52783-75-2; 3-bromoveratronitrile, 59116-12-0; 3-bromo-4,5-dimethoxyphenylacetic acid, 56982-10-6; 3,4-dimethoxyphenethylamine, 120-20-7; *N*-(3,4-dimethoxyphenethyl)-3-bromo-4,5-dimethoxyphenylacetamide, 65292-97-9; 1-(3-bromo-4,5-dimethoxybenzyl)-3,4-dihydro-2-methyl-6,7-methoxyisoquinolinium iodide, 65292-98-0; allyl bromide, 106-95-6; 2-bromo-3-benzyloxy-4-methoxyphenylacetic acid, 38849-42-2; 3,4-dimethoxy-6-chlorobenzaldehyde, 18083-05-5; 6-chloro-3,4-dimethoxybenzoic acid, 60032-95-3; 3-methoxyphenylacetaldehyde, 65292-99-1; α-hydroxy-5,4′-dimethoxy-2-methylbibenzyl, 65293-00-7; α-chloro-5,4′-dimethoxy-2-methylbibenzyl, 65293-01-8; 6′-chlorolaudanosine, 55954-20-6; 2-bromo-4-methoxytoluene, 36942-56-0.

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Methano-Bridged 14π-Electron Aromatic Annulenes. 1. 1,6-Methanofluorenyl and 9-Methyl-1,6-methanofluorenyl Anions

Ronald J. Hunadi[1] and George K. Helmkamp*

Department of Chemistry, University of California, Riverside, California 92521

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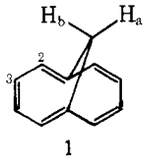
The syntheses of 1,6-methanofluorene, *syn*- and *anti*-9-methyl-1,6-methanofluorene, and their monoanions are described. The anions were shown by proton NMR to be delocalized aromatic systems existing in "cycloheptatriene" rather than "norcaradiene" forms.

Several methano-bridged 14π-electron aromatic systems have been described, namely *syn*-1,6-methano-8,13-oxido[14]annulene,[2] *syn*-1,6-methano-8,13-bismethano[14]-annulene,[3] 3,4-benzo-1,6-methano[10]annulene,[4] 1,7-methanododecapentaenyl dianion,[5] 1,6-methanododecapentaenyl dianion,[5] the dianion of 1-aza-2-methoxy-5,10-methano[12]annulene,[6] 2,3-benzo-1,6-methano[10]annulene,[7] and the 1,6-methanocarbazoyl anion.[8] Proton NMR spectroscopy showed delocalized aromatic π systems for all of these except the [11]annulene dianion, which decomposed before a spectrum could be recorded. In our initiation of a study of the effects of methano bridges on the physiological properties of psychoactive compounds (via reduction in aromaticity and alteration of steric factors) we found it necessary to investigate bridging procedures for various types of similar parent species. Included among them was fluorene, which can be considered a benzoannelated indene.

Benzoannelation reduces aromaticity of a molecule and its diamagnetic ring current. For example, Vogel[7] showed such a reduction for 2,3 annelation of 1,6-methanonaphthalene, **1**, with the observation that resonance signals for protons H_a and H_b are shifted 0.5 and 1.9 ppm, respectively, downfield on introduction of the additional ring.



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We now wish to report the syntheses of 1,6-methanofluorene (**2**) and 9-methyl-1,6-methanofluorene (**3**), and their corresponding anions **4** and **5**. The anions exhibited electron delocalization over the entire π system, but a decided downfield shift of bridge protons relative to those in the methanoindenyl anion[9] indicated a reduced diamagnetic ring current due to the additional ring.[10]

The key intermediate for the synthesis of 1,6-methanofluorene,[11] **2**, was ketone **6**, whose preparation from indene was already described.[13] It was readily reduced to the epimeric alcohols, **7**, which then were converted successively to the bridged *syn*-alcohol **8**, mesylate **9**, and mixture of elimination products **10** and **11**.

Previous experience showed that **10** should be preferred for the conversion to diene **2**. Since the **10**/**11** ratio from mesylate **9** was 60:40 (somewhat more favorable after chromatography

