Reduction of Bridgehead Halogens by an Intramolecular Electron Transfer Radical Mechanism†,[1]

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Reactions of 9,10-dibromo- and 9,10-diiodo-2-nitro-9,10-ethano-9,10-dihydroanthracene (**10** and **11**, respectively) with the tertiary carbanions, **1**, **3**, **5**, and **7**–**9**, proceed exclusively by reduction at the bridgehead with no substitution products being observed. It is proposed that the reduction process occurs by a radical chain mechanism including an intramolecular electron transfer step and β-hydrogen abstraction from alkyl substituents on the participating carbanions. These ethanoanthracenes contain halogens at bridgehead positions that are *meta*- and *para*-benzylic relative to an aromatic nitro group, thus allowing the determination of the relative reactivities of the two benzylic sites within the same molecule. Quantitative studies on the reaction of **11** with sodium salts of 2-ethylmalononitrile and diethyl 2-ethylmalonate reveal that the reduction process is regioselective, with reduction occurring more readily at the benzylic bridgehead position *para* to the nitro group than at the corresponding *meta*-benzylic position. The ratio of *meta*:*para* reduction products, determined for the reaction of the diiodide **11** with several carbanions, was in the range 1:(1.6 ± 0.2). This ratio contrasts with the differences in rate constants (approximately 2 orders of magnitude) determined for other nitrobenzylic systems, known to undergo $S_{RN}1$ substitution reactions with the same nucleophiles. These differences in the ratio of rate constants of regioselective reduction compared with those observed for substitution reactions is discussed in terms of the C–X bond at a bridgehead position lying orthogonal to the plane of the nitroaryl group. As a result of this geometry, the rate of intramolecular electron transfer is significantly reduced and the ratio of *para*-benzylic to *meta*-benzylic reactivity differs only by a factor of less than 2.

The $S_{RN}1$, radical anion, radical chain substitution mechanism is well established for systems as diverse as aromatic substrates,[2] *m*-nitro-,[3] and *p*-nitrobenzylic systems[4] and bridgehead substrates.[5] For nitrobenzylic substrates, the generally accepted steps in the $S_{RN}1$ mechanism are as summarized in eqs 1–4, Scheme 1 (Ar = *m*- or *p*-$O_2NC_6H_4$).

Our studies of the $S_{RN}1$ reactions of sterically hindered *p*-nitrobenzylic derivatives have revealed that not only are the regiochemistry[6] and stereochemistry[7] of this reaction subject to steric effects (specifically branching at the position α to the benzylic carbon), but also the rate constants of dissociation of the intermediate radical anions are greatly reduced in sterically hindered benzylic substrates.[8] This decrease in the rate constants of dissociation (resulting in an overall reduction in the rate constants of substitution) was ascribed to a steric effect. It was proposed that bulky α-substituents caused a preference for conformations in which the carbon–halogen bond (C–X bond) was increasingly in the plane of the aromatic ring, resulting in reduced orbital overlap between the unpaired electron in the π* orbital associated with nitroaryl radical anion and the σ* orbital of the C–X bond. We have demonstrated[3,9] that sterically hindered *m*- and *p*-nitrobenzyl chloride systems react with carbanions, such as those derived from α-alkylmalononitriles or from α-alkylmalonic esters, to give *C*-alkylated products, unless the steric constraints are very severe.

Scheme 1

$$ArCR^1R^2X + Nu^- \longrightarrow ArCR^1R^2X^{-\bullet} + Nu^\bullet \quad (1)$$

$$ArCR^1R^2X^{-\bullet} \longrightarrow ArR^1R^2C^\bullet + X^- \quad (2)$$

$$ArR^1R^2C^\bullet + Nu^- \longrightarrow ArCR^1R^2Nu^{-\bullet} \quad (3)$$

$$ArCR^1R^2Nu^{-\bullet} + ArCR^1R^2X \longrightarrow ArCR^1R^2Nu + ArCR^1R^2X^{-\bullet} \quad (4)$$

In the present work, we report the reactions of a variety of carbanions with substrates in which the carbon–halogen bonds are constrained, by molecular geometry, to be coplanar with the aromatic ring. This constraint was introduced by having the halogens at the bridgehead (and simultaneously at the benzylic position) in ethanoanthracene derivatives. The particular focus was to determine the effect of fixing of the angle between the aromatic ring and the C–X bond at a benzylic bridgehead position (*meta* or *para* to a nitro group on the aromatic ring, within the same molecule) on both the rate constants and preferred reaction pathway. It rapidly became apparent that reactions of compounds **12**-**15** with the carbanions **1**, **3**, **5**, and **7**–**9** resulted in a reduction process (replacement of the bridgehead halogen by hy-

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Table 1. Reactions of Dihalides 10, 11, and 17 with Carbanions 1–9[a]

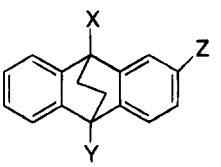
entry	substrate	nucleophile	conditions	isolated yields and product ratios (%)[b]
1[c]	**10**	**8**	60 °C/16 h	**12** *25*, **13** *62*, **16** *4*
2[c,d]	**10**	**8**	60 °C/18 h	**12** *2*, **13** *5*, **16** *89*
3	**11**	**1**	30 °C/45 min	**14** *38*, **15** *58*, **16** *3*
4[e]	**11**	**1**	40 °C/45 min	**14**:**15** = 1:1.83 ± 0.08
5[e,f]	**11**	**1**	30 °C/45 min	**14**:**15** = 1:1.73 ± 0.04
6[e,g]	**11**	**1**	30 °C/45 min	**14**:**15** = 1:1.73 ± 0.02
7[h,i]	**11**	**1**	30 °C/45 min	**11** *77*
8[j]	**11**	**1**	30 °C/45 min	**11** *73*, **14** *7*, **15** *15*
9[k]	**11**	**1**	30 °C/45 min	**11** *10*, **14** *27*, **15** *50*, **16** *7*
10	**11**	**2**	30 °C/45 min	**11** *92*
11	**17**	**1**	30 °C/45 min	**17** *86*
12	**17**	**1**	30 °C/3 h	**17** *59*, **18** *38*
13	**11**	**3**	50 °C/4 h	**11** *10*, **14** *29*, **15** *40*, **16** *12*
14[h]	**11**	**3**	50 °C/4 h	**11** *92*
15[i,j]	**11**	**3**	50 °C/4 h	**11** *79*, **14** *5*, **15** *14*
16[i]	**11**	**4**	50 °C/4 h	**11** *86*
17	**17**	**3**	50 °C/4 h	**17** *68*, **18** *30*
18[l]	**11**	**5**	50 °C/1 h	**11** *62*, **14**:**15** = 1:1.43
19	**11**	**6**	50 °C/4 h	**11** *93*
20[l]	**11**	**7**	50 °C/3 h	**11** *52*, **14**:**15** = 1:1.2.7
21[l]	**11**	**8**	30 °C/30 min	**11** 7, **14** 32, **15** 54, **16** 7
22[i]	**11**	**9**	40 °C/2.5 h	**11** <5, **14** + **19** *15*, **15** + **20** *27*, **16** + **21** + **22** + **23** *6*

