121–131 °C) was recrystallized from a mixture (80/20) of petroleum ether (bp 90–110 °C) and chloroform to give a 54% yield of **6a** [mp 147–148 °C; NMR ($CDCl_3$) δ 1.60 (s, 9, CH_3), 7.50 (m, 5, ArH), 7.90 (m, 4, ArH), 8.45 (broad s, 1, NH)].

Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.93; H, 6.52; N, 4.53.

Reactions of Isopropyl *p*-Bromobenzoate (1b). Reactions with isopropyl *p*-bromobenzoate [bp 80 °C (0.03 Torr), 86% yield from *p*-bromobenzoyl chloride and 2-propanol; composition analysis in agreement with $C_{10}H_{14}BrO_2$; NMR ($CDCl_3$) δ 1.45 (d, 6, CH_3), 5.40 (m, 1, CH), 7.50 (m, 3, ArH), 8.15 (m, 2, ArH)] were carried out as described for **1a.** Aliquots taken after 5 min showed considerable amounts of condensation products. The mixture was stirred for a total of 50 min at −105 °C and then poured into water. The organic product obtained from the dried ($MgSO_4$) ether extracts showed at least seven components by TLC. A portion (500 mg) of the product was purified by preparative TLC [silica gel, fluorescent indicator, petroleum ether (bp 30–60 °C) and ether mixture (90/10) as eluent] to give in order of decreasing R_f (1) isopropyl benzoate [9% yield; NMR ($CDCl_3$) δ 1.45 (d, 6, CH_3), 5.40 (m, 1, CH), 7.50 (m, 3, ArH), 8.15 (m, 2, ArH)]; (2) isopropyl *p*-bromobenzoylbenzoate [26% yield, mp 82–83 °C from petroleum ether (bp 60–90 °C); NMR ($CDCl_3$) δ 1.45 (d, 6, CH_3), 5.38 (m, 1, CH), 7.71 (s, 4, ArH), 7.85 (d, 2, ArH), 8.1 (d, 2, ArH) (Anal. Calcd for $C_{17}H_{15}BrO_3$: C, 58.81; H, 4.85; Br, 23.02. Found: C, 58.77; H, 4.42; Br, 23.16)]; (3) an oil, slightly impure alcohol corresponding to the product obtained by addition of *n*-butyllithium to isopropyl *p*-bromobenzoylbenzoate [19% yield; NMR ($CDCl_3$) δ 0.9 (t, 3, CH_3), 1.40 (d, ~6, CH_3), 1.40 (m, ~6, CH_2), 5.35 (m, 1, CH), 7.55 (m, 6, ArH), 8.10 (d, 2, ArH); ir (CCl_4) ν_{OH} 3440 cm^{-1}, $\nu_{C=O}$ 1710 cm^{-1}]; and (4) the major fraction, with low R_f, which was a complex mixture.

Reactions of Isopropyl *o*-Bromobenzoate (7). Isopropyl *o*-bromobenzoate [**7,** 83% yield from *o*-bromobenzoyl chloride and 2-propanol, bp 86–87 °C (0.01 Torr); NMR ($CDCl_3$) δ 1.38 (d, 6, CH_3), 5.13 (m, 1, CH), 7.43 (m, 4, ArH) (Anal. Calcd for $C_{10}H_{11}BrO_2$: C, 49.41; H, 4.56; Br, 32.87. Found: C, 49.18; H, 4.58; Br, 32.76)] was treated with *n*-BuLi as described for **1a.** Studies (NMR) of aliquots taken after 5 min showed absence of starting bromo ester and only isopropyl benzoate.

Lactone 9. To the solution prepared from bromo ester **7** (0.0206 mol) and *n*-BuLi stirred for 20 min at −105 °C was added cyclohexanone (0.03 mol) in dry THF (~25 ml) at −100 °C. The resulting solution was allowed to warm to 10 °C and was poured into dilute hydrochloric acid (~100 ml). The acidic solution was extracted with ether and the organic material obtained from the dried ($MgSO_4$) ether extracts was saponified (1.5 h) with hot 90% ethanolic KOH. The solution was cooled and extracted with ether (the ether extract contained 1.39 g of an oil which was resaponified and reprocessed to give 0.34 g, 9% yield, of lactone **9**). The alkaline mixture was made acidic (pH ~2) with concentrated hydrochloric acid and warmed at 50 °C for 5 min. The cooled solution was extracted with ether, which was subsequently washed rapidly with cold 5% aqueous NaOH. Lactone **9** (1.35 g, 34% yield, total yield 43%, mp and mmp[5] 79–80 °C) was obtained from the dried ($MgSO_4$) ether extract by recrystallization of the crude product from petroleum ether (bp 30–60 °C).