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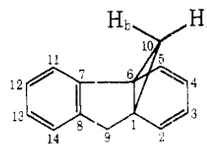
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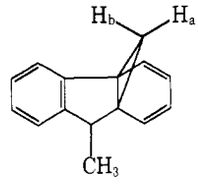
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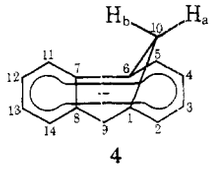
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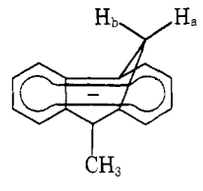
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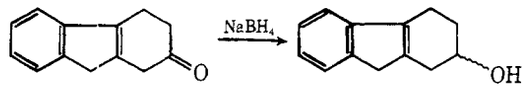
with silver nitrate on silica gel), attempts were made to improve the yield of the preferred monoene by carrying out eliminations on anti halides derived from **9**. Even though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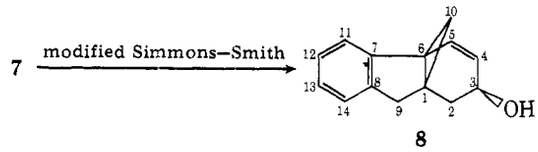
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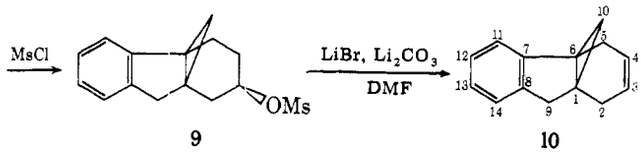
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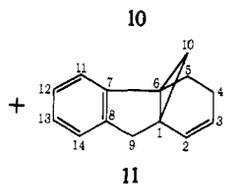

10 + 11 → 2 (dehydrogenation)

elimination by DBN in the iodo species yielded a 75:25 ratio, the overall yield of **10** was less than that directly obtained from the mesylate.

Among the unsuccessful routes for converting **11** to 1,6-methanofluorene were NBS bromination/elimination, DDQ dehydrogenation, and epoxidation/ring opening/elimination. However, addition of bromine to **10** at −78 °C followed by dehydrohalogenation with DBN/THF at 60 °C gave **2** in 75% distilled yield.

The bridged anion, **4**, was prepared by deprotonation of **2** with dimsyl-d_5 sodium in Me_2SO-d_6 using a modified procedure described originally by Rosen.[14] A 90-MHz proton NMR spectrum of the resulting solution thus prepared gave good resolution because of low concentration and viscosity.

Quenching of 4. Treatment of **4** with water regenerated **2** in near-quantitative yield, confirming the integrity of the carbon skeleton during proton transfers. Quenching instead with deuterium oxide gave *anti*-9-deuterio-1,6-methanofluorene, **12**. Similarly, methyl iodide converted **4** stereospecifically to *anti*-9-methyl-1,6-methanofluorene, **13**. These reactions are analogous to those previsouly described for the 1,6-methanoindenyl anion.[14] A difference between the methanoindenyl and methanofluorenyl systems appeared in the acidity of the remaining 9-proton of **13**. Even with a great excess of base no deprotonation of the methylated methanoindene had been noted, but under the same conditions **13** could be converted to its anion, **5**. Subsequent protonation of **5** yielded *syn*-9-methyl-1,6-methanofluorene, **14**, providing an interesting sequence for the generation of a pair of isomers.

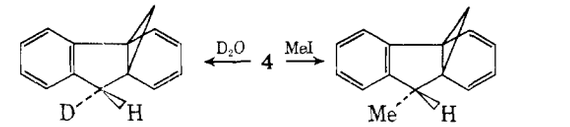
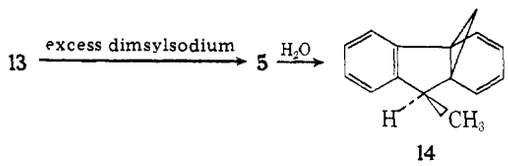

12 ← 4 → 13

Table I. 90-MHz Proton NMR Data for 4

Proton	Splitting pattern	Chemical shift, δ	Coupling constants, Hz
11	Double doublet	7.62	J = 7.55 J' = 1.46
14	Doublet	7.25	J = 8.06
5	Doublet	7.04	J = 7.18
2	Doublet	6.80	J = 8.21
13	Doublet of triplets	6.70	J = 8.21 J' = 1.46
12	Triplet	6.38	J = 7.20
3	Triplet	6.29	J = 8.35
9	Unresolved multiplet[a]	5.63	
4	Triplet	5.60	J = 7.62
10b	Doublet	−0.29	J = 7.33
10a	Double doublet	−0.84	J = 7.33 J' = 1.32

[a] W-coupled to 10a as shown by some sharpening of the band on decoupling.


13 → 5 → 14

Discussion

As in Rosen's observation with methanoindene,[15] deprotonation and subsequent anion quenching are stereospecific processes. This is confirmed in several ways. Of primary importance is the reported observation[16] that a proton syn to a methylene bridge is farther upfield than that of its anti counterpart. The benzylic proton that remains in **12** appears at δ 3.03, near the center of the doublet for the *syn*-benzylic proton of **2**. Furthermore, successive deprotonation and protonation of **12** resulted in virtually complete removal of the deuterium (only a small amount of **12** could be detected), demonstrating stereospecificity in both the original deuteration and subsequent deuterium loss. Finally, the clean inversion of the 9-methyl from syn to anti was consistent with preferential attack by the anion at its position opposite the bridge, and both isomers on deprotonation yielded the same anion as demonstrated by NMR spectra.