[a] Reactions were performed under sunlamp irradiation with substrate concentrations 0.05 M and with salt concentration 0.5 M in DMSO under an atmosphere of nitrogen unless otherwise stated. [b] Except where indicated yields quoted are those of isolated products. All reactions were duplicated and the reproducibility was ±3% of the figures quoted. [c] Reaction was performed in HMPA with 1,2-dimethoxybenzene as internal standard and yields are estimated by analytical reverse phase HPLC. [d] Reaction was performed in the dark. [e] Aliquots of reaction removed at regular time intervals and relative ratio **14**:**15** determined by analytical HPLC with 22% dichloromethane/light petroleum as eluent. [f] Reaction performed with salt concentration of 1 M and with substrate concentration of 0.05 M. [g] Reaction performed with salt concentration of 0.09 M and with substrate concentration of 0.05 M. [h] Reaction was performed with oxygen bubbling through the reaction mixture. [i] No other products were isolated from the reaction. [j] Reaction performed with 0.2 equiv of di-*tert*-butyl nitroxide present. [k] Reaction performed with d_6-DMSO as solvent. The relative ratio of products was determined by analytical HPLC on an isolated mixture of the iodo isomers **14** and **15** and was found to be **14**:**15** = 1:1.75. [l] Ratio of products determined by analytical HPLC, and no yields of isolated products were determined.

drogen) rather than a substitution reaction. This paper reports the scope and mechanism of this reductive process.

Results and Discussion

The carbanions **1**–**9** were allowed to react with the dihalogenated nitroethanoanthracenes **10** and **11**. The "mono-reduced" halides **12**–**15** and the "doubly-reduced" product, 2-nitro-9,10-ethano-9,10-dihydroanthracene (**16**) were produced in these reactions.



$Na^+ {}^-CRR^1R^2$

	R	R^1	R^2
1	Et	CN	CN
2	H	CN	CN
3	Et	CO_2Et	CO_2Et
4	H	CO_2Et	CO_2Et
5	Me	Ac	Ac
6	H	Ac	Ac
7	Me	Ac	CO_2Et
8	Me	CN	CN
9	CD_3	CN	CN

	X	Y	Z
10	Br	Br	NO_2
11	I	I	NO_2
12	H	Br	NO_2
13	Br	H	NO_2
14	H	I	NO_2
15	I	H	NO_2
16	H	H	NO_2
17	I	I	H
18	I	H	H
19	D	I	NO_2
20	I	D	NO_2
21	D	D	NO_2
22	D	H	NO_2
23	H	D	NO_2

The details of these reactions are collected in Table 1, together with those of the unnitrated diiodo compound **17**, which gave the monoiodo derivative **18**. The products in all of these reactions were separated from their respective starting materials by liquid chromatography and were characterized by comparison with authentic samples or by mass spectrometry.

The reaction of the dibromide **10** with the sodium salt **8** was performed using the polar solvent HMPA at high temperature (see entries 1 and 2, Table 1). Despite these harsh reaction conditions, conversion of the dibromide into the reduction products **12**, **13**, and **16** was slow and so subsequent reactions were carried out on the more reactive diiodide **11**. The reaction of **11** with the sodium salt **1** gave the iodo compounds **14** and **15** and the fully dehalogenated product **16** (see entry 3, Table 1). The percentage conversions into products for this reaction as a function of time are shown in Figure 1. Throughout the course of the reaction, the concentration of the isomer **15**, formed by replacement of iodine by hydrogen at the benzylic bridgehead position *para* to the nitro group, is greater than the concentration of isomer **14**, formed from replacement of iodine at the corresponding *meta* position.

During the time that the reaction was monitored (up to 180 min), and during which time the amount of **16** produced was <5%, the ratio of products **14**:**15** was 1:1.74 ± 0.02. This ratio was virtually unchanged by an increase in reaction temperature to 40 °C (see entry 4, Table 1) and was independent of the concentration of salt **1**. With either a 20-fold excess or with a 1.8-fold excess of **1**, the ratio **14**:**15** was unchanged (see entries 5 and 6, Table 1, respectively). The reaction of the diiodide **11** with the sodium salt **2** of malononitrile (see entry 10, Table 1), however, gave only starting material (92% recovery). The reaction of the diiodo compound **17**, with no nitro group present, with **1** also gave only starting material after 45 min incubation at 30 °C, but some conversion into the iodo compound **18** was apparent after 3 h at 30 °C. This reaction was much slower than that

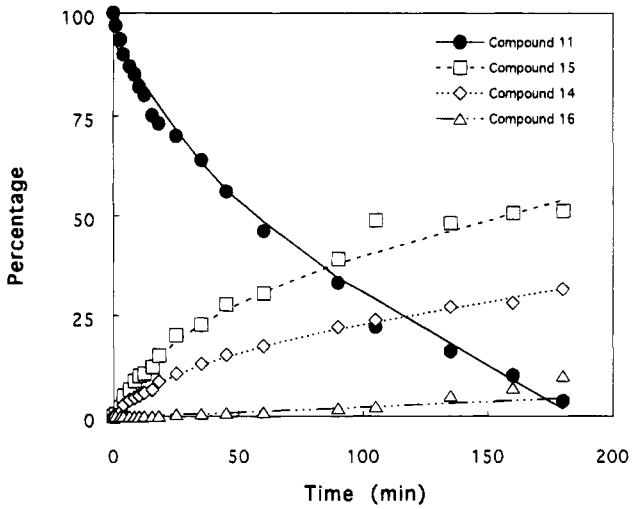


Figure 1. Time-course of the product distributions for the reaction of **11** (0.05 M in DMSO) with 3 mol equiv of the salt **1**, at 30 °C and under a N_2 atmosphere.

