

## METAL-AMMONIA REDUCTION—XIV FLUORANTHENE: CORRELATION OF PRIMARY PRODUCT STRUCTURE WITH HMO THEORETICAL PREDICTION<sup>1</sup>

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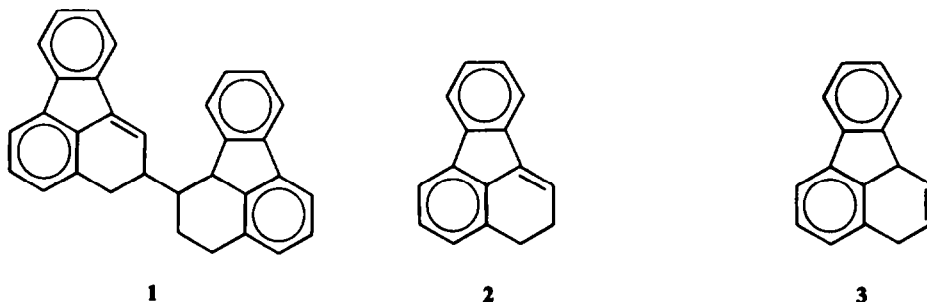
**Abstract**—Reduction of fluoranthene with lithium in liquid ammonia affords the previously undetected theoretically predicted product 3,10b-dihydrofluoranthene (3) in good yield, accompanied by minor amounts of the 2,3-dihydro isomer (2) which is shown to arise *via* base-catalyzed isomerization of 3. Analogous reductive methylation of fluoranthene with methyl bromide affords either 10b-methyl-3,10b-dihydrofluoranthene (4) or 3,10b-dimethyl-3,10b-dihydrofluoranthene (5), as the major product, depending upon use of lithium or sodium. Mechanism and stereochemistry of these transformations are discussed. NMR spectral analysis of the 3,10b-dihydrofluoranthene derivatives is reported; these compounds are distinguished by an unusual 1,4-cyclohexadiene ring system locked in a relatively rigid flattened boat conformation.

HIGHLY EFFICIENT, generally regiospecific reduction of polycyclic aromatic hydrocarbons is possible by means of solutions of alkali metals in liquid ammonia.<sup>1, 2a</sup> The structures of the dihydroaromatic products obtained by this means correlate to a remarkable degree with predictions of Hückel molecular orbital (HMO) theory.<sup>3</sup> Several apparent discrepancies in the earlier literature between prediction and experimental observation have been found upon recent reinvestigation to provide results in accord with theoretical expectation.<sup>1, 2a, 4, 5</sup>

Fluoranthene, the only non-alternant hydrocarbon investigated to date, is one of only two hydrocarbons† remaining for which anomalous results are reported. Streitwieser and Suzuki<sup>3a</sup> reported that treatment of fluoranthene with Na or Li in liquid NH<sub>3</sub> followed by addition of MeOH gave polymeric resin and 30–52% yield of a crystalline dimer (1); evidence was presented for origin of 1 from 2,3-dihydrofluoranthene (2) *via* Michael addition of its conjugate anion to itself. This result is not inconsistent with theory, since 2 may reasonably be expected to arise

† Reduction of fluorene, reported by Hückel and Schwen [*Chem. Ber.* **89**, 481 (1956)] to provide 3,9a-dihydrofluorene rather than the more probable 2,4a-dihydrofluorene<sup>3a</sup> is currently under investigation in this laboratory.

through base-catalyzed isomerization of 3,10b-dihydrofluoranthene (**3**), the predicted product.



It remained unsatisfactory, nevertheless, that **3** was never detected and that a major portion of the total product (i.e., the polymeric resin) remained uncharacterized, leaving open the possibility of a different dihydro isomer as its precursor. We now wish to report reinvestigation of this problem, including successful isolation and characterization of the elusive primary dihydro isomer **3**.