The 1,6-Methanofluorenyl Anion, 4. The pertinent proton NMR data for **4** are given in Table I. Assignments were made by comparison of chemical shifts with those of model systems that included the indenyl anion (**15**),[17] fluorenyl anion (**16**),[18] and 1,6-methanoindenyl anion (**17**).[9,14]

The cyclopropyl protons H_b and H_a of **4** are found at δ −0.29 and −0.84 as compared with δ −0.45 and −0.95 in **17**. The

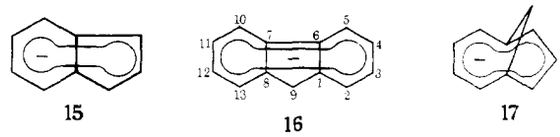

15 16 17

Table II. 90-MHz Proton NMR Data for 2

Proton	Splitting pattern	Chemical shift, δ
2,5	Complex multiplet	6.42
11,12,13,14	Sharp multiplet	6.87–7.53
3,4	Sharp multiplet	5.85
10b	Doublet (J = 3.6 Hz)	1.45
10a	Doublet (J = 3.6 Hz)	0.20
9a,9b	Doublets (J = 16.5 Hz)	2.90, 3.27

Table III. 90-MHz Proton NMR Data for 5

Proton	Splitting pattern	Chemical shift, δ	Coupling constants, Hz
11	Double doublet	7.55	J = 7.47, J' = 1.32
14	Double doublet	7.18	J = 7.91, J' = 1.17
2,5	Doublet	6.98	J = 7.18
13	Doublet of triplets	6.81	J = 8.06, J' = 1.47
12	Triplet	6.43	J = 6.96
3	Triplet	6.34	J = 8.50
4	Triplet	5.56	J = 7.69
Methyl	Singlet	1.93	
10b	Doublet	−0.26	J = 7.62
10a	Doublet	−0.88	J = 7.62

change is not as dramatic as that observed for the 2,3-benzoannelation of **1**, which causes shifts of 1.9 and 0.5 ppm.[7] Delocalization of charge over the 14 π system is shown by the downfield shift for protons in the six-membered aromatic ring when **2** is converted to **4**. In **2**, protons 11, 12, 13, and 14 appeared as a very complex multiplet at δ 6.87–7.53 (Table II) but shifted to as low as δ 6.38 for H-12 (Table I) in **4**. This kind of shift was described by Cox[18] when fluorene was converted to its anion, **16**.

HMO theory[17] predicted that, next to C-9, carbons C-4 and C-11 in **16** should have the highest electron density and C-5 and C-10 the lowest. Introduction of the methano bridge into **16** to give **4** caused an upfield shift in protons attached to positions 2, 3, 4, and 5 due to higher charge density, but relative density arrangements remained the same.

The 9-Methyl-1,6-methanofluorenyl Anion, 5. The proton NMR spectrum (Table III) for **5** is very similar to that of **4**. The inductive effect of the methyl group produced a downfield shift for H-2 and H-13, and the bridge proton over the six-membered ring no longer shows W coupling as it did in **4** because of the absence of any 9 proton.

During the interconversion of the anti to the syn form of 9-methylmethanofluorene via **5**, the methyl protons shifted from δ 1.49 to δ 1.18, showing that the cyclopropyl proton H-10b does have a shielding effect on the methyl group. This shielding concept is consistent with all of the stereochemical consequences proposed for all proton removals and quenchings in the methanofluorene system.

The structure for the methano-bridged fluorenyl anions (**4** and **5**) is shown in cycloheptatriene rather than norcaradiene (**18**) form. Primary justification for the assignment comes from ^{13}C NMR spectra. Pertinent data are given in Table IV.

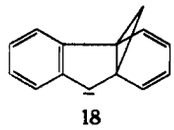


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Table IV. Carbon-13 Chemical Shifts for Bridged Fluorenes and Related Compounds

Compound	Registry no.	Chemical shifts, δ at 22.638 MHz C-1	C-6	C-10
Methanoindene[a]	174-44-7	40.07	48.07	28.01
Fluorene[19]	86-73-7	143.1	141.6	
2[a]	19540-84-2	39.57	45.57	26.47
15[b]	65150-09-6	128.1	(128.1)	
17[b]	65150-10-9	113.73	(113.76)	42.07
16[a]	12257-35-1	136.04	121.48	
4[b]	65150-11-0	119.17	101.30	39.83
8[a]	65150-12-1	32.76	26.54	24.60
10[a]	65167-98-8	32.67	26.15	24.62
11[a]	65150-13-2	36.59	26.32	26.09

[a] In chloroform/Me_4Si. [b] In Me_2SO-d_6/Me_4Si.

The effect of change in charge state is illustrated by the relatively small change in transforming fluorene to its anion, **16**. The very large change in the opposite direction in converting methanofluorene, **2**, to the methanofluorenyl anion, **4**, or methanoindene to methanoindenyl anion, **15**, must be ascribed to a change in hybridization of the carbon atoms at C-1 and C-6. Thus, a large reduction in s character in the anion would preclude consideration of a norcaradiene structure for these products.