***N*-Phenylphthalimide (10).** Phenyl isocyanate (0.05 mol) in dry THF (~25 ml) was added at −98 °C to the solution prepared from isopropyl *o*-bromobenzoate (0.020 mol) 5 min after the addition of *n*-BuLi. The mixture was allowed to warm to 25 °C and was poured into water (~100 ml). Phthalimide **10** (mp 208–210 °C, from ethanol/chloroform, mmp 206–209 °C, lit.[11] mp 208 °C) was obtained in 53% yield by recrystallization of the solid mixture obtained from the dried ($MgSO_4$) organic extracts. The concentrated mother liquor contained *N,N'*-diphenylurea (mp 237–242 °C dec, lit.[12] 239 °C, separated by trituration with petroleum ether in which the urea has limited solubility) and a product assumed to be slightly impure isopropyl *N*-phenylcarbamate [mp 85–86 °C, by preparative TLC with subsequent recrystallization from petroleum ether (bp 30–60 °C); lit.[13] mp 86 °C; NMR ($CDCl_3$) δ 1.30 (d, 6, CH_3), 5.05 (m, 1, CH), 6.6 (broad s, 1, NH), 7.20 (m, 5, ArH); ir (KBr) ν_{N-H} 3300 cm^{-1}, $\nu_{C=O}$ 1710 cm^{-1}].

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.82; N, 7.82. Found: C, 67.56; H, 7.24; N, 7.82.

Registry No.—1a, 59247-47-1; **1b,** 59247-48-2; **3a,** 774-65-2; **4a,** 59247-49-3; **5a,** 59247-50-6; **6a,** 59247-51-7; **7,** 59247-52-8; **9,** 5651-49-0; **10,** 520-03-6; *n*-butyllithium, 109-72-8; cyclohexanone, 108-94-1; benzophenone, 119-61-9; phenyl isocyanate, 103-71-9; *p*-bromobenzoyl chloride 586-75-4; 2-propanol, 67-63-0; isopropyl benzoate, 939-48-0; *o*-bromobenzoyl chloride, 7154-66-7; isopropyl *n*-phenylcarbamate, 122-42-9; isopropyl *p*-bromobenzoylbenzoate, 59247-53-9.

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Metal–Ammonia Reduction. 15. Regioselectivity of Reduction and Reductive Methylation in the Fluorene Series[1]

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Reduction of fluorene with alkali metals in ammonia affords initially 2,4a-dihydro- and 1,4-dihydrofluorene (**2, 3**) and not the 3,9a isomer previously reported. While **2** accords with molecular orbital prediction, **3** is only the second example of reduction contratheory. Analogous reductive methylation of fluorene with lithium and methyl bromide gave the 4a-methyl homologue of **2,** 4a-methyl-2,4a-dihydrofluorene, along with 9-methyl- and 9,9-dimethylfluorene. The products of similar reactions of 9,9-dimethylfluorene were principally the predicted 2,4a-dihydro derivatives accompanied by lesser amounts of the 1,4-dihydro isomers, namely 1,4-dihydro-9,9-dimethylfluorene and its 1-methyl homologue. Formation of the 2,4a-dihydro products is explicable in terms of the general mechanism previously proposed, while origin of the 1,4-dihydro compounds involves initial protonation unexpectedly at the 4 position. Formation of the 9-methylated derivatives of fluorene is ascribed to protonation by fluorene of the dianionic intermediate and methylation of the 9-fluorenyl anion.

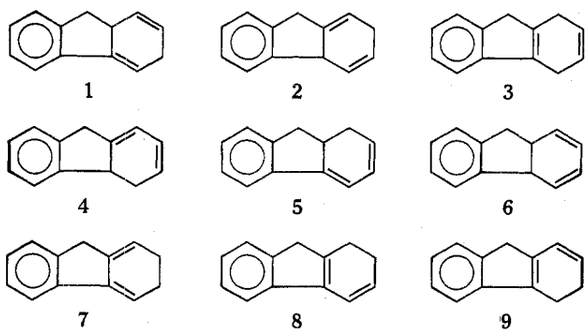
Reduction of polycyclic aromatic hydrocarbons by alkali metals in liquid ammonia has been shown in previous papers[1,3,4] to be controllable to the dihydro stage, to be regiospecific,[5] and to afford products in accord with predictions of

Table I. Reduction of Fluorene by Li and Ca in Ammonia[a]

Metal (mmolar equiv)	Temp, °C	Time, min	Product composition, % 2	3	Tetrahydro	Fluorene
Li (2.2)[b]	−78	5	39	37	8	11
Li (2.2)[b]	−33	5	29	35	10	26
Li (2.2)[c]	−78	5	43	30	4	20
Li (2.2)[c,d]	−33	30	27	46	1	25
Li (3.0)[b,e]	−78	10	31	27	0	36
Li (5.0)[b]	−33	20	38	2	51	2
Li (5.0)[b]	−33	30	27	3	62	1
Ca (2.2)[b]	−33	10	23	22	25	18

[a] Conditions are described in the Experimental Section. [b] The lithium metal was added last. [c] The lithium metal was dissolved before the addition of fluorene. [d] THF was employed in place of ether as cosolvent. [e] $FeCl_3$ (50 mg) was added before addition of fluorene.

