (the Wohl−Ziegler reaction[15]) was reported to afford 9-bromodibenz[*a,c*]anthracene (**1a**),[16a] the desired precursor to **1g**. We found that the nature of the products obtained from this reaction is sensitive to the reaction conditions.[1] This result led us to pursue the present study concerning the effects of

(1) Taken in part from the Ph.D. Dissertation of S. Duan, Department of Chemistry, Cleveland State University, 1996.

(2) Horner, L.; Winkelmann, E. H. *Angew. Chem.* **1959**, *71*, 349. Thaler, W. A. *Methods Free-Radical Chem.* **1969**, *2*, 121. Bovonsombat, P.; McNelis, E. *Synthesis* **1993**, 237.

(3) Bloomfield, G. F. *J. Chem. Soc.* **1944**, 114.

(4) Dauben, Jr., H. J.; McCoy, L. L. *J. Am. Chem. Soc.* **1959**, *81*, 4863.

(5) Incremona, J. H.; Martin, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 627. Kim, S. S.; Lee, C. S.; Kim, C. C.; Kim, H. J. *J. Phys. Org. Chem.* **1990**, *3*, 803. Day, J. C.; Katsaros, M. G.; Kocher, W. D.; Scott, A. E.; Skell, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 1950.

(6) Chow, Y. L.; Zhao, D. C. *J. Org. Chem.* **1987**, *52*, 1931.

(7) Braeuniger, H.; Kleinschmidt, E. G. *Pharmazie* **1969**, *24*, 140.

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(9) Gruter, G.-J. M.; Akkerman, O. S.; Bickelhaupt, F. *J. Org. Chem.* **1994**, *59*, 4473.

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(13) Newman, M. S.; Boden, H. *J. Org. Chem.* **1961**, *26*, 2525.

(14) Weinshenker, N. M. *Org. Prep. Proc.* **1969**, *1*, 33.

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(16) (a) Harvey, R. G.; Aboshkara, E.; Pataki, J. *Tetrahedron* **1997**, *53*, 15947. (b) The chemical shifts of **1a** appear at a higher field in the crude reaction mixture than in the isolated product and shift to a lower field as the reaction progresses, indicative of some dynamic process involving **1a**, such as shown in Scheme 1.

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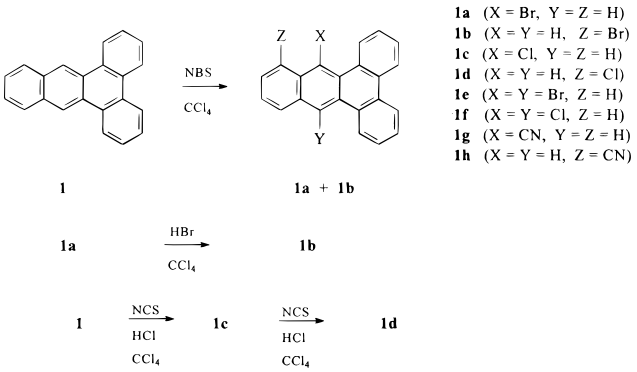
Scheme 1



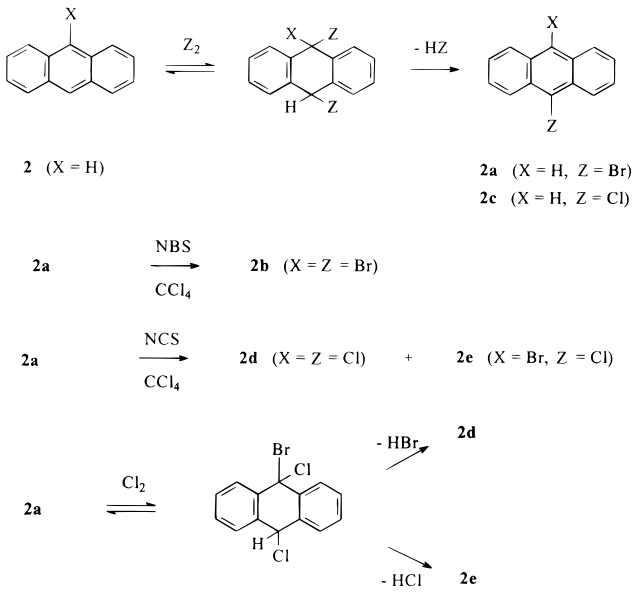
reaction conditions on the products obtained in halogenations of anthracene and its derivatives with NBS and NCS.