Experimental Section

Spectra were obtained as follows: 60-MHz NMR spectra on Varian A-60, A-60d, or T-60 spectrometers; 90-MHz ^1H NMR and 22.63-MHz ^{13}C NMR spectra on a Brüker HX-90 FT multinuclear spectrometer; infrared spectra on a Perkin-Elmer Model 137 spectrometer; ultraviolet spectra on a Cary-14 spectrometer; and mass spectra on a Finnigan mass spectrometer. Microanalyses were performed by C. F. Geiger and Chemalytics, Inc. High-resolution mass spectra were recorded by Dr. Kai Fang on an AEI MS-9 spectrometer.

Melting points, obtained on a Thomas-Hoover capillary melting point apparatus, are uncorrected. Evaporative bulb-to-bulb distillations were carried out on a Jumo SSP-O apparatus. High-pressure liquid chromatography was carried out on a Waters Associates liquid chromatograph Model 6000-A.

Grace-Davison grade 62 neutral silica gel, EM precoated PLC plates (silica gel 60 F-254) and 0.25-mm plates (EM silica gel 60 F-254) were used for preparative scale chromatography. Analytical thin-layer chromatography was performed using EM precoated TLC sheets (silica gel F-254, 0.25 mm on plastic support).

Tetrahydrofuran was redistilled from potassium benzophenone ketyl under nitrogen just prior to use; hexane and methylene chloride were distilled; all other solvents were used as obtained from Mallinckrodt.

2-Hydroxy-1,2,3,4-tetrahydrofluorene (7). To a stirred 0 °C solution of 33.5 g (0.182 mol) of ketone **6** (prepared from indene[13]) in 1200 mL of absolute ethanol was added 20.7 g (0.546 mol) of sodium borohydride (cautiously and slowly). The mixture was warmed to room temperature and kept there for 7.25 h. After solvent removal, the residue was taken up in 25% aqueous sodium hydroxide and stirred at room temperature overnight. The organic material was extracted into ether and washed with dilute hydrochloric acid and water. Drying over $MgSO_4$ followed by solvent removal and crystallization (hexanes/chloroform) gave 25.6 g (76%) of **7** as off-white plates: mp 103.5–104.5 °C; IR (KBr) 3.00 (OH), 3.45, 6.90, 9.70, 13.28, 1400 μm; NMR ($CDCl_3$/Me_4Si) δ 6.97–7.49 (m, 4 H), 3.88–4.31 (m, 1 H), 3.16 (broad s, 2 H), 2.31–2.79 (m, 5 H, allylic and hydroxyl protons), 1.74–2.18 (m, 2 H); MS m/e (rel intensity) 186 (16), 115 (100). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.47; H, 7.57.

***syn*-3-Hydroxy-7,8-benzotricyclo[4.3.1.0^{1,6}]dec-7-ene (8).** A zinc–copper couple[20] was prepared by heating to reflux 35.8 g (0.548 mol) of 30 mesh zinc and 0.5 g (0.0015 mol) of cupric acetate monohydrate in 125 mL of acetic acid for 10 min. After the acetic acid was decanted, the couple was washed five times with boiling ether and dried under nitrogen. The zinc–copper couple was transferred to a three-necked flask equipped with a mechanical stirrer, addition funnel, reflux condenser, and nitrogen inlet/outlet. The couple was

covered with 100 mL of ether. To the addition funnel was added 25.5 g (0.137 mol) of **7**, 147.0 g (0.548 mol) of methylene iodide, and 600 mL of ether. One crystal of iodine was added to the zinc–copper couple mixture and the addition of methylene iodide/**7** solution was started. The flask was heated (heat lamp) for 5 min to start the reaction. Then the addition rate was regulated to maintain a gentle reflux. After the addition was complete (50 min), the mixture was refluxed for an additional 10.5 h. The flask was cooled to 0 °C and saturated ammonium chloride solution was added. The aqueous phase was extracted with ether and the combined organic phases were washed twice with saturated ammonium chloride, twice with saturated sodium bicarbonate solution, and water. This extract was dried over $MgSO_4$, filtered, and concentrated. Chromatography (silica gel) of the residue gave 21.3 g (78%) of **8** as a viscous, yellow oil which could not be induced to crystallize. An analytical sample was obtained by preparative thick-layer chromatography (light yellow oil): R_f = 0.499 (100% ethyl ether); IR (film) 3.00 (OH), 3.31, 3.45, 3.53, 6.81, 9.55, 9.77, 10.28, 13.20, 13.70, 14.09 μm; NMR ($CDCl_3$/Me_4Si) δ 7.00–7.22 (m, 4 H), 3.35–3.90 (10-line m, 1 H), 3.11 (d, J = 17 Hz, 1 H, benzylic H anti to cyclopropane), 2.91 (d, J = 17 Hz, 1 H, benzylic proton syn to cyclopropane), 0.91–2.64 (m, 7 H), 1.05 (d, J = 4.4 Hz, 1 H, H-10b), 0.31 (d, J = 4.4 Hz, 1 H, H-10a); MS m/e (rel intensity) 200(56), 167(91), 128(61), 115(100). Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.73; H, 7.93.