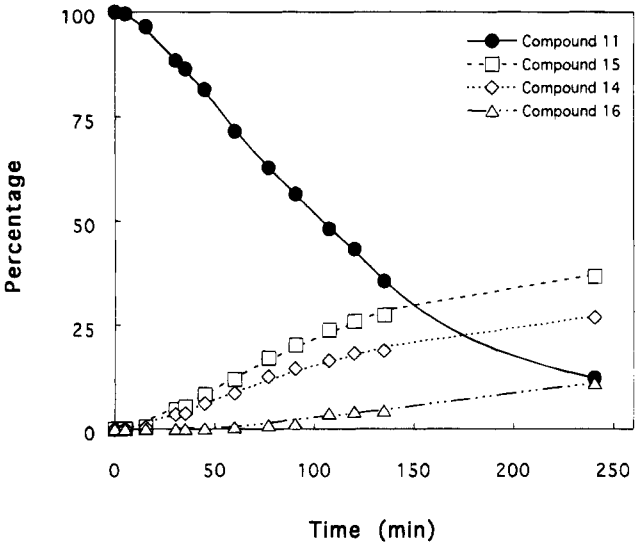


Figure 2. Time-course of the product distributions for the reaction of **11** (0.05 M in DMSO) with 10 mol equiv of the salt **3**, at 30 °C and under a N_2 atmosphere.

for nitro analogue **11** with the same salt (compare entry 3 with entry 12, Table 1).

The reaction of the diiodide **11** with the sodium salt **3** (see entry 13, Table 1 and Figure 2) again gave **14** and **15**, but under more vigorous conditions.

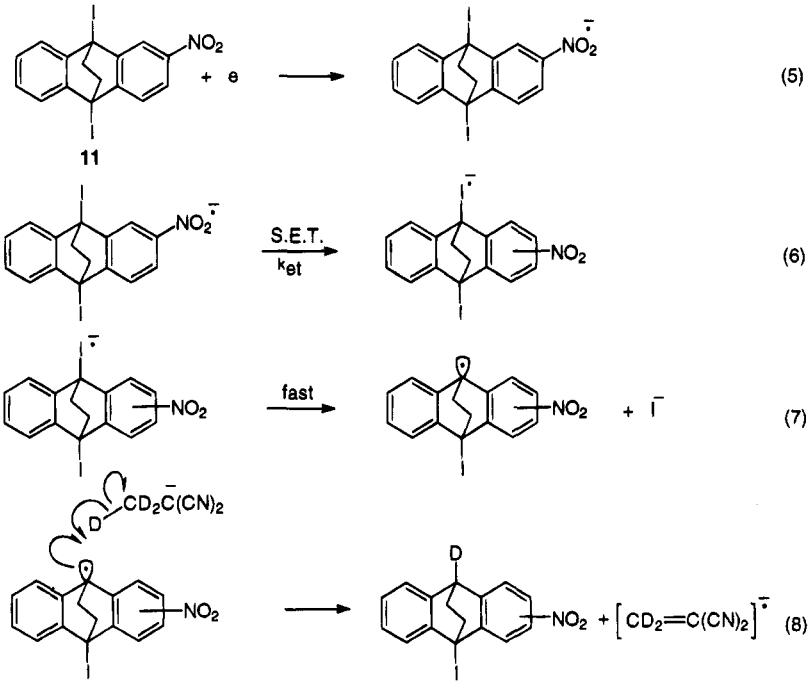
Clearly, from the data in Figure 2, compound **15** is produced at a greater rate than **14**. The ratio of **14** and **15** throughout the first 4 h was 1:1.34 ± 0.03. The reaction of the diiodide **11** with the sodium salt of diethyl malonate (**4**), however, gave 86% recovered starting material with no other products isolated (see entry 16, Table 1). The reaction of the diiodidé **17**, with no nitro group present, with the sodium salt of diethyl 2-ethylmalonate **3** gave the reduced product **18**, but this reaction was again slower than that for the nitro analogue **11** with the same salt (compare entries 13 and 17, Table 1). The reactions between **11** and the sodium salts **5** and **7** also gave **14** and **15** (see entries 18 and 20, Table 1), but with only 40 and 50% conversion of starting material, respectively. The reaction of the **11** with the sodium salt of acetylacetone **6** (see entry 19, Table 1), under identical reaction conditions to that used with the salt **5** gave only starting material. Treatment of **11** with the salt **8** showed similar rates of conversion of starting material into products to that observed for the reaction of **11** with **1** (see entry 21, Table 1).

The series of reactions of the dibromide **10**, and the diiodide **11** with various carbanions (as summarized in Table 1) to give only the corresponding mixtures of "reduced" products in reasonable yield is unusual in that these carbanions normally give substitution products by the $S_{RN}1$ process.[9] The observation that the reaction of **10** with **8** in HMPA also gave only reduction products with no C-alkylation (see entries 1 and 2, Table 1) discounts the remote possibility that the reduction process results from the change of solvent from HMPA[9] to DMSO in the majority of reactions in this present work.

The mechanism for this reduction process was examined by performing the reactions in the presence of traditional inhibitors of radical and radical anion processes. Thus it is clear from the results given in Table 1 that the reactions of **11** with **2** and **3** to give the reduction products **14**–**16** are completely inhibited by oxygen and strongly retarded by di-*tert*-butyl nitroxide (compare entry 3 with 7 and 8, and entry 13 with 14 and 15 in Table 1). These observations indicate that the reduction of **11** is probably taking place by a radical chain mechanism related to the $S_{RN}1$ process. A mechanism for the reduction process involves an initial one-electron reduction of the nitro group, followed by intramolecular single electron transfer from the π^* orbital of the nitroaryl moiety to the σ^* orbital of the carbon iodine (bridgehead) bond. Subsequent fission of this bond to release a halide leaves the bridgehead radical. This bridgehead radical may now react through one of two possible pathways. The first pathway would involve a second electron transfer to give an anion at the bridgehead followed by protonation by a suitable source to give the reduced product. A second pathway involves abstraction of a hydrogen atom from a suitable source to give the reduced product. In an attempt to determine which of the above two pathways was operating, the following additional reactions were performed.

Reaction of **11** with **1** in d_6-DMSO gave **14**–**16** (see entry 9, Table 1), none of which showed any signs of deuterium incorporation (by mass spectrometry). This result showed that DMSO was not the source of hydrogens for the reduction. The complete lack of reaction between **11** and the salts **2**, **4**, and **6**, derived from malononitrile, diethyl malonate, and acetylacetone, respectively, indicated that the alkyl substituent in the nucleophile was necessary for reduction to take place. This observation is consistent with the possibility that the alkyl group is the source of hydrogen needed for the radical chain reduction process. To test this hypothesis the reaction of **11** with the salt **9** of 2-(trideuteromethyl)-malononitrile was carried out. This reaction gave the deuterated products **19**–**23** and the undeuterated compounds **14**–**16** (see entry 22, Table 1). The percentage incorporation of deuterium into the inseparable mixture of compounds **14** and **19** was determined by mass spectroscopy and was found to be 89%. Similarly, the percentage incorporation of deuterium into the inseparable mixture of compounds **15** and **20** was found to be 87%. The ratio of the isomers {**14** + **19**}:{**15** + **20**} was determined by analytical HPLC and was found to be 1:1.53. The overall percentage of deuterium incorporated into the inseparable mixture of compounds **16**, **22**, and **23** could not be determined by mass spectroscopy due to the complexity of the mixture and instead was estimated by ^{1}H NMR spectroscopy and found to be approximately

Scheme 2



72%. This incorporation of deuterium into the reduction products **14** (to give **19**), **15** (to give **20**), and 2-nitro-9,-10-ethanoanthracene (**16**) (to give **21**–**23**) clearly shows not only that the β-hydrogen of 2-methylmalononitrile is a source of the hydrogen for the reduction process, but also that the reduction involves a radical abstraction step. Thus, in general, the β-hydrogens in the carbanions are the source of the hydrogen atoms in the reduction process. The mechanism proposed in Scheme 2 (illustrating the incorporation of deuterium) is consistent with the above and can be generalized to all of the reactions with tertiary carbanions with β-hydrogens (deuteriums).