Discussion

Bromination of anthracene (**2**) with NBS in CCl_4 affords 9-bromoanthracene (together with a small amount of 9,10-dibromoanthracene) in good yield. The reaction is accelerated markedly by the presence of iodine, a known retarder of free radical brominations.[4] Like anthracene, the meso (e.g., 9-) positions of dibenz[*a*,*c*]anthracene are the most reactive. Bromination of **1** with NBS in CCl_4 proceeds very slowly in the absence of iodine and affords a mixture of about 90% 9-bromodibenz[*a*,*c*]anthracene (**1a**) and 10% 10-bromodibenz[*a*,*c*]anthracene (**1b**) whether or not iodine is present (Scheme 1). Bromination at the less reactive 10-position of **1** likely is due to steric hindrance about the meso positions.[4] Over time, **1a** rearranges to afford **1b**. This rearrangement is promoted by additives that produce HBr, such as Br_2,[4] excess NBS, or HBr itself. These results are best explained by a mechanism involving reversible electrophilic addition of halogen to the arene,[17] followed by the elimination of hydrogen halide (Scheme 1).[16b] The effect of I_2 to accelerate, rather than retard, the reactions of **1** and **2** indicates that a free-radical process is not directly involved.

Under the same conditions, recrystallized NCS did not react with **1** unless a catalytic amount of HCl was added. In the presence of HCl, excess NCS and **1** afforded exclusively 9-chlorodibenz[*a*,*c*]anthracene, **1c** (Scheme 1), and 9,10-dichlorodibenz[*a*,*c*]anthracene from the subsequent reaction of **1c** with excess NCS. The regiochemistry of the reaction was verified by cyanation[12] of both **1a** and **1c** to the same **1g**.[18] The requirement for HCl presumably arises from the need to generate sufficient Cl_2 for the reaction to proceed. We attribute the lower reactivity of NCS compared to NBS to the greater strength of a N−Cl bond compared to a N−Br bond.[19] Thus, the amount of chlorine produced from NCS (in the absence of added HCl) will be much less than the amount of bromine

Scheme 2



produced from NBS under similar conditions. Furthermore, chlorine is smaller and more reactive than bromine, so that steric effects are less important.[20] Chlorination then occurs exclusively at the most reactive (meso) positions of **1**.

To test this mechanism, halogenations of several substituted anthracenes were examined. First, chlorination of 9-bromoanthracene (**2a**) by NCS in CCl_4 was examined. If halogenation of anthracenes with NBS and NCS generally proceeds by addition of halogen, then **2a** will afford 9,10-dichloroanthracene (**2d**) by elimination of HBr (Scheme 2). In fact, **2d** was the principal (65%) primary product from this reaction. A lesser amount of 9-bromo-10-chloroanthracene (35%), produced by elimination of HCl, also formed. The preferential elimination of HBr rather than HCl reflects the better leaving group ability of bromide compared to chloride.

Competition studies in reactions of anthracene, **2a**, and 9-chloroanthracene (**2c**) revealed that the reactivity of the haloanthracenes toward NCS in CCl_4 is comparable, and anthracene is about 20 times more reactive than either. This result may be explained by a combination of inductive and steric effects. The steric effect of a bromine substituent will be larger than that for chlorine, which would compensate for the greater deactivating inductive effect of a chlorine substituent. Importantly, **2c** was found *not* to be a significant product from chlorination of **2a**. Since **2a** and **2c** react at similar rates, substantial **2c** (if formed) should be observed at early times in the reaction of **2a** with NCS. This result rules out the intermediacy of **2c** in the formation of **2d** from chlorination of **2a**, and it is consistent with the observation of formation of **2d** as a primary product.