Methanesulfonate Ester 9. To a stirred solution (−5 to −10 °C) of 18.7 g (0.094 mol) of alcohol **8** and 15.6 g (0.154 mol) of triethylamine in 125 mL of methylene chloride was added 15.0 g (0.103 mol) of methanesulfonyl chloride over a period of 30 min. The mixture was kept at −5 to 0 °C for an additional 30 min and then stirred at room temperature for 2 h. The solution was cooled to 0 °C, 150 mL of water was added, and the mixture was warmed to room temperature. The aqueous phase was reextracted with methylene chloride. The combined organic phases were washed successively with water, 3 M hydrochloric acid (three times), saturated sodium bicarbonate solution (twice), and saturated sodium chloride solution. The organic extract was dried over $MgSO_4$, filtered, and evaporated to yield 24.4 g (94%) of an orange-yellow, viscous oil (R_f = 0.701 in 100% diethyl ether). A sample was purified by preparative thick-layer chromatography (eluting with 100% diethyl ether, run up twice) to yield a colorless oil which solidified to a near-colorless, waxy solid: mp 81–83 °C; IR (film) 3.34, 3.45, 6.83, 6.95, 7.51 (O=S=O), 8.58 (O=S=O), 10.62, 13.18, 13.73 μm; NMR ($CDCl_3$/Me_4Si) δ 6.94–7.34 (m, 4 H), 4.37–4.92 (m, 1 H), 3.10 (d, J = 17 Hz, 1 H), 2.94 (d, J = 17 Hz, 1 H), 2.87 (s, 3 H), 1.24–2.64 (m, 6 H), 1.08 (d, $J \cong$ 4.5 Hz, 1 H), 0.35 (d, $J \cong$ 4.5 Hz, 1 H); MS m/e (rel intensity) 278(9), 182(90), 167(100), 141(83). Anal. Calcd for $C_{15}H_{18}O_3S$: mol wt, 278.0976. Found: mol wt (MS), 278.0975.

7,8-Benzotricyclo[4.3.1.0^{1,6}]deca-3,7-diene (10) and 7,8-Benzotricyclo[4.3.1.0^{1,6}]deca-2,7-diene (11). Mesylate Method. A mixture of 16.2 g (0.058 mol) of mesylate **9**, 21.6 g (0.292 mol) of lithium bromide, and 7.6 g (0.088 mol) of lithium carbonate in 400 mL of dimethylformamide was stirred under nitrogen for 4 h at 125 °C. At room temperature water was added. An ether extract was washed four times with water, dried over $MgSO_4$, filtered, and evaporated to give 9.3 g (88%) of a dark brown oil. The crude product was chromatographed on 10% silver nitrate-impregnated silica gel. Elution with 2% diethyl ether/98% hexanes gave 4.07 g (44%) of **10** as a light yellow oil (R_f = 0.730, 3:1 benzene/diethyl ether on 10% silver nitrate-impregnated silica gel). An analytically pure sample was obtained by evaporative bulb-to-bulb distillation (92.5 °C, 0.075 mm). Compound **10** was obtained as a colorless oil: IR (film) 3.30, 3.46, 3.53, 6.73, 6.97, 13.13, 13.76 μm; NMR (CCl_4/Me_4Si) 6.84–7.41 (m, 4 H, aromatic), 5.53 (m, 2 H, vinyl), 3.09 (d, J = 17 Hz, 1 H, benzylic H anti to cyclopropane), 2.90 (d, J = 17 Hz, 1 H, benzylic H syn to cyclopropane), 1.89–2.92 (m, 4 H, allylic), 1.06 (d, J = 3.8 Hz, H-10b), 0.24 (d, J = 3.8 Hz, 1 H, H-10a); MS m/e (rel intensity) 182(31), 167(40), 165(22), 128(100). Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.15; H, 8.06.