#### RESULTS

The experimental procedures developed for synthesis and isolation of other unstable dihydroaromatics, notably dihydropyrene,<sup>4</sup> were utilized herein. Treatment of a solution of fluoranthene in ether with Li in liquid  $\text{NH}_3$  at  $-33^\circ$  followed after 10 min by addition of solid  $\text{NH}_4\text{Cl}$  and rapid isolation of the product by partition between ether and water afforded a crude product containing **3** (84%) and **2** (12%) by NMR analysis. Separation of the dihydro isomers was prevented by the instability of **3** which decomposed on attempted purification by recrystallization or chromatography. The integrated NMR spectrum of **3** (minor components subtracted out) was consistent with the assigned structure, displaying an aromatic multiplet at  $\delta$  6.8–7.7 (7H), vinyl protons centered at 6.05 (2H), a complex methine signal at 3.95 (1H), and a methylene signal at 3.20 (2H, apparent triplet,  $J \sim 4$  Hz). Homoallylic coupling between the methine and methylene protons was indicated by collapse of the methylene signal to a broad single peak on irradiation at  $\delta$  3.95; conversely, irradiation at  $\delta$  3.20 sharpened considerably the methine signal. The observed coupling constant ( $J \sim 4$  Hz) agrees with the value reported for homoallylic coupling in the related compound, 1,4-dihydro-1-naphthoic acid.\*<sup>6</sup>

Analogous reduction of fluoranthene with Na, or with Li in  $\text{NH}_3$  in the absence of cosolvent, also furnished **2** and **3**, albeit in somewhat different proportion. More significantly, a lithium-fluoranthene reaction quenched with MeOH afforded **2** virtually exclusively. Reactions under other conditions utilizing different proportions, cosolvents, reaction times, quenching agents, etc., proved considerably less satisfactory providing more complex product mixtures.

Although instability of **3** prevented isolation in a pure state, it underwent smooth base-catalyzed isomerization with NaOMe in refluxing MeOH to **2**. The latter was a

\* A general resemblance of the vinyl, methine, and methylene patterns of **3** to those of 1,4-dihydro-1-naphthoic acid was observed.

crystalline solid, m.p. 67.5–68.5° (lit.<sup>3a</sup> 63–65°) whose NMR spectrum showed aromatic, vinylic, benzylic, and allylic protons in the expected ratio. Saturation of the multiplet at  $\delta$  2.85 in the benzylic-allylic region resulted in collapse of the vinyl complex at  $\delta$  6.45 into a singlet, while irradiation at  $\delta$  6.45 transformed the higher field multiplet into a symmetrical AA'BB' pattern with four major peaks. The observed chemical shifts proved sensitive to concentration, signals being shifted 0.1–0.2 ppm upfield in more concentrated solution.

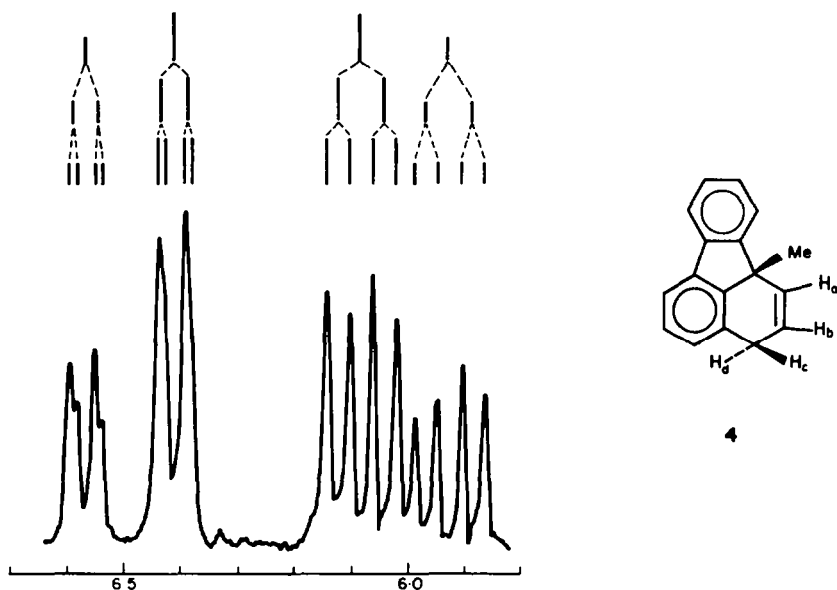
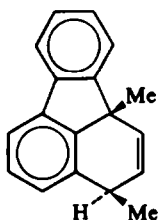
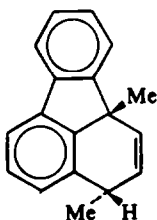
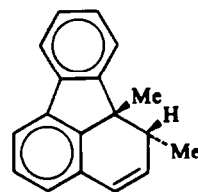