Halogenation of 9-methylanthracene (**3**) was investigated to address the effect of iodine on the reaction. Reaction of **3** with NBS in CCl_4 occurs slowly in the absence of iodine to afford solely 9-(bromomethyl)anthracene, **3b** (Schemes 3). **3b** reacts even more slowly

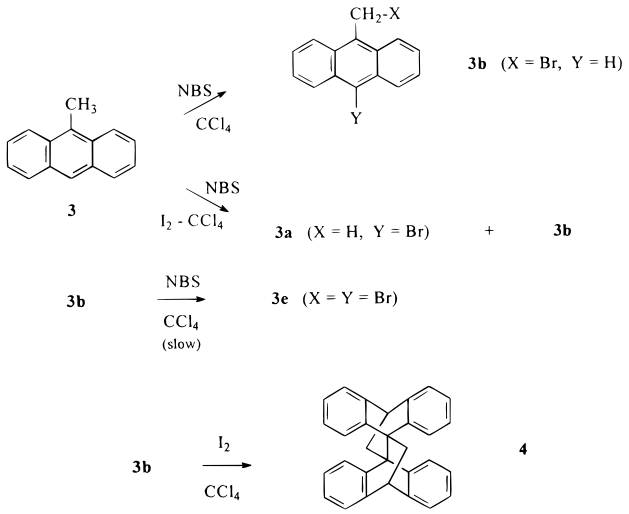
(17) (a) Halogenations of anthracenes proceed, at least in part, by addition intermediates: de la Mare, P. B. D.; Ridd, J. H. *Aromatic Substitution*; Academic Press: New York, 1959; p 174. (b) Although ionic mechanisms cannot be ruled out, nonionic reactions should be preferred in solvents of low polarity (such as CCl_4): Hubig, S. M.; Jung, W.; Kochi, J. K. *J. Org. Chem.* **1994**, *59*, 6233.

(18) Single-crystal X-ray analysis of **1g** demonstrated the presence of steric crowding near the cyano group, which is slightly bent (the C−C≡N bond angle is 174.3(7)°), and the aromatic system is highly nonplanar.

(19) The homolytic dissociation energy of N−Cl bonds is about 0.7 eV larger than that of the corresponding N−Br bonds: Andrieux, C. P.; Differding, E. D.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1993**, *115*, 6592.

(20) Kaeding, W. *J. Org. Chem.* **1961**, *26*, 4851.

Scheme 3



with NBS to afford 9-bromo-10-(bromomethyl)anthracene. Addition of iodine not only accelerates the rate of reaction of NBS with **3** but also affords a new product, 9-bromo-10-methylanthracene (**3a**), in 67% yield, together with a lesser amount (31%) of **3b**. These products do not interconvert under the reaction conditions.[21] Benzylic bromination of **3** in CCl_4 in the absence of iodine occurs by a free radical mechanism. The sluggish reaction of the **3b** product by a subsequent nuclear bromination, rather than by a second benzylic halogenation to form 9-(dibromomethyl)anthracene, probably is due to the conformation of the bromomethyl substituent, which precludes alignment of the methylene hydrogens with the anthracene π system, as observed for 9-alkylanthracenes.[23] Comparison of relative reaction rates indicates that iodine promotes nuclear bromination by accelerating the aromatic substitution. This may happen by generation of hydrogen halide (HI or HBr), which increases the amount of free Br_2 present. The observation that **1a** and **1b** form in essentially the same ratio from **1** in the presence and absence of iodine, even though reaction is accelerated in the presence of iodine, suggests that the same halogenating agent is responsible for the nuclear brominations whether iodine is present or not.[24] This mechanism is in agreement with studies of methylbenzenes and NBS, which indicate that nuclear halogenation occurs by electrophilic aromatic substitution.[7,9] Similar product ratios in reactions of anthracene using NBS and molecular bromine also are consistent with this proposal. Chlorination of **3** with NCS in the presence of a catalytic amount of HCl afforded analogous nuclear (9-chloro-10-methylanthracene, **3c**, 65%) and radical-derived (9-(chloromethyl)anthracene, **3d**, 35%) products. However, iodine did not affect the yield for nuclear chlorination; the main effect of iodine was to divert formation of **3d** to lepidopterene. The 9-(halomethyl)anthracenes were shown independently to react slowly in the presence of iodine to form lepidopterene (Scheme 3).[21] Preferred nuclear substitution by chlorine, and the absence of an effect of iodine on this process, may be due to the presence of a relatively high concentration of Cl_2 formed by the addition of HCl to the reaction medium.[25]

Conclusion

Dibenz[*a*,*c*]anthracene halogenates with NBS in CCl_4 to afford 9- and 10-monobromination products **1a** and **1b** in the ratio 90:10. The reaction is accelerated by iodine, and HBr effects rearrangement of **1a** to the sterically less crowded **1b**. The mechanism is proposed to involve reversible addition of Br_2, followed by elimination of HBr. Reaction of NCS with **1** requires addition of HCl and affords exclusively meso chlorination. The difference in reactivities of NBS and NCS is ascribed to the relative amounts of free halogen produced (due to differences in bond strengths involving Br and Cl), and the different sizes of the halogens. The 9- and 10-halodibenzanthracenes can be cyanated with CuCN to afford the respective cyano derivatives without rearrangement.