Continued elution with 4% diethyl ether/96% hexanes yielded 2.48 g (27%) of **11** as an orange-red oil. This oil was purified by short-path distillation to give 1.76 g (17%) of a colorless oil: bp 58–60 °C (0.1 mm); R_f = 0.651, 3:1 benzene/ether on 10% silver nitrate-impregnated silica gel; IR (film) 3.34, 3.48, 3.55, 5.85, 6.83, 13.18, 13.80, 14.28 μm; NMR (CCl_4/Me_4Si) δ 6.87–7.33 (m, 4 H, aromatic), 6.10 (dd, J = 10 Hz, J' = 2 Hz, 1 H, vinyl), 5.37 (ddt, J = 10 Hz, J' = 6 Hz, J'' = 2 Hz, 1 H, vinyl), 3.14 (d, J = 16.5 Hz, 1 H, benzylic H anti to cyclopropane), 2.97 (d, J = 16.5 Hz, 1 H, benzylic H syn to cyclopropane), 1.50–2.60 (m, 4 H), 1.38 (d, J = 4.2 Hz, 1 H, H-10b), 0.49 (d, J = 4.2 Hz, 1 H, H-10a); MS m/e (rel intensity) 182(100), 167(66), 165(50), 141(80). Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 91.94; H, 8.02.

An attempted elimination reaction on mesylate **9** using potassium *tert*-butoxide in dimethyl sulfoxide yielded a 41:59 mixture of **10** and **11** and other unidentified materials.

Halide Method for 10 and 11. A solution of 218 mg (0.784 mmol) of mesylate **9** and 420 mg (3.136 mmol) of lithium iodide in 10 mL of acetone was refluxed under nitrogen for 20 h. Acetone was removed under reduced pressure, water was added to the residue and the organic materials were extracted into methylene chloride. The extracts were dried over $MgSO_4$, filtered, and concentrated to give 219 mg (90%) of a green oil. Preparative thick-layer chromatography of this crude product yielded 120 mg (49%) of a yellow oil (R_f = 0.642 in 100% ether). This oil was shown by proton NMR analysis to be a mixture of *anti*-3-iodo-7,8-benzotricyclo[4.3.1.0^{1,6}]dec-7-ene (**19**) and **10** (minor component). The IR (film) showed bands at 3.45, 3.58, 3.65, 6.82, 6.90, 6.98, 7.05, 13.13, 13.40, and 13.68 μm.

The mixture of iodide **19** and **10** was reacted with 120 mg (1.07 mmol) of DBN in 10 mL of dry tetrahydrofuran at 60 °C for 11.3 h under nitrogen. After tetrahydrofuran was removed under reduced pressure, water was added and the organic materials were extracted into methylene chloride and washed with dilute hydrochloric acid (three times), dilute aqueous sodium hydroxide (twice), water (twice), and saturated sodium chloride solution. The methylene chloride extracts were dried over $MgSO_4$, filtered, and concentrated to give 75 mg (53%) of an orange oil. Proton NMR (CCl_4/Me_4Si) analysis of this material showed it to be a 70.5:29.5 mixture of **10** and **11** (this corresponded to a 37% unisolated yield of **10** from **9**). The same general procedure was used for the preparation of **10** and **11** from **9** via the bromide and chloride.

1,6-Methanofluorene (2). To a stirred solution (−78 °C) of 546 mg (3.0 mmol) of olefin **10** in 30 mL of methylene chloride under nitrogen was added 600 mg (3.3 mmol) of bromine in 25 mL of methylene chloride over a period of 45 min (the stirring bar was treated successively with fuming nitric acid, 50% aqueous sodium hydroxide, and water before use to minimize iron-catalyzed aromatic substitution). After an additional 20 min at −78 °C about 2 g of sodium sulfite and 5 mL of methanol were added. The mixture was allowed to warm to room temperature and 20 mL of water was added. The organic phase was washed with water (twice) and saturated sodium chloride solution. Drying over $MgSO_4$ followed by filtration and concentration gave 966 mg (94%) of **19** (the dibromide of **10**) as a yellow oil: R_f = 0.653 in 1:1 benzene/ether; IR (film) 3.48, 6.84, 7.05, 8.58, 13.18, 13.78 μm; NMR (CCl_4/Me_4Si) δ 7.08 (m, 4 H), 4.12–4.64 (m, 2 H), 3.15 (d, J = 15.5 Hz, 1 H), 2.95 (dd, J = 15.5 Hz, J' = 3 Hz, 1 H), 1.70–2.93 (m, 4 H), 1.43 (dd, J = 4.4 Hz, J' = 2.2 Hz, 1 H), 0.49 (d, J = 4.4 Hz, 1 H).