Hückel molecular orbital (HMO) theory.[7] Several apparent discrepancies in the earlier literature were resolved upon reinvestigation.[1,3,6,8,9] Fluorene is the sole remaining hydrocarbon for which anomalous results have been reported. According to Hückel and Schwen,[10] fluorene upon treatment with sodium in liquid ammonia affords an unstable dihydrofluorene assigned the 3,9a-dihydro structure (**1**) on the basis of chemical evidence. On the other hand, HMO calculations[3,7] predict the 2,4a-dihydro structure (**2**) as the primary product;[11] **2** would also be expected by analogy with biphenyl from which 1,4-dihydrobiphenyl is the initial product.[3,8,12] Therefore, we undertook to reinvestigate this problem.

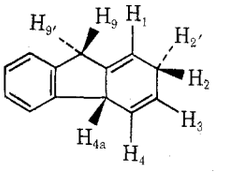


Results

Interaction of lithium metal with fluorene in liquid ammonia following the general technique developed earlier[1,8] furnished two dihydro derivatives (**2, 3**) along with tetrahydrofluorene and recovered fluorene. Product ratios were determined by GLC analysis and found to be markedly dependent upon reaction conditions (Table I). Reaction for 5 min at −78 °C quenched with NH_4Cl and worked up rapidly by extraction with ether afforded **2** (39%) and **3** (37%) accompanied by tetrahydrofluorene (8%) and fluorene (11%).

The structural assignments of the dihydro isomers, which were trapped off the GLC column, are based on the following considerations. The integrated NMR spectrum of the isomer assigned the 1,4-dihydro structure **3** exhibited a sharp allylic singlet at δ 3.05 (4 H), a benzylic singlet at 3.20 (2 H), an AB quartet (J = 9 Hz) in the vinyl region at 5.84 (2 H), and an aromatic multiplet at 6.96–7.33 (4 H) consistent with this relatively symmetrical structure. Structures **1** and **2** and the alternative structures **4, 5,** and **6** may be ruled out immediately, since the integrated proton ratios are inconsistent with these assignments. The ultraviolet spectrum of **3** had λ_{max} 259 nm (ϵ 11 000) compatible with the indene chromophore present in this ring system.[13] Further reduction of **3** with lithium in ammonia took place smoothly to afford a tetrahydrofluorene derivative, the NMR spectrum of which still displayed two vinylic protons. This behavior is in accord with previous experience[1,3] that conjugated styrene-type double bonds undergo facile reduction, while isolated double bonds are resistant to further transformation with alkali metals in ammonia. The alternative 2,3-dihydrofluorene structure **7** may be rejected on several grounds. The observed chemical shift of the allylic protons (δ 3.05) occurs at unexpectedly low field for **7** and is more compatible with the doubly allylic protons of **3.** Also, the AB quartet pattern (J = 9 Hz) of the vinylic protons is unexpected for **7.** Moreover, reduction of **7,** presuming that it could be limited to the tetrahydro stage, should furnish a tetrahydrofluorene with at most one vinyl hydrogen atom.[15] Therefore, structure **7** may be rejected. The two additional structures **8** and **9** can also be ruled out since the observed chemical shift (δ 3.05) of the allylic protons is much more consistent with the doubly allylic assignment of **3.** The ultraviolet spectral data are also incompatible with **8** or **9,** since the maximum absorption of these more conjugated chromophores is anticipated to occur at considerably longer wavelength than observed.[17]

The 2,4a-dihydro structure **2** was assigned the second dihydro isomer on the basis of the integrated ^1H NMR spectrum. The benzylic proton at H_{4a}, uniquely characteristic of this structure, appeared as a multiplet at δ 3.69, while the two additional benzylic protons at H_9 were found as an AB quartet at δ 3.50 (J = 18 Hz). An analysis of the vinyl region showed an apparent singlet at δ 5.58, a multiplet at 5.86, and a doublet at 6.09 assigned to H_1, H_3, and H_4, respectively. The downfield signal assigned at H_4 was part of a basic AB pattern ($J_{3,4}$ = 9.7 Hz) which exhibited additional coupling to the allylic proton(s) δ 2.72 (J = 2.6 Hz). Irradiation of the allylic protons at δ 2.72 simplified the signal at 5.86 to a doublet of doublets ($J_{3,4}$ = 9.7 and $J_{3,4a}$ = 3.3 Hz). This general pattern is consistent with that observed for analogous 1,4-dihydroaromatic molecules,[1] and for the 4a-methyl homologue of **2** discussed in following paragraphs.