The first step in the mechanism, eq 5, involves a one-electron reduction of the nitroaryl group. The source of this electron is a tertiary carbanion (initiation) or the radical anion produced by the β-hydrogen abstraction as shown in eq 8 (propagation). This step is followed by an intramolecular single electron transfer process (S.E.T.), with a rate constant, k_{et}, from the nitro radical anion to either of the bridgehead iodines (eq 6) with subsequent formation of the bridgehead radical species shown in eq 7. The bridgehead radical abstracts a β-hydrogen (deuterium) from a molecule of the tertiary carbanion to give the mixture of deuterated isomers **19** and **20**, while also generating a radical anion, *e.g.*, that of 1,1-dicyanoethylene, as shown in eq 8. The doubly reduced compound **21** is produced by subsequent reduction of the isomers **19** and **20** by a mechanism similar to that given in eq 5–8. The radical anion derived from the tertiary carbanion, *e.g.*, that produced from 1,1-dicyanoethylene (see equation 8), acts as a chain carrier providing the electron for the reduction process in eq 5.

The incomplete incorporation of deuterium into **19**, **20**, and **23** of 89, 87, and 72%, respectively, indicate that there is an alternate source of hydrogen in these reduction reactions. Even "dry" DMSO may contain some water, and if this water is associated with the deuterated carbanion by strong hydrogen bonding, hydrogen abstraction may take place to give the reduced product (RH) and the chain carrier ($[CD_2C(CN)_2]^{\bullet-}$) by the process shown in Figure 3.

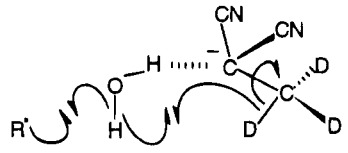


Figure 3. Bridgehead radical (R$^{\bullet}$) abstracting a hydrogen from the water molecule, which is hydrogen bonded to the carbanion of 2-(trideuteromethyl)malononitrile.

The dibromide **10** and the diiodide **11** each react with carbanions to give reduction preferentially at the bridgehead position *para* benzylic to the nitro group (that is, the ratio *para*:*meta* $\approx$ 1.4–1.8). The reactivity of the *para*-benzylic position is expected to be greater than that of the *meta*-benzylic position by analogy with the reactivity of *m*- and *p*-nitrobenzylic substrates in reactions that take place by an $S_{RN}1$ process.[3,10] It is evident, however, that the *magnitude* of this difference in this study is substantially smaller (by approximately 2 orders of magnitude) than the difference in reactivity between the *meta*- and the *para*-benzylic positions as measured by the rate constants for the intramolecular electron transfer in nitrobenzyl halide radicals[8] and in the observed reaction rates for analogous *m*- and *p*-nitrobenzylic substrates involved in $S_{RN}1$ reactions.[3,10] The much smaller difference (less than 2-fold) in this present study can be attributed to the orthogonal nature of the C–X σ^* orbital with the π^* orbital of the nitroaryl group. This orthogonality effectively reduces the extent of orbital overlap between the electron donor and acceptor groups, and as a result the rate constants of intramolecular electron transfer and consequent dissociation (see eqs 6 and 7) are substantially reduced.

The reactions involving the diiodide **17** (with no nitro group present) with carbanions **1** and **3** indicate that competitive direct reduction of the bridgehead C–I bond can occur (see entries 12 and 17, Table 1). These results suggest that the difference between intramolecular (one-electron) reduction and outer-sphere direct (one-electron)

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reduction of the C–X bond, for the reactions of the diiodide **11** and carbanions **1**–**9**, is approximately 1 order of magnitude. This difference could be explained readily if the nitroaryl radical anion of **11** catalyzes intermolecular electron transfer. Thereby, another mechanism explaining the reduction reaction involves the reduction of the C–I bond at the bridgehead of one molecule by intermolecular electron transfer from the nitroaryl radical anion of another molecule of **11**. Such intermolecular electron transfer processes would also need to be regioselective in nature, favoring the *para*-benzylic position over the corresponding *meta* position, to explain our observations, but this mode of reduction is less likely for the reaction of the diiodide **11** with the salts **1**–**9** than for the corresponding reactions of the bromo analogue **10** due to the greater reactivity of the iodo system. The fact that there is only 1 order of magnitude difference in the rates of intramolecular and intermolecular reductions of **11** and **17**, respectively, under similar reaction conditions again points to the importance of the orthogonality of the σ^* orbital of the C–X bond and the π^* orbital of the nitroaryl group in controlling the intramolecular electron-transfer rate constant. In other systems where there is greater overlap of these σ^* and π^* orbitals, there is a much greater discrimination in favor of the intramolecular reduction (substitution).

In an attempt to determine whether there was an intrinsic difference in reactivity between the *meta* and *para* bridgehead halogens, the dihalides **10** and **11** were treated with tributyltin hydride under standard reaction conditions.[11] Quantitative analysis of the reaction products from reaction of **10** and **11** with tributyltin hydride showed that the reactions gave the reduction products **12** and **13**, and **14** and **15**, in the ratios 1:1.11 ± 0.07 and 1:1.06 ± 0.08, respectively. These results indicate a lack of discrimination in the direct reduction of the carbon halogen bond at the bridgehead, *i.e.*, halogens at either the *meta*- or *para*-benzylic positions show equal probability within experimental error toward replacement by hydrogen when treated with external reducing agents. Thus it would appear that the difference in rate constants of reduction at *meta*- and *para*-benzylic positions of **10** and **11** are the result of a regioselective electron transfer from the radical anion of the nitroaryl group to the bridgehead halogens. That is, the nitroaryl group is playing some significant role in the regioselective reduction of **10** and **11**.