Consistent with the proposed mechanism, NCS chlorinates 9-bromoanthracene to afford mostly 9,10-dichloroanthracene. 9-Methylanthracene affords exclusively 9-(bromomethyl)anthracene with NBS in the absence of iodine, but mainly 9-bromo-10-methylanthracene in the presence of iodine. Iodine also accelerates the nuclear bromination of **3**, as well as that of anthracene itself, when the reaction is performed with NBS in the absence of added HBr. Acceleration of nuclear bromination by iodine probably is due to an increase in the amount of bromine produced in the presence of iodine.

Experimental Section

Materials. Anthracene (MCB), dibenz[*a*,*c*]anthracene (Aldrich), 9-chloroanthracene (Aldrich), 9,10-dichloroanthracene (Aldrich), 9-methylanthracene (Aldrich), 9-(chloromethyl)anthracene (Aldrich, *N*-bromosuccinimide (Aldrich), iodine (Fisher), and anhydrous carbon tetrachloride (Aldrich) were used as received. *N*-Chlorosuccinimide (Aldrich) was recrystallized from benzene. 9-Bromoanthracene was prepared by bromination of anthracene with NBS.[10] 9-Bromodibenz[*a*,*c*]anthracene and 10-bromodibenz[*a*,*c*]anthracene were prepared by a literature procedure.[16a]

Products were identified by mixed mp (mmp) and by ^1H and ^{13}C NMR spectra (spiking the samples with small amounts of authentic materials), and volatile products (haloanthracenes) were identified by GC/MS. Crude products were quantified by ^1H NMR, as well as by GC/MS where indicated for the halogenated anthracenes.

Bromination of Dibenz[*a*,*c*]anthracene. To dibenz[*a*,*c*]-anthracene, **1**, (84 mg, 0.30 mmol) and *N*-bromosuccinimide (53 mg, 0.30 mmol) in carbon tetrachloride (5 mL) was added a catalytic amount of iodine (one drop of a solution containing 0.2 g of iodine in 10 mL of CCl_4[10]). The reaction mixture was heated at reflux for 24 h under a nitrogen atmosphere. The warm mixture was filtered through a Hirsch funnel and the effluent concentrated under reduced pressure. Analysis of the

(21) In the presence of iodine, 9-(bromomethyl)anthracene slowly is transformed into lepidopterene,[22] a process characteristic of the formation of the 9-anthrylmethyl radical. The failure to observe 1,2-di(9-anthryl)ethane can be ascribed to the low concentration of alkyl radicals, which discourages dimerization. For example, a low concentration of 9-anthrylmethyl radicals may add to the 10- position of 9-(bromomethyl)anthracene as the first step in formation of lepidopterene, Scheme 4.

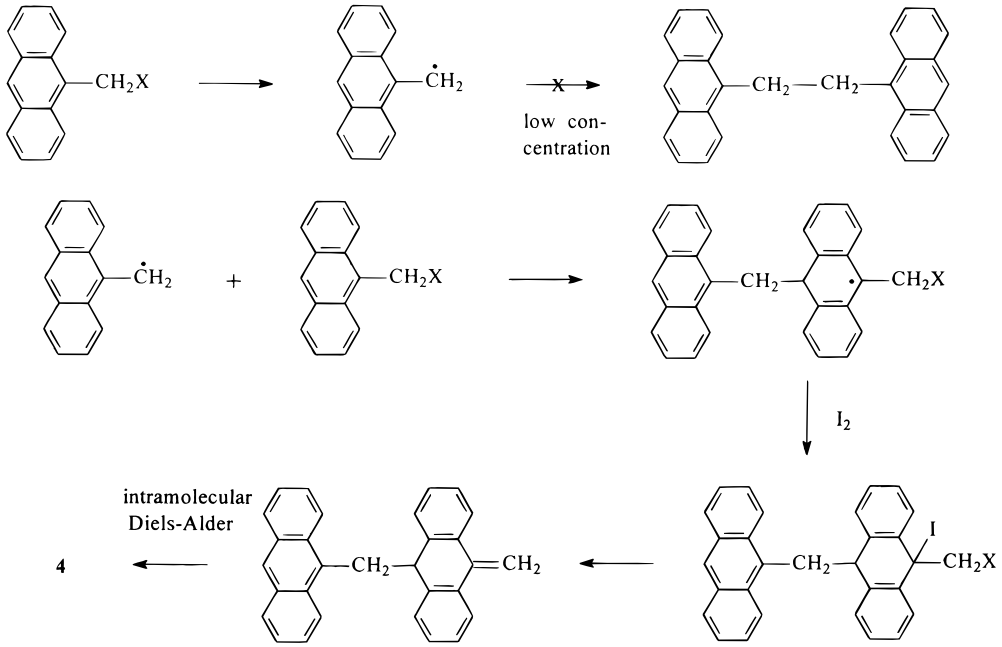
(22) Becker, H.-D.; Andersson, K.; Sandros, K. *J. Org. Chem.* **1980**, *45*, 4549.