FIG 1. Vinyl region of NMR spectrum of 4

Confirmation of the structure of 3 was provided by reductive methylation of fluoranthene. Reaction of the latter with Li in liquid  $\text{NH}_3$  followed by MeBr gave in good yield the 10b-methyl homolog of 3, 10b-methyl-3,10b-dihydrofluoranthene, (4) its integrated NMR spectrum was consistent with this assignment. The aromatic protons appear as a complex multiplet centered at  $\delta$  7.32 (7H), the methylene protons as a multiplet at 3.26 (2H), and the methyl hydrogen as a singlet at 1.26 (3H). An analysis of the vinyl region (Fig 1) shows a basic AB pattern (2H,  $J_{ab} = 9.3$  Hz). The downfield proton, assigned as  $H_a$ , shows two additional couplings, presumably with the allylic pseudoaxial and pseudoequatorial protons,  $H_c$  ( $J_{ac} \sim 2.6$  Hz) and  $H_d$  ( $J_{ad} \sim 0.8$  Hz). The upfield proton,  $H_b$ , shows two additional couplings assigned as  $J_{bc} = 2.4$  Hz, and  $J_{bd} = 5.0$  Hz on the following basis.  $H_c$  and  $H_d$  are geminal methylene protons in a 1,4-cyclohexadiene ring locked in a relatively rigid flattened boat conformation. Since  $J_{vic}$  decreases<sup>7</sup> as the dihedral angle approaches  $90^\circ$ , the coupling constant of larger magnitude must involve the pseudoequatorial proton,  $H_d$ . The methylene protons of 1,4-dihydro-1-naphthoic acid were previously assigned on similar grounds.<sup>6</sup>

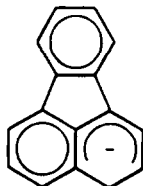
Accompanying **4** were minor amounts of the dimethyl homologs, *cis*- and *trans*-3,10b-dimethyl-3-10b-dihydrofluoranthene (*cis*- and *trans*-**5**), and *trans*-1,10b-dimethyl-1,10b-dihydrofluoranthene (**6**) (Table 1). Substitution of Na or K for Li drastically altered product distribution to favor these dimethylated products. A similar metal effect on reductive methylation of naphthalene was noted earlier.<sup>8</sup>

*cis*-**5***trans*-**5****6**

Conversely, dimethylated products were entirely excluded by half-quenching (i.e., addition of sufficient water to consume all but one equivalent of added metal) the lithium fluoranthene reaction prior to methylation. The structures assigned the dimethylated products are based on NMR and mass spectral data in comparison with related compounds (Discussion).

#### DISCUSSION

The general mechanistic concepts developed in preceding studies<sup>1,3,8</sup> adequately explain the foregoing results. In these terms, initial protonation of a dianionic intermediate\* is expected to take place regiospecifically in the 3-position with formation of the stable dihydrofluoranthene monanion **7**. Further protonation of the