Experimental Section

Melting points were determined thermoelectrically on a Reichert hot-stage melting point apparatus and are uncorrected. ^{1}H NMR spectra were determined on either a Bruker AMX400 (400 MHz) or a Bruker AC200 (200 MHz) spectrometer on 5–10% solutions in $CDCl_3$. ^{1}H chemical shifts are quoted in ppm downfield from $SiMe_4$. Infrared spectra were recorded using either a Biorad 20-80 FTIR or Perkin-Elmer 1600 series FTIR spectrophotometers in the solvent specified and ultraviolet spectra were recorded using a Hitachi 150-20 spectrophotometer in the solvent specified. Mass spectra were determined using an AEI model MS902 at 70 eV and are expressed in percentage abundance relative to the base peak. Microanalyses were carried out by either the Chemical and Micro Analytical Service Pty. Ltd., Melbourne, or the Microanalysis Unit at the University of New South Wales, Sydney. Reaction mixtures were "worked up" by diluting with water followed by two-fold extraction with ethyl acetate, washing the organic phase with water and brine, drying with anhydrous sodium sulfate, and removal of solvent under reduced pressure to give the crude product. Flash chromatography[12] was performed on Merck silica gel 60 (230–240 mesh). Light petroleum refers to the fraction of bp 65–70 °C and all other solvents were redistilled prior to use. Anion precursors, malononitrile, 2-methylmalononitrile, 2-ethylmalononitrile, diethyl 2-ethylmalonate, diethyl malonate, 3-methyl-2,4-pentanedione, acetylacetone, and ethyl 2-methyl-3-oxobutanoate were commercial samples and were purified by distillation under reduced pressure using a Kugelrohr apparatus prior to use.

Preparation of Starting Materials and Authentic Samples. 2-(Trideuteromethyl)malononitrile: A solution of freshly distilled malononitrile (1.0 g, 15.2 mmol) in THF (10 mL) was treated with sodium hydride (400 mg, 16.7 mmol) at 20 °C and the reaction stirred for 10 min. Methyl iodide (99.9% deuterium, 2.21 g, 15.2 mmol) was added dropwise and the reaction mixture stirred until no precipitate remained. The mixture was quenched with water and worked up in the usual fashion. The crude product (0.89 g) was purified by HPLC using 20% ethyl acetate/light petroleum as eluent and the least polar component was distilled under reduced pressure to give 2-(trideuteromethyl)malononitrile (330 mg, 27%), mp 31–33 °C (mp 32–34 °C).[13] ^{1}H NMR spectroscopy confirmed ≥99.5% deuterium in the methyl group.

9,10-Dibromo-2-nitro-9,10-ethano-9,10-dihydroanthracene (10). 9,10-Dibromo-9,10-ethano-9,10-dihydroanthracene (**19**)[14] (2.0 g, 5.5 mmol) was dissolved in acetic anhydride (30 mL) at 20 °C and rapidly added to a finely ground suspension of copper(II) nitrate trihydrate (6 g, 25 mmol, 4.5 equiv) in acetic anhydride (40 mL) at 20 °C. After 72 h the reaction was quenched with water and worked up. The crude product (3.6 g) was chromatographed on silica gel with 15% ethyl acetate/light petroleum as eluent. Recrystallization of the least polar component (1.61 g) from ethanol gave pure **10** (1.43 g, 65%), mp 109–111 °C. ^{1}H NMR (400 MHz): δ 2.42 (s, 4H), [AA'XX' pattern] 7.30 (m, 2H), 7.75 (m, 2H); 7.92 (d, 1H, H4, $J_{3,4}$ = 8.40 Hz), 8.12 (dd, 1H, H3, $J_{1,3}$ = 2.20, $J_{3,4}$ = 8.40 Hz), 8.62 (d, 1H, H1, $J_{1,3}$ = 2.20 Hz). IR (EtOH) 1590, 1515, 1490, 930 cm^{-1}. UV (EtOH) 271 nm (ϵ 6.2 × 10^3). Mass spectrum *m/z* 411 (M + 4, 4), 409 (M + 2, 13), 407 (M, 6), 475 (100), 384 (9), 383 (46), 382 (20), 381 (100), 380 (10), 379 (53), 338 (8), 337 (10), 336 (23), 335 (17), 334 (15), 256 (20), 254 (25), 202 (20). Anal. Calcd for $C_{16}H_{11}Br_2NO_2$: C, 47.0; H, 2.7; N, 3.4%. Found: C, 47.4; H, 2.8; N, 3.3%.

9,10-Diiodo-2-nitro-9,10-ethano-9,10-dihydroanthracene (11). 9,10-Diiodo-9,10-ethano-9,10-dihydroanthracene (**17**) (1.0 g, 2.2 mmol) was dissolved in hot acetic anhydride (50 mL). The mixture was chilled to 0 °C, nitric acid (10 mL, 70% w/w) was added, and the mixture was stirred at 0 °C for a further 5 min. The reaction mixture on workup gave a crude product (1.31 g) which was chromatographed on silica gel with 10% ethyl acetate/light petroleum as eluent. The more polar product (1.08 g) on recrystallization from methanol/ethyl acetate gave **11** (0.79 g, 72%), mp 140–142 °C. ^{1}H NMR (200 MHz): δ 2.63 (s, 4H), [AA'XX' pattern] 7.28 (m, 2H), 7.67 (m, 2H); 7.91 (d, 1H, H4, $J_{3,4}$ = 8.36 Hz), 8.08 (dd, 1H, H3, $J_{1,3}$ = 2.22, $J_{3,4}$ = 8.36 Hz), 8.62 (d, 1H, H1, $J_{1,3}$ = 2.22 Hz). IR ($CHCl_3$) 1590, 1526, 1415, 906 cm^{-1}. UV ($CHCl_3$) 274 nm (ϵ 7.7 × 10^3). Mass spectrum *m/z* 504 (M + 1, 1%), 503 (M, 5), 475 (100), 429 (10), 376 (50), 302 (45), 249 (35), 203 (35), 202 (92), 176 (25), 175 (45), 127 (10), 101(25), 88 (10), 75 (8). Anal. Calcd for $C_{16}H_{11}I_2NO_2$: C, 38.1; H, 2.2; N, 2.8%. Found: C, 38.4; H, 2.1; N, 2.7%.