(23) Thus, an "inverted" reactivity order was reported for hydrogen atom abstraction by bromine from 9-alkylanthracenes, with reactivity decreasing for methyl (1.00) > ethyl (0.063) ≫ isopropyl (<0.0001): Tanko, J. M.; Mas, R. H. *J. Org. Chem.* **1990**, *55*, 5145.

(24) Other halogenating agents, such as IBr, also may be expected to afford nuclear bromination. For example, chlorination is reportedly the sole reaction of ICl with anthracene: Turner, D. E.; O'Malley, R. F.; Sardella, D. J.; Barinelli, L. S.; Kaul, P. *J. Org. Chem.* **1994**, *59*, 7335.

(25) It also is possible that chlorine has a greater propensity toward addition to methylanthracene, or the addition may be less reversible, than bromine.

Scheme 4



crude reaction mixture by ^{1}H NMR revealed 70% conversion to a 90:10 mixture of **1a**:**1b**. Reactions under otherwise identical conditions but containing no iodine afforded after 7 days 10% conversion to an 85:15 mixture of **1a**:**1b**.

Prolonged reflux of the crude product mixture led to a gradual change in the isomer distribution. For example, after 7 days, this ratio was 60:40 for the reaction performed in the presence of iodine. The rate of isomerization was accelerated by HBr. When the reaction was performed (without iodine) in the presence of a catalytic amount of bromine (a drop of a dilute solution in CCl_4) or a small excess (0.06 mmol) of NBS, the initial product (by ^{1}H NMR) was predominantly the 9-bromo isomer. However, continued reflux for 18 h afforded conversion to mostly 10-bromodibenz[*a*,*c*]anthracene. Thus, repeated column chromatography of this product using Woelm (activity I) alumina eluting fractionally with petroleum ether and dichloromethane eventually afforded 16 mg (15%) of pure 9-bromodibenz[*a*,*c*]anthracene (**1a**), 81 mg (76%) of 10-bromodibenz[*a*,*c*]anthracene (**1b**), and 4 mg (5%) of recovered **1**, identified by comparison with authentic samples.[16a] A trace amount (about 1 mg) of a compound tentatively identified as 9,14-dibromodibenz[*a*,*c*]anthracene (**1e**) [with ^{1}H NMR: 8.99 (2H, dd, 8.3,1.3 Hz), 8.60 (2H, dd, 6.6,3.2 Hz), 8.31 (2H, dd, 7.9,1.3 Hz), 7.71 (2H, dd, 6.6,3.2 Hz), 7.59 (2H, m), 7.48 (2H, m)] also was isolated.

Chlorination of Dibenz[*a*,*c*]anthracene. A stirred mixture of **1** (477 mg, 1.71 mmol) and *N*-chlorosuccinimide (457 mg, 3.42 mmol) and a catalytic amount (5−10 μL) of concentrated hydrochloric acid in carbon tetrachloride was heated to reflux under a nitrogen atmosphere. The progress of the reaction was routinely checked by TLC (Whatman silica gel 60 Å plates) and NMR. (Reactions under the same conditions but containing no added HCl afforded no product.) After 2 days, the warm mixture was filtered and the filtrate concentrated under reduced pressure. Purification of the residue by repeated chromatography (Woelm activity I alumina) eluting fractionally with petroleum ether−dichloromethane afforded 342 mg (64%) of **1c**, 150 mg (25%) of **1f**, and 48 mg (10%) of recovered **1**.