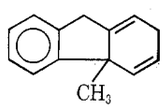
Analogous reductive methylation of fluorene with lithium in liquid ammonia followed by methyl bromide gave the 4a-methyl homologue of **2,** 4a-methyl-2,4a-dihydrofluorene (**10**), along with 9-methylfluorene and 9,9-dimethylfluorene, the relative proportions of which proved dependent upon reaction conditions (Table II).

The NMR spectrum of **10** closely resembled that of **2,** exhibiting a pair of allylic protons as a multiplet at δ 2.65, an AB quartet (J = 19 Hz, δ_A 3.73, δ_B 3.28) assigned to the benzylic

Table II. Reductive Methylation of Fluorene with Lithium and Methyl Bromide in Liquid Ammonia[a]

Time, min	Temp, °C	10	Product composition, % 9-Methylfluorene	9,9-Dimethylfluorene	Fluorene
5[b]	−78	38	37	5	12
5[c]	−78	45	26	13	4
10[b]	−78	33	36	21	1
30[b]	−33	40	0	30	1

[a] Conditions are described in the Experimental Section. [b] Lithium metal was added last. [c] Lithium metal was dissolved before addition of fluorene.



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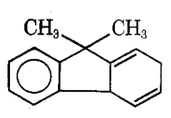
protons, three vinylic protons as multiplets at 5.52 (H_1) and 5.70 (H_3) and a doublet of doublets at 6.14 (H_4), and an aromatic multiplet (4 H) at 6.95–7.18. On decoupling by irradiation at δ 2.65, the H_3 and H_4 signals sharpened to clear doublets (J = 10.5 Hz for each) and the H_1 multiplet collapsed to a sharp singlet. The ultraviolet spectrum showed λ_{max} 256 nm (ϵ 2650), confirming the lack of conjugation with the aromatic ring.[18]

The origin of the side products, 9-methylfluorene and 9,9-dimethylfluorene, which accompany **10** is not immediately evident. Their formation, however, is indicative of involvement of the relatively acidic benzylic protons of fluorene in the foregoing reactions. It was of interest, therefore, to investigate the analogous transformations of 9,9-dimethylfluorene. Reduction of the latter with lithium in ammonia under conditions similar to those employed with fluorene afforded the anticipated analogue of **2**, i.e., 9,9-dimethyl-2,4a-dihydrofluorene (**11**), along with a second dihydro isomer characterized as 9,9-dimethyl-1,4-dihydrofluorene (**12**). Compound **11**, like the related dihydrofluorene isomer **2**, proved relatively unstable, undergoing spontaneous reversion to the parent hydrocarbon. The failure of Huckel and Schwen[10] to detect appreciable reaction between sodium and 9,9-dimethylfluorene in liquid ammonia is probably a consequence of decomposition of the dihydro products to 9,9-dimethylfluorene during the more prolonged and drastic workup procedure employed by these authors. Owing to its instability, **11** could not be obtained entirely free of **12** and 9,9-dimethylfluorene. The structural assignment, therefore, is based upon its NMR spectrum in the mixture, which closely resembled that of **2** and **10**, and upon characterization of its 4a-methyl analogue obtained as the major product of analogous reductive methylation.

Assignment of the structure of **12** is based on the NMR and



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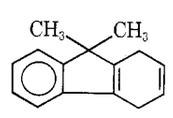

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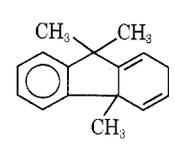

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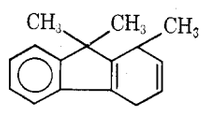

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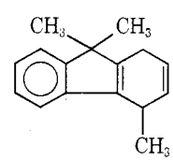

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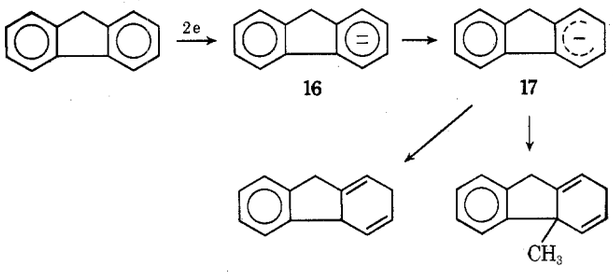
uv spectral data and upon characterization of the analogous product of reductive methylation of 9,9-dimethylfluorene as 1,9,9-trimethylfluorene (**14**). The uv spectrum of **12** had λ_{max} 262 nm (ϵ 12 200), which is consistent with **3** (λ_{max} 259 nm, ϵ 11 000)[13] and inconsistent with the alternative structures[17] analogous to **4–9**, which are thereby eliminated from consideration. The integrated NMR spectrum of **12** exhibited methyl, allylic, vinylic, and aromatic protons in the ratio of 6:4:2:4. The alternative 3,9a-dihydro structures analogous to **1**, as well as the 4,4a-, 1,9a-, and 4a,9a-dihydro structures analogous to **4**, **5**, and **6**, are expected to exhibit different patterns, and may therefore be rejected. Thus, **12** remains as the only structure consistent with the data.