9-Bromo-3-nitro-9,10-ethano-9,10-dihydroanthracene (12) and 9-Bromo-2-nitro-9,10-ethano-9,10-dihydroanthracene (13). Fuming nitric acid (0.40 g) was added slowly to a solution of glacial acetic acid (0.20 g) and acetic anhydride (0.20 g) cooled at 5–10 °C. This reagent was added dropwise over 2 min to a stirred solution of 9-bromo-9,10-

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ethano-9,10-dihydroanthracene[15] (0.48 g) in acetic anhydride (3.0 mL) cooled to 0 °C. The reaction mixture was stirred at 0–5 °C for a further 3 h, by which time all of the starting material had dissolved. The reaction mixture was diluted with water and worked up in the usual way by extraction with chloroform. The crude product was chromatographed on silica gel with 30% ethyl acetate/light petroleum as eluent to separate the mixture of **12** and **13** from the dinitrated material. Chromatography of the mononitrated compounds on silica gel with 10% ethyl acetate/light petroleum as eluent gave **12** as the less polar isomer. Recrystallization from ethanol gave white crystals of **12** (82 mg, 15%), mp 123–125 °C. ^{1}H NMR (200 MHz): δ 1.92 (m, 2H), 2.31 (m, 2H), 4.48 (t, 1H, H10, J = 2.7 Hz), 7.23 (m, 2H), 7.29 (m, 1H), 7.72 (dm, 1H, H8, $J_{7,8}$ = 6.15 Hz), 7.88 (d, 1H, H1, $J_{1,2}$ = 8.25 Hz), 8.13 (dd, 1H, H2, $J_{1,2}$ = 8.25 Hz, $J_{2,4}$ = 2.18), 8.17 (d, 1H, H4, $J_{2,4}$ = 2.18 Hz). IR ($CHCl_3$) 1515, 1455, 1340, 1295, 1150, 1080, 900 cm^{-1}. UV ($CHCl_3$) 272 nm (ϵ 8.4 × 10^3). Mass spectrum *m/z* 331 (M + 2, 7%), 329 (M, 6), 304 (17), 303 (95), 302 (12),301 (100), 258 (16), 257 (19), 256 (24), 255 (16), 245 (7), 243 (5), 202 (15), 176 (83), 88 (43). Anal. Calcd for $C_{16}H_{12}BrNO_2$: C, 58.2; H, 3.7; N, 4.2%. Found: C, 57.9; H, 3.8; N, 4.0%. The more polar component on recrystallization from ethanol gave **13** (280 mg, 51%), mp 166–168 °C. ^{1}H NMR (200 MHz): δ 1.92 (m, 2H), 2.30 (m, 2H), 4.48 (t, 1H, H10, J = 2.8 Hz), 7.24 (m, 2H), 7.29 (m, 1H), 7.43 (d, 1H, H4, $J_{3,4}$ = 8.10 Hz), 7.76 (dm, 1H, H8, $J_{7,8}$ = 6.9 Hz), 8.09 (dd, 1H, H3, $J_{1,3}$ = 2.25, $J_{3,4}$ = 8.10 Hz), 8.62 (d, 1H, H1, $J_{1,3}$ = 2.25 Hz). IR ($CHCl_3$) 1590, 1515, 1450, 1345, 1155, 1080, 905 cm^{-1}. UV ($CHCl_3$) 279 nm (ϵ 8.7 × 10^3). Mass spectrum *m/z* 331 (M + 2, 8%), 329 (M, 9), 304 (15), 303 (93), 302 (16), 301 (100), 273 (4), 271 (2), 258 (9), 257 (15), 256 (6), 255 (17), 245 (6), 243 (8), 202 (14), 176 (58), 88 (22). Anal. Calcd for $C_{16}H_{12}BrNO_2$: C, 58.2; H, 3.7; N, 4.2%. Found: C, 58.5; H, 4.0; N, 4.0%.

9-Iodo-3-nitro-9,10-ethano-9,10-dihydroanthracene (14) and 9-iodo-2-nitro-9,10-ethano-9,10-dihydroanthracene (15). 9-Iodo-9,10-ethano-9,10-dihydroanthracene (**18**)[16] (2.1 g, 6.4 mmol) was dissolved in acetic anhydride (20 mL). This solution was rapidly added to a stirred, finely ground suspension of copper(II) nitrate trihydrate (2.3 g, 9.6 mmol, 1.5 equiv) in acetic anhydride (10 mL). The reaction mixture was stirred at 20 °C for 10 min, quenched with water, and worked up, and the crude orange oil (1.30 g) was chromatographed on silica gel with a 5–10% ethyl acetate/light petroleum gradient eluent. The least polar component on recrystallization from methanol/ethyl acetate gave starting material **18** (0.21 g). The next more polar component (0.53 g) on recrystallization from methanol/ethyl acetate gave **14** (0.47 g, 20%), mp 124–125.5 °C. ^{1}H NMR (200 MHz): δ 1.89 (m, 2H), 2.47 (m, 2H), 4.5 (t, 1H, H10, J = 2.74 Hz), 7.22 (m, 3H), 7.69 (m, 1H), 7.87 (d, 1H, H1, $J_{1,2}$ = 8.38 Hz), 8.05 (dd, 1H, H2, $J_{2,4}$ = 2.22, $J_{1,2}$ = 8.38 Hz), 8.09 (d, 1H, H4, $J_{2,4}$ = 2.22 Hz). IR ($CHCl_3$) 1588, 1546, 1502, 1476, 1347, 907 cm^{-1}. UV ($CHCl_3$) 275 nm (ϵ 9.3 × 10^3). Mass spectrum *m/z* 378 (M + 1, 3%), 377 (M, 8), 350 (18), 349 (100), 304 (28), 303 (10), 291 (8), 203 (9), 202 (12), 177 (10), 176 (26), 101 (8), 88 (22), 69 (12), 57 (8). Anal. Calcd for $C_{16}H_{12}INO_2$: C, 50.9; H, 3.5; N, 3.6 %. Found: C, 51.3; H, 3.5; N, 3.6%. The more polar component (1.32 g) on recrystallization from methanol/ethyl acetate gave **15** (1.23 g, 51%), mp 163.5–164 °C. ^{1}H NMR (200 MHz): δ 1.93 (m, 2H), 2.50 (m, 2H), 4.52 (t, 1H, H10, J = 2.72 Hz), 7.22 (m, 3H), 7.39 (d, 1H, H4, $J_{3,4}$ = 8.03 Hz), 7.71 (m, 1H), 8.07 (dd, 1H, H3, $J_{1,3}$ = 2.40, $J_{3,4}$ = 8.03 Hz), 8.62 (d, 1H, H1, $J_{1,3}$ = 2.40 Hz). IR ($CHCl_3$) 1522, 1460, 1349, 1210, 904 cm^{-1}. UV ($CHCl_3$) 282 nm (ϵ 8.7 × 10^3). Mass spectrum *m/z* 378 (M + 1, 1%), 377 (M, 2), 350 (18), 349 (100), 303 (11), 291 (8), 203 (8), 202 (13), 176 (45), 164 (8), 101 (12), 88 (18), 75 (8). Anal. Calcd for $C_{16}H_{12}INO_2$: C, 50.9; H, 3.5; N, 3.6%. Found: C, 51.4; H, 3.3; N, 3.6%.