9-Chlorodibenz[*a*,*c*]anthracene (1c): mp 155−156 °C; ^{1}H NMR 9.40 (1H, dd, 8.1,1.5 Hz), 8.98 (1H, s), 8.63 (2H, m), 8.50 (2H, m), 8.08 (1H, dt, 8.8, 0.6 Hz), 7.64 (6H, m); ^{13}C NMR 132.24, 131.75, 131.10, 130.35, 130.09, 130.02, 129.74, 128.93, 128.79, 128.31, 128.12, 128.01, 127.74, 127.33, 126.89, 126.57, 125.64, 125.36, 123.69, 123.25 (broad, possibly two peaks overlapping), 120.71. Anal. Calcd for $C_{22}H_{13}Cl$: C, 84.48; H, 4.20. Found: C, 84.02; H, 4.15.

9,14-Dichlorodibenz[*a*,*c*]anthracene (1f): mp 200−201 °C; ^{1}H NMR 9.08 (2H, dd, 8.3, 1.3 Hz), 8.60 (2H, dd, 6.6, 3.2 Hz), 8.35 (2H, dd, 8.0, 1.2 Hz), 7.73 (2H, dd, 6.5, 3.3 Hz), 7.60 (2H, td, 7.6, 1.3 Hz), 7.50 (2H, td, 7.7, 1.4 Hz); ^{13}C NMR 131.56, 130.78, 129.35, 129.12, 129.03, 128.71, 127.84, 126.51, 126.19, 125.50, 123.62. Anal. Calcd for $C_{22}H_{12}Cl_2$: C, 76.10; H, 3.48. Found: C, 76.78; H, 3.41.

The structure of **1c** was verified by chemical conversion to 9-cyanodibenz[*a*,*c*]anthracene (**1g**), which was identical to **1g** prepared from **1a** (see below).

9-Cyanodibenz[*a*,*c*]anthracene (1g). A stirred mixture of **1a** (5.0 mg, 0.014 mmol), cuprous cyanide (2.5 mg, 0.028 mmol), and dimethylformamide (1 mL) was heated at reflux overnight. The resulting brown complex of nitrile and cuprous halide was poured into a solution of ferric chloride and concentrated hydrochloric acid in water. The reaction mixture was maintained at 60−70 °C for 30 min to decompose the complex, after which the layers were separated. Extraction with dichloromethane afforded a dark brown organic layer that was filtered through a short column of silica gel, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was recrystallized from benzene−ethanol to give 3.8 mg (90%) of **1g** as pale yellow needles: mp 210−211 °C; ^{1}H NMR 9.64 (1H, td, 8.1, 2.4 Hz), 9.25 (1H, s), 8.66 (1H, dd, 6.3, 3.4 Hz), 8.58 (2H, m), 8.52 (1H, m), 8.13 (1H, d, 8.2 Hz), 7.74 (4H, m), 7.68 (2H, m); ^{13}C NMR 133.82, 132.95, 131.66, 131.04, 130.03, 129.71, 129.14, 128.93, 128.78, 128.73, 128.53, 128.06, 127.90, 127.63, 127.36, 127.30, 127.26, 125.65, 123.56, 123.54, 123.49, 119.99, 104.17; EI-MS (20 eV), 303 *m*/*z* (100% RA). X-ray (from dichloromethane-toluene): space group *Pna*2$_1$, a = 7.5703(5) Å, b = 9.5106(12) Å, c = 20.2404(14) Å. Anal. Calcd for $C_{23}H_{13}N$: C, 91.06; H, 4.32; N, 4.62. Found: C, 91.19; H, 4.36; N, 4.45.

Alternatively, 350 mg (1.1 mmol) of **1c**, 200 mg (2.2 mmol) cuprous cyanide in 10 mL of *N*-methylpyrrolidone could be used. (No reaction was observed in the lower boiling DMF solvent.) The yield of **1g** was 310 mg (93%) after flash chromatography on silica gel (Baker, 43 μm), eluting fractionally with petroleum ether and dichloromethane. This product had mmp and NMR spectra identical to those of **1g** prepared from **1a**.