A mixture of 966 mg (2.82 mmol) of **19**, 1414 mg (12.64 mmol) of DBN and 45 mL of tetrahydrofuran was stirred at 60 °C under argon for 40.8 h. After 5 mL of water was added the tetrahydrofuran was removed under reduced pressure. The residue was treated with methylene chloride and water and the aqueous phase was further extracted twice with methylene chloride. The combined organic phases were washed with dilute hydrochloric acid (twice), 10% sodium hydroxide solution (twice), water (twice), and saturated sodium chloride solution, dried over $MgSO_4$, filtered, and concentrated to give 483 mg (91%) of a brown oil. This crude product was purified by evaporative bulb-to-bulb distillation (92 °C (0.075 mm)) to give 407 mg (80%) of **2** as a light yellow oil (R_f = 0.625, 1:1 benzene/ether). Alternatively, purification could be accomplished by short-path distillation to give **2** as a colorless oil (51%) (bp 64–66 °C (0.09 mm)) which subsequently solidified, mp 57.0–58.5 °C. The residue of this distillation was subjected to evaporative bulb-to-bulb distillation (103–112 °C (0.075 mm)) to yield additional **2** as a yellow oil, which raised the overall yield to 64%. The spectral data for **2** are as follows: IR (film) 3.28, 3.43, 3.51, 6.76, 6.87, 6.99, 9.85, 13.72, 13.92 μm; NMR (CCl_4/Me_4Si) δ 6.87–7.53 (m, 4 H, aromatic), 6.42 (m, 2 H, vinyl), 5.85 (m, 2 H, vinyl), 3.21 (d, J = 16.5 Hz, 1 H, benzylic H anti to cyclopropane), 2.94 (d, J = 16.5 Hz, 1 H, benzylic H syn to cyclopropane), 1.45 (d, J = 3.6 Hz, 1 H, H-10b), 0.20 (d, J = 3.6 Hz, 1 H, H-10a); UV (THF) 236 (ε 5140), 268 (sh, ε 4260), 273 (ε 4380), 300 nm (sh, ε 1470); MS m/e (rel intensity) 180 (100), 179(51), 165(90). Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.32; H, 6.52.

Generation of the 1,6-Methanofluorenyl Anion (4). To a dry, thin-walled (5 mm) NMR tube covered with a septum was added 28 mg (0.154 mmol) of diene **2** in 0.4 mL of Me_2SO-d_6. This solution was degassed by repetitive freeze–thaw cycles and the air replaced by argon. Dimsyl-d_5 sodium was prepared by heating 5 mg (0.21 mmol) of sodium hydride in 0.6 mL of degassed Me_2SO-d_6 for 1 h at 70–80 °C (under nitrogen). After the solution cooled to room temperature it was transferred to the tube via syringe and kept under argon. Immediately a deep, orange-red color formation was noted and the NMR tube was shaken a few times to ensure complete mixing. The 90-MHz

proton NMR was recorded within 15–30 min. The anion was stable at room temperature for approximately 4 h, after which extensive polymerization began. The 90-MHz ^1H NMR (Me_2SO-d_6/Me_4Si) is summarized in Table I. The UV spectrum (*n*-BuLi/THF) showed λ_{max} at 250 (ϵ 69 700), 297 (ϵ 86 900), and 340 nm (sh, ϵ 20 500).

***anti*-9-Methyl-1,6-methanofluorene (13).** To a stirred solution of 100 mg (0.556 mmol) of diene **2** in 15 mL of tetrahydrofuran (under argon) were added successively 0.20 mL (1.112 mmol) of HMPA and 0.16 mL (1.112 mmol) of diisopropylamine. The resulting solution was cooled to 0 °C and 0.71 mL (1.112 mmol) of a 1.56 M solution of *n*-butyllithium/hexane was added. With continuous stirring the cooling bath was removed after 21 min at 0 °C and 0.49 mL (1.51 mmol) of methyl iodide was added; then after an additional 75 min at room temperature, 5 mL of saturated ammonium chloride solution was added. The aqueous phase was separated and extracted with ether. The combined organic phases were washed with water (four times) and saturated sodium chloride, dried over $MgSO_4$, filtered, and concentrated to give 103 mg (96%) of an orange oil. Purification was accomplished by evaporative bulb-to-bulb distillation (96 °C (0.02 mm)) to yield 57 mg (53%) of **13** as a pale yellow oil: R_f = 0.606 in 10% ethyl acetate/90% hexanes; IR (film) 3.30, 3.38, 3.42, 3.49, 6.78, 6.88, 8.37, 9.82, 12.58, 13.35, 13.79, 14.29 μm; UV (THF) 236 (ϵ 5430), 273 (ϵ 4100), 301 nm (sh, ϵ 1670); 90-MHz NMR ($CDCl_3$/Me_4Si) δ 7.44 (m, 1 H, aromatic), 7.15 (m, 3 H, aromatic), 6.49 (m, 2 H, vinyl), 5.93 (m, 2 H, vinyl), 3.03 (m, 1 H, benzylic), 1.55 (d, J = 3.52 Hz, 1 H, H-10b), 0.26 (d, J = 3.52 Hz, 1 H, H-10a); MS *m/e* (rel intensity) 194(39), 180(12), 179(100), 178(57). Anal. Calcd for $C_{15}H_{14}$: mol wt, 194.1095. Found: mol wt (MS), 194.1098.