**7**

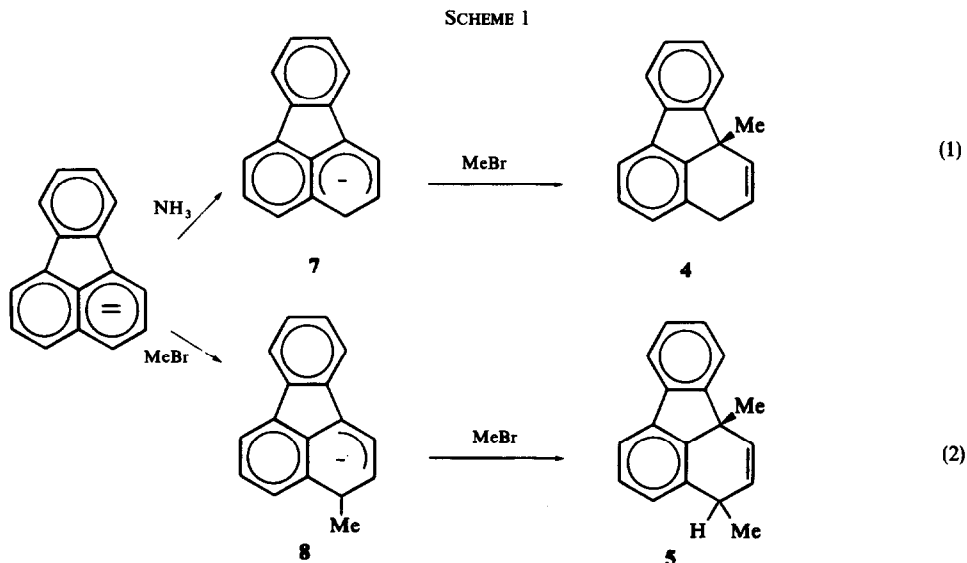
latter by a sufficiently acidic proton source, such as  $\text{NH}_4\text{Cl}$ , occurs at the site of maximum charge density, the 10b-position, to afford the primary dihydro product (**3**). Origin of the second dihydro isomer (**2**), through partial protonation at position-2 might appear reasonable since the calculated<sup>3a</sup> charge density at the 2-position of **7** ( $q_r = 1.216$ ) is close to that at the 10b-position ( $q_r = 1.246$ ). Available evidence, however, is more consistent with the view that **2** arises solely *via* isomerization of **3**.

\* Although direct evidence is lacking whether protonation takes place at the radical-anion or dianion stage, previous studies with the related biphenyl system indicate protonation of the former to be considerably slower than addition of a second electron followed by proton addition to the latter.

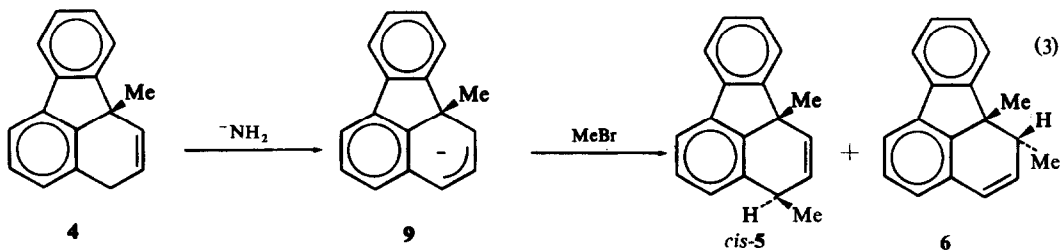
In particular, the corresponding methyl derivative of 2, 2-methyl-2,3-dihydrofluoranthene, was not detected (by NMR) in any of the products of reductive methylation.

The rather different product distribution obtained by the previous investigators<sup>3a</sup> (utilizing Na or Li in liquid NH<sub>3</sub> followed by addition of MeOH) would appear to be primarily a consequence of (a) methoxide-catalyzed isomerization of 3 to 2 during prolonged exposure to base in the workup procedure, and (b) dimerization and polymerization of 2 at the relatively high concentrations employed.