10-Cyanodibenz[*a*,*c*]anthracene (1h). A stirred mixture of 10-bromodibenz[*a*,*c*]anthracene (32 mg, 0.090 mmol), cuprous cyanide (16 mg, 0.18 mmol), and dimethylformamide (2 mL) was heated at reflux overnight. The resulting brown complex of nitrile and cuprous halide was poured into a solution of ferric chloride and concentrated hydrochloric acid

in water. The reaction mixture was maintained at 60−70 °C for 30 min to decompose the complex, after which the layers were separated. Extraction with dichloromethane afforded a dark brown organic layer that was filtered through a short column of silica gel, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was recrystallized from benzene−ethanol to give 26 mg (95%) of 10-cyanodibenz[*a*,*c*]anthracene as a pale yellow powder: mp 206−207 °C; ^{1}H NMR 9.09 (1H, s), 8.79 (1H, s), 8.63 (1H, m), 8.50 (1H, m), 8.42 (2H, m), 8.11 (1H, d, 8.4 Hz), 7.89 (1H, dd, 7.0, 1.0 Hz), 7.61 (4H, m), 7.48 (1H, dd, 8.4, 7.1 Hz); ^{13}C NMR 133.31, 132.93, 131.00, 130.32, 130.15, 130.09, 129.53, 128.95, 128.90, 128.42, 128.20, 127.67, 127.48, 124.48, 123.99, 123.53, 123.33, 123.27, 123.23, 122.61, 119.00, 117.99, 109.91. Anal. Calcd for $C_{23}H_{13}N$: C, 91.06; H, 4.32; N, 4.62. Found: C, 91.10; H, 4.30; N, 4.59.

Bromination of Anthracene with NBS. The effect of iodine on the bromination of anthracene (**2**) was studied by following the literature procedure[10] in the presence as well as the absence of iodine. Although 9-bromoanthracene (**2a**) was the major product (75% yield) in both cases (together with about 10% 9,10-dibromoanthracene, **2b**, and 5% anthraquinone, 10% unreacted **1** was recovered), the reaction was slower by at least severalfold in the absence of iodine. This was indicated by complete consumption of NBS within 1 h in the presence of iodine, but only about 30% in the absence of iodine; several additional hours were required for the NBS to be consumed in the latter reaction. The isolated yield of 9-bromoanthracene from the literature procedure was 60% (although anthracene and dibromoanthracene were not removed by the workup described).

Bromination of Anthracene with Bromine. Bromination of **2** with 1 equiv of molecular bromine at 0 °C afforded essentially the same product mixture as reaction with NBS. Recrystallization from ethanol failed to separate the anthracene and dibromoanthracene from bromoanthracene. Careful column chromatography (activity I Woelm alumina, eluting fractionally with petroleum ether and dichloromethane) afforded 6.5 g (45%) of relatively pure (≥95%) **2a** from a preparative scale reaction starting with 10 g (56 mmol) of **2**.

Chlorination of 9-Bromoanthracene. A stirred mixture of **2a** (50 mg, 0.19 mmol), *N*-chlorosuccinimide (5.2 mg, 0.039 mmol), and a catalytic amount (5−10 μL) of concentrated hydrochloric acid in carbon tetrachloride (1 mL) was heated to reflux under a nitrogen atmosphere. The progress of the reaction was monitored by removal of a small aliquot and analysis by ^{1}H NMR. The crude reaction mixture was subjected to NMR and GC/MS analysis to determine the identities of the products and their ratio, which was invariant with reaction time at low conversions of **2a**. The products 9,10-dichloroanthracene (**2d**) and 9-bromo-10-chloroanthracene[26] (**2e**) were identified by comparison with authentic compounds, and their ratio was found to be 65:35. 9-Chloroanthracene (**2c**) was ruled out as a potential product by comparison of the ^{1}H NMR spectrum of the crude reaction mixture with that of authentic **2c**.

No reaction between HCl and **1a** occurred under these conditions.