9,10-Diiodo-9,10-ethano-9,10-dihydroanthracene (17). 9,10-Diiodoanthracene[17] (4.76 g, 11 mmol) was suspended in toluene (40 mL) in an autoclave (315 mL) and treated with ethylene at 160 °C using the method of Wilhelm and Schmidt.[18] After 48 h the reaction vessel was cooled, the excess of ethylene was vented, and the mixture was poured onto water. The reaction was worked up and the crude product (5.8 g) was chromatographed on silica gel with 15% ethyl acetate/light petroleum as eluent and on recrystallization from methanol/ethyl acetate gave pure **17** (4.25 g, 84%), mp 149–151 °C. ^{1}H NMR (200 MHz) δ 2.58 (s, 4H), [AA'XX' pattern] 7.20 (m, 4H); 7.66 (m, 4H). UV ($CHCl_3$) 240 nm (ϵ 3.8 × 10^3), 256 (4.0 × 10^3). Mass spectrum *m/z* 459 (M + 1, 4%), 458 (M, 17), 431 (17), 430 (100), 384 (20), 352 (23), 331 (44), 304 (25), 205 (12), 204 (60), 203 (35), 202 (48), 176 (40), 102 (20), 101 (50), 88 (40). Anal. Calcd for $C_{16}H_{12}I_2$: C 42.0; H, 2.6%. Found: C, 42.3; H, 2.8%.

Reactions of 10, 11, and 17 with Carbanions. General Procedure. These reactions were carried out under the general conditions specified in Table 1. The general procedure involved dissolving the substrate in DMSO, deoxygenating the solution by passage of dry nitrogen gas through the solution for 5 min, and addition of a solution of the appropriate salt directly to the reaction mixture. Sodium salts were generated *in situ* immediately prior to use by the addition of an excess of sodium hydride (60% dispersion in oil) to a solution of the corresponding conjugate acid in DMSO. After 10 min the solution was filtered under positive nitrogen pressure and deoxygenated by passing a stream of dry nitrogen through the solution for 5 min. Reactions performed under irradiation were carried out in a flask 0.5 m from a Philips 240 V, 500 W sunlamp. All reactions were carried out under an atmosphere of dry nitrogen unless otherwise stated (see Table 1). Reactions performed under "oxygen" were performed with oxygen bubbling through the reaction mixture, and reactions in the presence of di-*tert*-butyl nitroxide[19] (0.2 mol/mole of substrate, see Table 1) were performed with introduction of the nitroxide prior to addition of the solution of the carbanion. Reaction temperatures were regulated by an external water bath and are believed to be accurate to ±1 °C. The volumes of DMSO in the component solutions were chosen to give a final volume of DMSO such that the resulting concentrations were as given in Table 1. Reaction mixtures were worked up by quenching with water followed immediately by three-fold extraction into dichloromethane, washing the organic phase with water and brine, drying with anhydrous sodium sulfate, and removal of solvent under reduced pressure to give the crude product. Unless otherwise stated, flash chromatography and analytical HPLC analysis were performed using 22% dichloromethane/light petroleum as eluent. All isolated products were shown to be identical with corresponding authentic samples by TLC, and IR, and ^{1}H NMR spectroscopy. Where quantitative measurements were obtained using analytical HPLC, a measured amount of a stock solution of the appropriate internal standard was added to aliquots of the reaction mixture taken at various time intervals during the course of the reaction. These reaction samples were diluted with either methanol or dichloromethane where appropriate and chromatographed in the solvent of choice. The quantitative analysis for the "reduction" of **10** with **1** used 1,2-dimethoxybenzene as internal standard, and for **11** with **1** and **3** used *p*-nitroanisole as internal standard. Quantitative measurements were obtained using a Hewlett Packard 3393A integrator system. The quantitative analysis of the reaction of **11** with **3**, given in Figure 1, was carried out using **3** (0.15 M, 3 mol equiv) to ensure a conveniently measurable rate of conversion of **11** into products, otherwise reaction conditions remained identical with those reported for entry 3, Table 1.

Reaction of 10 with 8 (see entries 1 and 2, Table 1). At the appropriate time interval an aliquot of reaction mixture (50 μL) was removed and analyzed by reverse phase analytical HPLC with 80% methanol/water eluent to estimate yields of the reduced products **12**, **13** and 2-nitro-9,10-ethano-9,10-dihydroanthracene (**16**).[20]

Reactions of 11 with 1 or 2 (see entries 3–10, Table 1). Entry 3: The crude product from the reaction of **11** with

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1 (total volume of DMSO = 6.0 mL) was chromatographed on silica gel, and the isolated products on recrystallization gave **14** (43 mg, 38%) from methanol/ethyl acetate, **15** (66 mg, 58%) from methanol/ethyl acetate, and **16** (2 mg, 3%) from methanol. **Entries 4–6**: Aliquots from the reaction mixture resulting from treatment of **11** with **1** (total volume of DMSO = 6.0 mL) were removed at various time intervals and analyzed by analytical HPLC. The relative ratio of the isomers **14**:**15** throughout the 45 min the reaction was monitored were found to be 1:1.83 ± 0.08, 1:1.73 ± 0.04 and 1:1.73 ± 0.02, for entries 4–6 (Table 1), respectively. **Entry 7**: An experiment performed using identical reaction conditions with that of entry 3, but with oxygen bubbling through the reaction mixture was chromatographed on silica gel and on recrystallization gave only starting material **11** (115 mg, 77% recovery) from methanol. No other products were observed. **Entry 8**: Another experiment using identical reaction conditions with that of entry 3, but with di-*tert*-butyl nitroxide (0.2 equiv) added, was chromatographed on silica gel and on recrystallization gave starting material **11** (110 mg, 73% recovery) from methanol, and the products **14** (8 mg, 7%) and **15** (17 mg, 15%) each from methanol/ethyl acetate. **Entry 9**: A third experiment was performed using the reaction conditions specified in entry 3, but with d_6-DMSO (2 mL) as the reaction solvent. After 45 min the reaction was quenched and the ratio **14**:**15** estimated as 1:1.75 by analytical HPLC. The remaining crude product (70 mg) was chromatographed on silica gel and on recrystallization gave starting material **11** (5 mg, 10% recovery) from methanol, **14** (10 mg, 27%) and **15** (18 mg, 50%) each from methanol/ethyl acetate and **16** (2 mg, 7%) from methanol. **Entry 10**: The crude product from the reaction of **11** with **2** (total volume of DMSO = 4.2 mL) was chromatographed on silica gel with 5% ethyl acetate/light petroleum as eluent and on recrystallization from methanol gave only starting material **11** (98 mg, 92% recovery). No other products were isolated.