The observed metal effect on methylated product distribution is explicable in terms of facile monoprotection of the dilithio dianion by ammonia (eq. 1) and slow protonation of the corresponding disodio intermediate; dimethylation of the latter affords *cis* and *trans* 5 (eq. 2), while methylation of 7 provides 4. The dependence of the kinetic basicity of the dianion on the cation apparently reflects important differences in covalent character or tightness of ion pair association in the respective intermediates.<sup>9</sup> Ion pair association has been implicated previously as a major determinant of product structure in reductive alkylation of both naphthalene<sup>8</sup> and *p*-terphenyl.<sup>1</sup>



The alternative pathway to dimethylated products, i.e., "back reaction"\* *via* proton abstraction from 4 (eq. 3), was ruled out by demonstration that 4 upon



\* Back reaction is the major source of di- and trimethylated products from biphenyl.<sup>10</sup>

treatment with amide ion and MeBr afforded markedly different *cis-trans* and product ratios, with the *cis* isomer of **5** and **6** (2:1) predominating. The greater steric preference exhibited by the back reaction undoubtedly reflects the greater rigidity imposed on the reduced ring of **9** by the angular methyl substituent. The latter tends to fix the

TABLE 1. REDUCTIVE METHYLATION OF FLUORANTHENE<sup>a</sup>

Metal	Temp (°C)	Product composition, <sup>b</sup> %				fluoranthene
		<b>4</b>	<i>cis</i> - <b>5</b>	<i>trans</i> - <b>5</b>	<b>6</b>	
Li	-33	86	7	2	3	0
Li <sup>c</sup>	-33	71	11	4	5	6
Na	-78 <sup>d</sup>	29	42	24	3	0
Na <sup>e</sup>	-78	37	38	20	3	0
Li <sup>f</sup>	-78	71	13	8	2	6
Li <sup>g</sup>	-78	88	0	0	0	10
K <sup>e</sup>	-78	20	50	22	4	2
Li <sup>g</sup>	-33	96	0	0	0	3

<sup>a</sup> Reaction conditions described in Experimental Section.

<sup>b</sup> Percentages based on NMR data supported by integrated peak values from GLPC.

<sup>c</sup> No cosolvent employed.

<sup>d</sup> For reactions at -78° a 10 min cooling period was allowed between addition of the solution of fluoranthene and the metal, except in this experiment.

<sup>e</sup> Reaction time 5 min.

<sup>f</sup> Reaction time 20 min.

<sup>g</sup> Reaction was half-quenched after 10 min by addition of water in THF over a 10 min period before introduction of gaseous MeBr after an additional min.

ring into the flattened boat structure characteristic of fused-ring 1,4-cyclohexadienes,\* and localize the negative charge at the 3-position in an orbital axially oriented for maximum overlap.† *Cis* stereospecific alkylation predicted on this basis is in accord with observation. Similarly, the lower stereoselectivity of reductive dimethylation (eq. 2) is in accord with the less sterically constrained structure of the intermediate monoanion (**8**). In the latter, equatorial-peri interaction may be expected to dictate a modest preference for axial orientation of the methyl group, leading to *cis*-stereoselectivity. Other factors‡ potentially exerting a controlling influence over product stereochemistry include a *steric approach factor* and an *ion pair factor*. Involvement of ion pairs is suggested by the observed variation in *cis-trans* ratios with the metal.

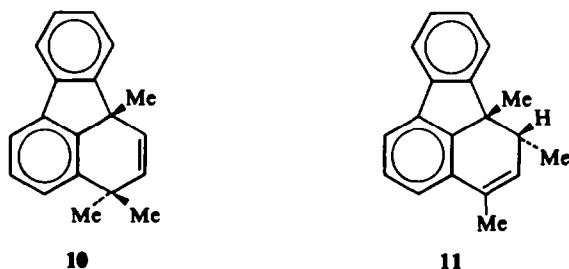
\* Both 9-alkyl-9,10-dihydroanthracene<sup>11</sup> and 1,4-dihydro-1-naphthoic acid<sup>6</sup> have recently been shown to exist in nonplanar boat conformation. The generality of this rule remains to be established.