Chlorination of 9-Bromoanthracene and Anthracene. A stirred mixture of **2a** (18.2 mg, 0.071 mmol), **2** (6.4 mg, 0.036), *N*-chlorosuccinimide (5.7 mg, 0.043 mmol), and a catalytic amount (5−10 μL) of concentrated hydrochloric acid in carbon tetrachloride (1 mL) was heated to reflux under a nitrogen atmosphere. The progress of the reaction was monitored by ^{1}H NMR, and aliquots were sampled after about 5%, 10%, 15%, and 20% conversion. The disappearance of bromoanthracene initially was much slower than that of anthracene, and after about 20% of the NCS was consumed, most of the original bromoanthracene remained. ^{1}H NMR analysis of the products revealed formation of **2c** (92% based on NCS consumed), **2d** (4%), and 9-bromo-10-chloroanthracene, **2e** (2%).

Chlorination of 9-Bromoanthracene and 9-Chloroanthracene. A stirred mixture of **2a** (9.3 mg, 0.036 mmol), **2c** (6.3 mg, 0.030 mmol), *N*-chlorosuccinimide (2.9 mg, 0.022 mmol), and a catalytic amount (5−10 μL) of concentrated hydrochloric acid in carbon tetrachloride (1 mL) was heated to reflux under a nitrogen atmosphere. The progress of the reaction was monitored by ^{1}H NMR, and aliquots were sampled after about 5%, 10%, and 30% conversion. The initial rates of disappearance of the haloanthracenes were nearly the same, and proportional amounts (ratio 1.1:1) remained after about 30% of the NCS was consumed.

Bromination of 9-Methylanthracene in the Presence of Iodine. To a suspension of 54 mg (0.28 mmol) of 9-methylanthracene (**3**) and 50 mg (0.28 mmol) of NBS in 0.4 mL of carbon tetrachloride was added a catalytic amount of iodine (one drop of a solution containing 0.2 g of iodine in 10 mL of CCl_4[10]). The mixture was heated at reflux for 1 h. Analysis by ^{1}H NMR revealed 97% conversion to 9-bromo-10-methylanthracene,[27,28] **3a** (67%), 9-(bromomethyl)anthracene,[27,29] **3b** (31%), and 9-bromo-10-(bromomethyl)anthracene,[30] **3e** (2%). Purification by column chromatography (activity III Woelm alumina eluting fractionally with hexanes and dichloromethane, and then methanol) afforded 40 mg (53%) of **3a** and 10 mg of (13%) **3b**, along with 10 mg (17%) of its hydrolysis product 9-(hydroxymethyl)anthracene.

Bromination of 9-Methylanthracene in the Absence of Iodine. A suspension of 54 mg (0.28 mmol) of **3** and 50 mg (0.28 mmol) of NBS in 0.4 mL of carbon tetrachloride was heated at reflux for 1 h, after which ^{1}H NMR analysis revealed 8% conversion to **3b**.[27] Reflux for an additional 23 h followed by analysis by ^{1}H NMR revealed clean conversion to **3b** in 98% yield, together with 2% of **3e**.[30]

At this point, addition of a catalytic amount of iodine (one drop of a solution containing 0.2 g of iodine in 10 mL of CCl_4[10]) followed by reflux for 24 h resulted in no isomerization. However, prolonged reflux in the presence of iodine resulted in the gradual conversion of to lepidopterene, **4**.[22] The residue was taken up in hot cyclohexane and filtered and the filtrate concentrated to afford 61 mg (80%) of **3b**.

Use of 2 equiv of NBS in the absence of iodine accelerated the initial formation of **3b**, which was followed by a very slow reaction to form **3e**.[30]

Chlorination of 9-Methylanthracene. A suspension of 54 mg (0.28 mmol) of **3**, 37 mg (0.28 mmol) of NCS in 0.4 mL of CCl_4, and a catalytic amount (5−10 μL) of concentrated hydrochloric acid was heated at reflux for 1 h. Analysis by ^{1}H NMR revealed conversion of 66% to form mostly (70%) 9-chloro-10-methylanthracene,[28,31] **3c**, and 30% of either 9-(chloromethyl)anthracene,[29] **3d**, in the absence of iodine or **4**[22] in the presence of iodine. Column chromatography (activity III Woelm alumina, eluting fractionally with petroleum ether and dichloromethane) of the reaction performed in the absence of iodine afforded 20 mg (32%) of **3c** and 6 mg (9%) of **3d**.

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Supporting Information Available: Instrumentation and tables of crystallographic data, atomic coordinates, and bond distances and angles for 9-cyanodibenz[*a*,*c*]anthracene. This material is available free of charge via the Internet at http://pubs.acs.org.

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