Reductive methylation of 9,9-dimethylfluorene was carried out in order to trap the unstable **11** in the form of its 4a-methyl derivative. As anticipated, the major product (50–80% yield) was 4a,9,9-trimethyl-2,4-dihydrofluorene (**13**). It was accompanied by a second new compound identified as **14**. In confirmation of the structure of **13**, the integrated NMR spectrum exhibited the pattern seen for other 2,4a-dihydrofluorene derivatives, displaying methyl singlets at δ 1.28, 1.39, and 1.43 (9 H), an allylic multiplet centered at 2.72 (2 H), vinyl protons (2 H) as a multiplet at 5.63–5.97 (H_1 and H_3) and as a doublet (J = 9.5 Hz) at 6.26 (H_4), and an aromatic multiplet (4 H). The ultraviolet spectrum showed λ_{max} 271 nm (ϵ 2000), confirming the lack of conjugation between the olefinic groups and the aromatic ring.[13] Compound **14**, identified as 1,9,9-trimethyl-1,4-dihydrofluorene, exhibited an NMR spectral pattern resembling that of **12**, the minor product of reduction of 9,9-dimethylfluorene. To establish with greater certainty the position of attachment of the third methyl group in **14**, the latter was dehydrogenated with *o*-chloranil. The resulting trimethylfluorene (mass spectrum *m/e* 208) was a colorless oil which exhibited methyl peaks at δ 1.55 (6 H) and 2.50 (3 H) in the NMR spectrum. It was identified as 1,9,9-trimethylfluorene by comparison with an authentic sample synthesized from 1-methylfluorene through reaction with *n*-butyllithium and methyl bromide. The NMR spectra and retention times on GLC and TLC of both samples were identical. Since the alternative 4,9,9-trimethyl-1,4-dihydrofluorene structure (**15**) was also compatible with the uv and NMR spectral data for **14**, it was necessary to synthesize also 4,9,9-trimethylfluorene. This was accomplished through oxidative rearrangement of **13** with trityl fluoroborate according to the method described previously.[19] The NMR spectrum of 4,9,9-trimethylfluorene differed from that of the 1,9,9 isomer in several respects, notably the chemical shifts of the methyl singlets which appeared at δ 1.43 (6 H) and 2.65 (3 H). The retention times on GLC were also different. Therefore, **15** can be excluded as the structure of the second trimethyldihydrofluorene isomer, which is thereby established unequivocally as **14**.

Discussion

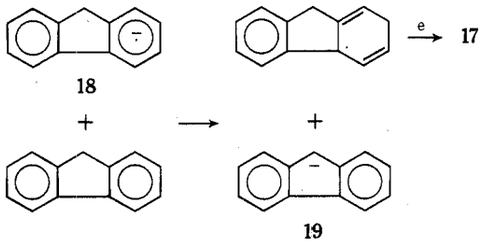
The principal products of both reduction and reductive methylation of fluorene and 9,9-dimethylfluorene are the 2,4a-dihydrofluorene derivatives (i.e., **2**, **10**, **11**, **13**). This is in accord with HMO theoretical prediction and contrary to the claim of Huckel and Schwen.[10] The mechanism of these transformations, based on the detailed study of the analogous transformations of the closely related biphenyl ring system,[8] can be presumed to involve (1) rapid addition of two electrons to form the fluorenyl dianion (**16**); (2) fast protonation by the medium in the 2 position, the site of maximum electron density; and (3) survival of the resulting monoanion (**17**) sufficiently long to undergo either kinetic protonation by a more acidic proton source (e.g., NH_4Cl) or alkylation with methyl bromide at the benzylic position.

The origin of the minor products is of considerable interest,

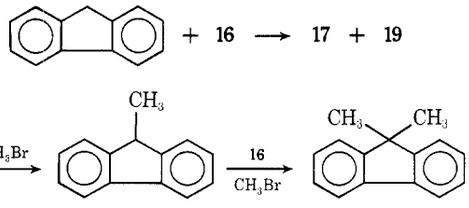


since reduction partially contrary to HMO theoretical prediction is clearly documented for only *p*-terphenyl.[6] In the present case, the principal minor products of reduction and reductive methylation are the respective 1,4-dihydrofluorene derivatives **3, 12,** and **14.** Evidently, initial protonation takes place at either the 1 or the 4 positions. Characterization of the minor product of reductive methylation of 9,9-dimethylfluorene as the 1-methyl derivative, **14,** indicates that protonation in the 4 position is preferred in this case. It would be unsafe, however, to generalize on the basis of this single example. In the case of *p*-terphenyl it was shown that protonation contrary to prediction was a consequence of ion pair association, and by appropriate variation of the cation, solvent, and other parameters the site of proton addition could be controlled.[6] In the present case, attempts to demonstrate similar effects (Table I) gave inconclusive results.