† This argument is applicable to the minor isomer **6** which apparently arises via *trans* axial alkylation of **9** at the 1-position; *trans* axial attack may be partially a consequence of steric interference from the 10b-methyl group and/or partial cation induced charge localization at the 1-position.

‡ The importance of *conformational* and *steric approach* factors in controlling the stereochemistry of metal-ammonia reduction of polycyclic hydrocarbons has been previously established;<sup>2ab, 4, 12</sup> more recently, the additional importance of an *ion pair association* factor has also been recognized.<sup>1, 8, 12</sup> Evidence that similar factors are operable during reductive alkylation has also been obtained.<sup>2a, 8, 13</sup>

However, the data is inadequate to reach definitive conclusion concerning the importance of either of these effects.

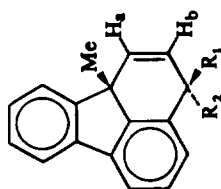
The structures assigned the dimethylated products **5** and **6**, as stated earlier, are based primarily on NMR and mass spectral data (Table 2). The 3,10b-dihydrofluoranthene ring system of *cis*- and *trans*-**5** presents an interesting example of a "frozen" 1,4-cyclohexadiene structure, unique in permitting relatively straightforward analysis and assignment of chemical shifts and coupling constants. NMR spectral analysis of **5** and **6** was achieved in comparison with the spectra of two trimethylated compounds, assigned the structures **10** and **11**, and obtained as major products from further methylation of a mixture of mainly **4** and **5** (from reaction with K, Table 1).



In the vinyl region, the mono-, di-, and trimethyl derivatives of 3,10b-dihydrofluoranthene (i.e., **4**, **5**, and **10**) exhibit basic AB patterns with similar coupling constants ( $J_{ab} = 9.3\text{--}9.8$  Hz). *Cis*- and *trans*-**5** are distinguishable on the basis of the magnitude of the secondary couplings exhibited by the vinyl protons. The upfield proton of *cis*-**5** shows only the expected additional coupling with the pseudoequatorial proton  $H_d$  ( $J_{bd} = 5.1$  Hz), while no additional couplings are evident for the downfield proton. In contrast, the upfield proton of *trans*-**5** displays a smaller additional coupling with the allylic proton  $H_c$  ( $J_{bc} = 1.6$  Hz) consistent with its pseudoaxial orientation, while the remaining vinyl proton  $H_a$  exhibits additional coupling with  $H_c$  of the expected magnitude ( $J_{ac} \sim 3.3 \pm 0.8$  Hz).

Similarly, the NMR spectral patterns of the di- and trimethyl derivatives of 1,10b-dihydrofluoranthene (i.e., **6** and **11**) are consistent with one another and with their assigned structures (Table 2). In particular, the magnitude of the vicinal coupling constant  $J_{ac}$  (5.8 Hz) in **6** supports the pseudoequatorial assignment of  $H_a$  and hence, *trans*-diaxial orientation of the methyl groups. Also, the chemical shifts of the allylic methyl groups of **6** and **11** are quite distinctive ( $\delta = 0.40$  and  $0.44$ , respectively), appearing at considerably higher field than any of the other methyl resonances in these series of compounds; the presence of this high field methyl doublet in the NMR spectrum of **6** confirms the correctness of assignment of structures *cis*-**5** and **6**, which otherwise might possibly be reversed. Also, the allylic protons,  $H_c$ , of **6** and **11** appear upfield ( $\delta$  2.78 and 2.73) from the allylic-benzylic protons of **4** and **5** ( $\delta$  3.24–3.48) in further support of the assigned structures.