Reaction of 17 with 1 or 3 (see entries 11, 12 and 17, Table 1). Entry 11: The crude product from the reaction of **17** with **1** (total volume of DMSO = 6.1 mL) was chromatographed on silica gel with 5% ethyl acetate/light petroleum as eluent and on recrystallization from methanol gave only starting material **17** (120 mg, 86% recovery). No other products were isolated. **Entry 12**: The crude product from the reaction of **11** with **3** (total volume of DMSO = 4.7 mL) was chromatographed on silica gel with 5% ethyl acetate/light petroleum as eluent and on recrystallization of each product from methanol gave starting material **17** (64 mg, 59% recovery) and the monoiodide **18** (28 mg, 36%). **Entry 17**: The reaction between **17** and the salt **3** (total volume of DMSO = 6.5 mL) followed by workup as above gave starting material **17** (103 mg, 68% recovery) and the monoiodide **18** (32 mg, 30%).

Reaction of 11 with 3 or 4 (see entries 13–16, Table 1). Entry 13: The reaction between **11** and the salt **3** (total volume of DMSO = 6.0 mL) followed by workup as above gave starting material **11** (15 mg, 10% recovery) from methanol, **14** (33 mg, 29%) and **15** (46 mg, 40%) each from methanol/ethyl acetate and **16** (9 mg, 12%) from methanol. **Entry 14**: An experiment performed using identical reaction conditions with those for entry 13, but with a total reaction volume of 2.3 mL and performed with oxygen bubbling through the reaction mixture, gave only starting material **11** (54 mg, 92% recovery) from methanol after the usual workup. No other products were observed. **Entry 15**: A further experiment under identical reaction conditions with those for entry 13, but with di-*tert*-butyl nitroxide (0.2 equiv) added on workup and separation of the components in the usual way gave starting material **11** (119 mg, 79% recovery) from methanol, and **14** (6 mg, 5%) and **15** (16 mg, 14%) each from methanol/ethyl acetate. **Entry 16**: The reaction between **11** and the salt **4** (total volume of DMSO = 2.0 mL) followed by workup as above gave starting material **11** (43 mg, 86% recovery) from methanol. No other products were isolated.

Reaction of 11 with 5 or 6 (see entries 18 and 19, Table 1). Entry 18: The reaction between **11** and the salt **5** (total volume of DMSO = 4.0 mL) followed by workup as above gave starting material **11** (62 mg, 62% recovery) from methanol. The remaining component (22 mg) was determined to be a mixture of the isomers **14** and **15** in the ratio 1:1.43 as estimated by analytical HPLC. **Entry 19**: The reaction between **11** and the salt **6** (total volume of DMSO = 8.0 mL) followed by workup as above gave only starting material **11** (186 mg, 93% recovery) from methanol. No other products were isolated.

Reaction of 11 with 7 (see entry 20, Table 1). The reaction between **11** and the salt **7** (total volume of DMSO = 4.0 mL) followed by workup as above gave starting material **11** (53 mg, 52% recovery) from methanol and a mixture (46 mg) of the isomers **14** and **15** in the ratio 1:2.7 (estimated by analytical HPLC).

Reaction of 11 with 8 or 9 (see entries 21 and 22, Table 1). Entry 21: The reaction between **11** and the salt **8** (total volume of DMSO = 2.0 mL) followed by workup gave a crude product (47 mg) that was analyzed by analytical HPLC and shown to be a mixture of starting material **11** (7%), products **14** and **15** in the ratio 1:1.71, and **16** (7%). **Entry 22**: The reaction between **11** and the salt **9** (total volume of DMSO = 3.0 mL) followed by workup as above gave a reaction mixture that was analyzed by analytical HPLC and shown to be a mixture of starting material **11** (<5%), products **14** and **15** in the ratio 1:1.53, and **16** (10%). The remaining crude material (≈40 mg) was purified by HPLC, and the least polar component was an inseparable mixture of 10-deutero-9-iodo-3-nitro-9,10-ethano-9,10-dihydroanthracene (**20**) and 9-iodo-3-nitro-9,10-ethano-9,10-dihydroanthracene (**14**) (7.8 mg, 15%), mp 122–124 °C. Mass spectrum *m/z* 379 (0.5%), 378 (4), 377 (0.5), 351 (22), 350 (100), 304 (23), 302 (12), 204 (11), 203 (18), 178 (13), 177 (43), 176 (14), 88 (11), 89 (11), 69 (16), 57 (13). The next more polar component eluted was an inseparable mixture of 10-deutero-9-iodo-2-nitro-9,10-ethano-9,10-dihydroanthracene (**20**) and 9-iodo-2-nitro-9,10-ethano-9,10-dihydroanthracene (**15**) (14 mg, 27%), mp 160–162 °C. Mass spectrum *m/z* 379 (0.5%), 378 (2.4), 377 (0.4), 351 (5), 350 (100), 349 (26), 304 (28), 302 (14), 292 (10), 205 (11), 204 (20), 203 (30), 178 (20), 177 (84), 165 (10), 89 (18). The most polar component eluted was determined by ^{1}H NMR spectroscopy (identical, except for diminished absorption for the bridgehead protons with an authentic sample of **16**[20]) TLC and MS to be a mixture of 9-deutero-2-nitro-10-protio-9,10-ethano-9,10-dihydroanthracene (**22**), 10–deutero-9-protio-2-nitro-9,10-ethano-9,10-dihydroanthracene (**23**), 9,10-dideutero-2-nitro-9,10-ethano-9,10-dihydroanthracene (**21**) and 2-nitro-9,10-ethano-9,10-ethano-9,10-dihydroanthracene (**16**) (2 mg, 6%). Mass spectrum[21] *m/z* 254 (1%), 253 (8), 252 (6), 251 (2), 226 (18), 225 (100), 224 (42), 223 (30), 180 (10), 179 (50), 178 (38), 177 (30), 176 (11), 167 (13), 152 (10).

Tributyltin Hydride Reduction of 10 and 11. The dibromide **10** (50 mg, 0.12 mmol) was dissolved in dry benzene (2 mL) and stirred at room temperature. Tributyltin hydride (150 μL, 0.7 mmol, 5.5 equiv) was added to the reaction, and the mixture was heated under reflux. Aliquots of reaction mixture were removed at intervals and were analyzed by analytical HPLC with 10% ethyl acetate/light petroleum as eluent. The ratio of the bromo products **12** and **13** over 60 min was monitored and was determined to be 1:1.11 ± 0.07. After 60 min, degradation of the products occurred and the ratio of monobromides is based only on aliquots removed up to 60 min.

The diiodide **11** (50 mg, 0.09 mmol) was dissolved in dry benzene (2 mL) and treated as above. The ratio of iodo products **14** and **15** was determined to be 1:1.06 ± 0.08. The monoiodo products showed no signs of degradation over the 24 h period the reaction was monitored.

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(21) The peaks at *m/z* 253, 252, and 251 principally correspond to the parent ions of **21**, **22**/**23**, and **16**, respectively. The presence of significant M + 1 peaks and the coincidence of the peaks from **22** and **23** do not allow determination of the ratio of these products.