An unusual feature of fluorene with respect to hydrocarbons previously investigated is the relative acidity of the benzylic protons (pK_a 25).[20] Reaction of fluorene with lithium metal in THF has been shown to afford 9-lithiofluorene (**19**) and a mixture of tetra- and hexahydrofluorenes.[16] The mechanism proposed involves protonation by fluorene of the radical anion **18** produced on interaction of lithium and fluorene, followed by addition of a second electron from unreacted lithium to the resulting radical to form the anion **17** capable of metalating another molecule of fluorene. In liquid ammonia with excess



lithium present a similar mechanism is unlikely, since the radical anion would be expected to undergo facile transformation to the dianion.[8] However, protonation of the dianion directly by fluorene to furnish the monoanions **17** and **19** is quite reasonable, since the relative acidity of fluorene (pK_a = 25)[20] exceeds that of ammonia (pK_a = 34).[20] Methylation of **19** leads to 9-methylfluorene, which in turn can undergo further reaction on the remaining benzylic hydrogen in similar



manner to provide 9,9-dimethylfluorene. This mechanism accounts most satisfactorily for the relatively large proportions of the methylfluorenes formed in reductive methylation (Table II).

The observed facility of 1,4-dihydrofluorene to undergo further reduction to tetrahydrofluorene deserves comment, since overreduction is not generally a serious complication when the standard procedures developed earlier in our laboratory[1,6,8] are employed. These procedures take advantage of the stability and resistance to further electron addition of many hydrocarbon anions in liquid ammonia by withholding addition of the protonating agent until the end of the reaction period, then adding a relatively acidic proton source (usually NH_4Cl) rapidly to quench reaction. The diminished effectiveness of this technique in this case suggests that the monoanion of 1,4-dihydrofluorene must itself be protonated already to some extent by the medium. The styrene-type double bond of the neutral hydrocarbon should, of course, undergo facile further reduction.

Experimental Section

Physical Data. ^1H NMR spectra were obtained on Varian T-60 and Bruker HX 270 spectrometers. Chemical shifts are reported relative to Me_4Si in CCl_4 unless specified otherwise; integration was consistent with all assignments. Microanalyses for C and H correct to ±0.3 were obtained for all new compounds and were submitted for review, except the dihydrofluorene derivatives **2** and **11,** which were too unstable to provide meaningful microanalytical data. GLC analyses were performed on a F & M Model 500 chromatograph employing a 6 ft × 0.25 in. 20% DEGS column on 60–80 mesh Chromosorb W at 125 and 135 °C with 20 psi helium pressure and 50 ml/min flow rate. Mass spectra were determined on a Finnigan 1015 mass spectrometer at 70 eV. Ultraviolet spectra were taken on a Cary Model 14 spectrometer.

Reactions in Liquid Ammonia. All reactions were conducted under helium (to avoid formation of lithium nitride) in a three-neck Morton flask fitted with a Dewar condenser. Precautions described in preceding papers[6,8] for the exclusion of impurities (moisture, air, peroxides in solvents, and metallic salts in ammonia) known to often have a deleterious effect on reactions in ammonia were scrupulously observed. Fluorene was recrystallized from methanol and dried in vacuo. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ before use. Ammonia was distilled into the reaction vessel through a column of barium oxide (10–20 mesh). Lithium wire (Lithco) was freshly cut and washed free of oil with hexane before use. Methyl bromide was purified by passage of the gas through a tube of silica gel and sand into the reaction vessel. Products were isolated rapidly by partition between ether and water to minimize isomerization and other secondary processes. NMR spectra were taken immediately upon isolation of products and before GLC or other procedures in order to detect any decomposition occurring during these processes.

9-Methylfluorene. *n*-Butyllithium (15% in hexane) (105 mmol) was added to a solution of fluorene (16.6 g, 100 mmol) in THF (300 ml) at −40 °C over a period of 10 min. The resulting orange solution was stirred at −40 °C for 80 min, then decolorized by a stream of gaseous methyl bromide bubbled into the solution (flow rate 60 mmol/min) over a period of 2 min. Then NH_4Cl (50 g in 300 ml of water) was added, followed by ether (200 ml), and products were isolated by conventional procedure. Recrystallization of the product from methanol afforded 9-methylfluorene (17.65 g, 98%) as colorless needles: mp 45–46 °C (lit.[21] 45–46 °C); NMR δ 1.50 (d, 3, CH_3), 3.85 (q, 1, H_9), and 7.73–7.06 ppm (m, 8, aromatic).