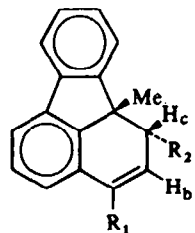
TABLE 2. NMR SPECTRA. A. MONO-, DI-, AND TRIMETHYL-3,10b-DIHYDROFLUORANTHENE



Compound	Chemical shifts <sup>a</sup> (ppm) and signal multiplicity <sup>b</sup>					Coupling constants, <sup>c</sup> Hz					
	H <sub>a</sub>	H <sub>b</sub>	R <sub>1</sub>	R <sub>2</sub>	Me	J <sub>ab</sub>	J <sub>ac</sub>	J <sub>ad</sub>	J <sub>bc</sub>	J <sub>bd</sub>	J <sub>11',12'</sub>
4, R <sub>1</sub> = H <sub>c</sub> R <sub>2</sub> = H <sub>d</sub> <i>cis</i> -5	6.48, m	6.02, m	3.48, m	3.24, m	1.30, s	9.3	2.6	0.8	2.4	5.0	19.5
R <sub>1</sub> = Me R <sub>2</sub> = H <sub>d</sub> <i>trans</i> -5	6.46, d	5.94, d of d	1.52, d	3.35, m	1.42, s	9.6	—	small	—	5.1	7.5
R <sub>1</sub> = H <sub>c</sub> R <sub>2</sub> = Me 10'	6.44, d of d	5.80, d of d	3.35, m	1.45, d	1.31, s	9.3	3.3 ± 0.8	—	1.6	—	7.4
R <sub>1</sub> = R <sub>2</sub> = Me	6.39, d	5.69, d	1.56, s	1.43, s	1.36, s	9.8	—	—	—	—	—



TABLE 2—Continued  
 B. DI- AND TRIMETHYL-1,10b-DIHYDROFLUORANTHENE



Compound	R <sub>1</sub>	H <sub>b</sub>	H <sub>c</sub>	R <sub>2</sub>	Me	J <sub>ab</sub>	J <sub>bc</sub>	J <sub>bc</sub>	J <sub>br1</sub>	J <sub>cr1</sub>	J <sub>cr2</sub>
6 <sup>d</sup> , R <sub>1</sub> = H, R <sub>2</sub> = Me	6.48, d	6.06, d of d	2.78, m	0.44, d	1.37, s	9.6	small	5.8	—	—	7.2
11 <sup>e</sup> , R <sub>1</sub> = R <sub>2</sub> = Me	2.12, d of d	5.84, d of q	2.73, m	0.40, d	1.34, s	—	—	6.2	1.4	0.7	7.3

<sup>a</sup> Chemical shifts relative to TMS in CCl<sub>4</sub> at ~0.4M conc unless indicated otherwise. Higher concentrations led to upfield shifts of vinyl, benzylic, and methyl resonances to as much as 9.6, and 4–6 Hz, respectively, at 2.0M concentration.

<sup>b</sup> s = singlet; d = doublet; m = multiplet.

<sup>c</sup> Coupling constants reliable to ±0.1 Hz unless indicated otherwise.

<sup>d</sup> Concentration ~0.1M.

<sup>e</sup> Concentration ~0.2M.

## EXPERIMENTAL

All reactions in liquid  $\text{NH}_3$  were conducted under helium in a three neck flask fitted with a Dewar condenser. Precautions for the exclusion of impurities (moisture, air, peroxides, metallic salts in ammonia) described in preceding papers<sup>1</sup> were scrupulously observed. Products were isolated rapidly by partition between ether and water without waiting for evaporation of  $\text{NH}_3$ , and NMR spectra were taken immediately on crude products.

Proton NMR spectra were obtained on Varian A-60 and T-60 spectrometers; chemical shifts are reported relative to TMS in  $\text{CCl}_4$  at concentrations of  $\sim 0.4$  M unless indicated otherwise. Chemical shifts exhibited concentration dependence: increasing the concentration from  $\sim 0.4$  M to  $\sim 2.0$  M resulting in upfield shifts of vinylic, benzylic and methyl protons of 9.6 and 4–6 Hz, respectively. Integration was in all cases consistent with the assigned structures. GLPC analyses were performed on a F & M Model 500 chromatograph employing either an  $8' \times 0.25''$  20% DEGS on 60–80 Chromosorb W column at  $200^\circ$ , a  $6' \times 0.25''$  5% butanediol succinate on 70–80 Varaport 30 column at  $180^\circ$ , or a  $3' \times 0.25''$  5% Apiezon column at  $210^\circ$ . Mass spectra were obtained on a Finnigan 1015 mass spectrometer at 70 eV except where otherwise indicated.

**3,10b-Dihydrofluoranthene (3).** A solution of fluoranthene (0.51 g, 2.5 mmol) in 75 ml anhydrous ether was added to 150 ml refluxing  $\text{NH}_3$ , followed by Li metal (5.5 mg-atm). After 10 min, reaction was quenched by addition of solid  $\text{NH}_4\text{Cl}$  (20 g) all at once. The product proved unstable, decomposing on attempted purification; the integrated NMR spectrum (see preceding section) was consistent with the presence of **3** (84%) and **2** (12%).

Analogous reduction in the absence of the cosolvent afforded **3** (74%), and **2** (22%), while reaction at  $-78^\circ$  with ether as cosolvent furnished **3** (83%), **2** (5%), and recovered fluoranthene (12%).

**2,3-Dihydrofluoranthene (2).** Crude **3** in MeOH (50 ml) was added to a solution of NaOMe (23 mg Na, 1 mmol) in MeOH (50 ml) under  $\text{N}_2$ . The resulting solution was refluxed for 2 hr, decomposed by addition of 100 ml of water, and extracted with hexane. Recrystallization of crude **2** ( $\sim 95\%$ ) from MeOH– $\text{H}_2\text{O}$  afforded pale yellow crystals of pure **2**, m.p.  $67.5$ – $68.5^\circ$  (lit.<sup>3a</sup>  $63$ – $65^\circ$ ) which gradually darkened on standing: UV (cyclohexane) 325.5 ( $\epsilon$  7250), 312.5 (7140), 300 (6350), 293 (7290), 281 (8050), 259.5 (46,900), 255.5 (20,200), 249.5 (32,400), and 234.5  $\mu\text{m}$  (45,500); mass spectrum (70 eV)  $m/e$  204 (72%, parent ion), 203 (100%), 202 (51%); mass spectrum (10 eV), 204 (100%); NMR (see discussion). (Calc. for  $\text{C}_{16}\text{H}_{12}$ : C, 94.08; H, 5.92. Found: C, 93.58; H, 5.84%.)

Direct preparation of **2** from fluoranthene was achieved under essentially the same conditions employed for reduction to **3** except that reaction was quenched after 10 min with sufficient MeOH to decolorize the solution. Solid  $\text{NH}_4\text{Cl}$  (20 g) was added and the product isolated in the usual manner. The integrated NMR spectrum showed **2** ( $\sim 70\%$  by NMR) and recovered fluoranthene (10%) along with an unidentified substance(s), probably dimeric and/or polymeric products reported previously.<sup>3a</sup>

**10b-Methyl-3,10b-dihydrofluoranthene (4).** Reductive methylation of fluoranthene (0.51 g, 2.5 mmol) with Li in ether– $\text{NH}_3$  was carried out essentially according to the procedure described for reduction except that reaction was quenched after 10 min by introduction of gaseous MeBr (flow rate = 60 mmol/min). NMR analysis of the crude product indicated the presence of **4** (88%) and a second component (12%) tentatively identified as the dimethyl homolog, 3,10b-dimethyl-3,10b-dihydrofluoranthene. Repetition in the absence of cosolvent gave a slightly lower yield of **4** (81%) while similar reaction of fluoranthene (5 mmol) with Li (12.5 mg-atm) in glyme (50 ml)– $\text{NH}_3$  (150 ml) for 30 min afforded **4** ( $\sim 80\%$  by GLPC). The analytical sample of **4** obtained by chromatography on silica gel was an oil. (Calc. for  $\text{C}_{17}\text{H}_{14}$ : C, 93.54; H, 6.46. Found: C, 93.64; H, 6.31%.)

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