9,9-Dimethylfluorene. Reaction of 9-methylfluorene (7.98 g, 44 mmol) with *n*-butyllithium and methyl bromide following essentially the same procedure employed for monomethylation furnished 9,9-dimethylfluorene (8.44 g, 98%) as colorless needles: mp 96–97 °C (lit.[21,22] 95–96 °C); NMR δ 1.45 (s, 6, CH_3) and 7.67–7.05 ppm (m, 8, aromatic); uv (CH_3OH) λ 258 nm (ε 15 900) 262 (16 900), 265 (16 400), 272 (12 900), 289 (6600), 294 (5050), and 300 (11 000).

Reduction of Fluorene. A solution of fluorene (830 mg, 5 mmol) in ether (75 ml) was added to 150 ml of liquid ammonia in a dry ice bath at −78 °C followed by lithium wire (76 mg, 11 mmol), and 5 min later the deep brown solution was quenched by addition of solid NH_4Cl (20 g). Addition of water and ether followed by the workup procedure recommended above gave a solid product (820 mg) consisting of **2** (39%), **3** (37%), tetrahydrofluorene (8%), and recovered fluorene (11%) by NMR and GLC analysis; GLC retention times at 135 °C were 4.2, 6.4, 2.2, and 8.4 min, respectively. The relative yields of the product components were highly dependent upon reaction conditions (cf. Table I).

Samples of **2** and **3** were trapped off the GLC column. Compound **2** had NMR δ 2.72 (m, 2, allylic), 3.50 (AB quartet, 2, J = 18 Hz, δ_9,

3.59, δ_9 3.41, $H_{9',9}$), 3.69 (m, 1, H_{4a}), 5.58 (apparent s, 1, H_1), 5.86 (m, 1, H_3) (decoupling the allylic protons at δ 2.72 simplified the signal at 5.86 to a doublet of doublets, $J_{3,4}$ = 9.7, $J_{3,4a}$ = 3.3 Hz), 6.09 (d of d, 1, $J_{3,4}$ = 9.7, $J_{4,4a}$ = 2.6 Hz, H_4), and 6.95–7.28 ppm (m, 4, aromatic); mass spectrum *m/e* 168 (parent ion). Compound **3** had mp 110–111 °C; NMR δ 3.04 (s, 4, allylic), 3.20 (s, 2, benzylic), 5.84 (AB quartet, 2, J = 9.0 Hz, δ_A 5.88 δ_B 5.78, vinylic), and 6.96–7.33 ppm (m, 4, aromatic); uv λ_{max} (CH_3OH) 259 nm (ϵ 11 000).

Reductive Methylation of Fluorene. Reaction was conducted as described for reduction except that prior to quenching with ammonium chloride a stream of gaseous methyl bromide was passed into the reaction vessel for 1 min to decolorize the solution (flow rate 60 mmol/min). GLC analysis of the product (871 mg) gave 4a-methyl-2,4a-dihydrofluorene (**10**), 9,9-dimethylfluorene, 9-methylfluorene, and recovered fluorene, having retention times at 135 °C of 3.0, 5.0, 7.2, and 8.4 min, respectively. The yields of each of these components were dependent upon reaction conditions (Table II).

Compound **10** trapped off the GLC column was a colorless liquid: NMR δ 1.18 (s, 3, CH_3), 2.65 (m, 2, allylic), 3.51 (AB quartet, 2, J = 19 Hz, δ_A 3.73, δ_B 3.28, H_9), 5.52 (m, 1, H_1), 5.70 (m, 1, H_3), 6.14 (d of d, 1, H_4), and 6.95–7.18 ppm (m, 4, aromatic); when the allylic protons were decoupled the H_3 and H_4 signals became doublets (J = 10.5 Hz) and the H_1 multiplet collapsed to a sharp singlet; uv (CH_3OH) λ 249 nm (ϵ 2390), 256 (2650, 262 (2450), 278 (550), and 291 (380).

Reduction of 9,9-Dimethylfluorene. Reaction of 9,9-dimethylfluorene (970 mg, 5 mmol) with lithium (76 mg, 11 mmol) in ammonia following the procedure described for similar reaction of fluorene afforded a product (950 mg) shown by GLC to contain **11** (38%), **12** (24%), and recovered dimethylfluorene (31%); GLC retention times at 125 °C were 4.4, 5.2, and 6.8 min, respectively. Samples of both **11** and **12** were trapped off the GLC column. The instability of **11** with respect to decomposition back to 9,9-dimethylfluorene prevented detailed analysis of its NMR spectrum which in the mixture resembled closely that of **2** and **10**. Compound **12** was an oil: NMR δ 1.21 (s, 6, CH_3), 2.85 (t, 2, J = 8.25 Hz, $H_{1',1}$), 3.06 (t, 2, J = 8.25 Hz, $H_{2',2}$), 5.87 (s, 2, vinylic), and 7.00–7.39 ppm (m, 4, aromatic); uv (CH_3OH) λ 262 nm (ϵ 12 200), 272 (9300), 282 (3370), 288 (2230), and 299 (2380).

Analogous reaction in THF with 2.5 equiv of lithium at −33 °C for 30 min gave **11** (60%), **12** (25%), and recovered dimethylfluorene (4%).

Reductive Methylation of 9,9-Dimethylfluorene. Reaction of 9,9-dimethylfluorene (970 mg, 5 mmol) with lithium and methyl bromide in ammonia according to the procedure employed with fluorene gave a product (985) mg) shown by GLC to consist of **13** (49%), **14** (12%), **11** (2%), and recovered 9,9-dimethylfluorene (33%); GLC retention times were 3.2, 5.5, 4.4, and 6.8 min, respectively. Distillation through a spinning band column furnished pure **13** as a colorless oil: bp 117 °C (10 mm); NMR δ 1.28 (s, 3, 4a-CH_3), 1.39 (s, 3, 9-CH_3), 1.43 (s, 3, 9-CH_3), 2.62–2.83 (m, 2, allylic), 5.63–5.97 (m, 2, $H_{1,3}$), 6.26 (d, 1, J = 9.5 Hz, H_4), and 7.08–7.27 ppm (m, 4, aromatic); uv (CH_3OH) λ 259 nm (ϵ 316), 264 (630), 271 (2000), and 289 (466). Compound **14** trapped off the GLC column was an oil: NMR δ 1.30 (d, 3, J = 6 Hz, 4-CH_3), 1.28 (s, 3, 9-CH_3), 1.42 (s, 3, 9-CH_3), 3.12 (m, 2, $H_{1',1}$), 3.28 (m, 1, H_2), 5.79 (AB quartet, 2, J = 12 Hz, δ_A 5.84, δ_B 5.74, $H_{3,4}$), and 7.03–7.36 ppm (m, 4, aromatic); uv (CH_3OH) λ 266 nm (ϵ 10 955) and 293 (1365).

Similar reaction in which 2.5 equiv of lithium, THF, −33 °C, and 2.5 h were employed afforded **13** (80%), **14** (9%), and recovered 9,9-dimethylfluorene (9%).

1,9,9-Trimethylfluorene. Reaction of 1-methylfluorene (720 mg, 4 mmol) with a sixfold excess of *n*-butyllithium and methyl bromide following essentially the same procedure employed for the preparation of 9,9-dimethylfluorene furnished 1,9,9-trimethylfluorene (817 mg, 3.93 mmol, 98%) as a colorless oil: NMR δ 1.55 (s, 6, 9-CH_3), 2.50 (s, 3, 1-CH_3), and 6.80–7.70 ppm (m, 7, aromatic); it showed one spot on TLC on silica gel and a single sharp peak on GLC.

Dehydrogenation of 1,9,9-Trimethyl-1,4-dihydrofluorene (14). A solution of **14** (17 mg) and *o*-chloranil (30 mg) in benzene (4 ml) was refluxed for 1 h. After cooling to room temperature, the residue was chromatographed on Florisil eluted with hexane to afford 1,9,9-trimethylfluorene as a colorless oil, mass spectrum (70 eV) *m/e* 208. Its NMR spectrum and retention times on TLC and GLC were identical with those of the authentic compound.

Dehydrogenation of 4a,9,9-Trimethyl-2,4a-dihydrofluorene (13). A solution of **13** (120 mg) and trityl fluoroborate (220 mg) in acetic acid (6 ml) was heated at refluxed for 1 h. Conventional workup furnished an oil (157 mg), NMR and GLC analysis of which indicated quantitative conversion to triphenylmethane and 4,9,9-trimethylfluorene. The latter was extracted from the mixture by its greater solubility in benzene. Pure 4,9,9-trimethylfluorene trapped off the GLC column was a colorless oil: NMR δ 1.43 (s, 6, 9-CH_3), 2.65 (s, 3, 4-CH_3), and 6.90–7.90 ppm (m, 7, aromatic); mass spectrum (70 eV) *m/e* 208.

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Registry No.—**2,** 59247-36-8; **3,** 55297-18-2; **10,** 59247-37-9; **12,** 59247-38-0; **13,** 59247-39-1; **14,** 59247-40-4; methyl bromide, 74-83-9; fluorene, 86-73-7; 9-methylfluorene, 2523-37-7; 9,9-dimethylfluorene, 4569-45-3; 1-methylfluorene, 1730-37-6; 1,9,9-trimethylfluorene, 59247-41-5; 4,9,9-trimethylfluorene, 59247-42-6; lithium, 7439-93-2; calcium, 7440-70-2; ammonia, 7664-41-7.

References and Notes

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