***anti*-9-Deuterio-1,6-methanofluorene (12).** Diene **2** (23 mg, 0.128 mmol) in 0.5 mL of Me_2SO-d_6 was treated with about 0.1 mL of 5.2 M dimsyl-d_5 sodium/Me_2SO-d_6 (about 0.5 mmol) under argon until no further color change could be detected. After approximately 30 min, 0.5 mL (27.7 mmol) of deuterium oxide was added and the mixture was allowed to stand for an additional 30 min. An ether extract was washed three times with water, dried over $MgSO_4$, filtered, and concentrated, to give 11 mg (48%) of a yellow oil. Purification was accomplished by preparative thin layer chromatography to yield 4.4 mg (19%) of **12** as a light yellow oil: IR (film) 3.43, 3.57, 4.71 (C–D), 6.82, 6,93, 8.42, 9.58, 9.85, 13.05, 13.90 μm; NMR ($CDCl_3$/Me_4Si) δ 6.94–7.54 (m, 4 H, aromatic), 6.15–6.79 (m, 2 H, vinyl), 5.75–6.11 (m, 2 H, vinyl), 3.36 (q, J = 7 Hz, 1 H, benzylic), 1.49 (d, J = 7 Hz, 3 H, methyl), 1.45 (d, J = 3.6 Hz, 1 H, H-10b), 0.09 (d, J = 3.6 Hz, 1 H, H-10a); UV (THF) 236 (ϵ 4820), 273 nm (ϵ 3580). Anal. Calcd for $C_{14}H_{11}D$: mol wt, 181.1002. Found: mol wt (MS), 181.0999.

Preparation of 1,6-Methanofluorene (2) from *anti*-9-Deuterio-1,6-methanofluorene (12). To a dry, thin-walled (5 mm) NMR tube covered with a septum was added 51 mg (0.282 mmol) of **12** (91% deuterated as estimated by NMR) in 0.4 mL of Me_2SO-d_6 under argon. The NMR tube was degassed as outlined for generation of **4**, and 0.15 mL (0.757 mmol) of 5.05 M dimsyl-d_5 sodium in Me_2SO-d_6 was added (solution immediately turned deep red). Proton NMR analyses showed that the resulting anion, which contained very little deuterium as determined from integration of the spectrum, consisted mainly of **4**. After water (0.5 mL, 0.02 mol) was added, the mixture was extracted into ether, washed with water (four times), dried over $MgSO_4$, filtered, and concentrated, to yield 33 mg (62%) of a light orange oil. Proton NMR analysis ($CDCl_3$/Me_4Si) indicated that this oil contained only a small amount of **12** (less than 10%) and was comprised mainly of **2**.

Generation of the 9-Methyl-1,6-methanofluorenyl Anion (5) from *anti*-9-Methyl-1,6-methanofluorene (13). Anion **5** was prepared in an analogous manner to **4** using 37 mg (0.191 mmol) of **13** in 0.2 mL of Me_2SO-d_6 and 0.20 mL (1.01 mmol) of 5.05 M dimsyl sodium in Me_2SO-d_6 solution. The deep red anion generation was considerably slower than that of **4**. Anion **5** was stable at room temperature for approximately 1 h and exhibited the 90-MHz NMR data summarized in Table III.

***syn*-9-Methyl-1,6-methanofluorene (14).** *anti*-9-Methyl diene **13** (37 mg, 0.191 mmol) in 0.2 mL of Me_2SO-d_6 was treated with 0.20 mL of 5.05 M dimsyl-d_5 sodium in Me_2SO-d_6 (1.01 mmol) under argon. After about 30 min, 0.5 mL (0.022 mol) of water was added. The mixture was extracted into ether, washed with water (four times), dried over $MgSO_4$, filtered, and concentrated, to yield 23 mg (62%) of an orange oil. Evaporative bulb-to-bulb distillation (95–130 °C (0.037–0.080 mm)) followed by preparative thin-layer chromatography (silica gel, run up three times) yielded 5 mg (14%) of a near-colorless oil: R_f = 0.667 in 15% ethyl acetate/85% hexanes; IR (film) 3.40, 3.43, 3.50, 6.65, 6.77, 12.98, 13.18, 13.40, 13.66 μm; 90-MHz NMR ($CDCl_3$/Me_4Si) δ 7.39 (m, 1 H), 7.14 (m, 3 H), 6.51 (m, 2 H), 5.96 (m, 2 H), 3.41 (q, J = 7.35 Hz, 1 H), 1.54 (d, J = 3.52 Hz, 1 H), 1.18 (d, J = 7.04 Hz, 3 H), 0.24 (d, J = 3.52 Hz, 1 H); MS *m/e* (rel intensity) 194(9), 167(100). Anal. Calcd for $C_{15}H_{14}$: mol wt, 194.1095. Found: mol wt (MS), 194.1101.

Generation of the 9-Methyl-1,6-methanofluorenyl Anion (5) from *syn*-9-Methyl-1,6-methanofluorene (14). Anion **5** was prepared in the same manner outlined for **4** using 4.0 mg (0.021 mmol) of the *syn*-methyl diene **14** in 0.4 mL of Me_2SO-d_6 and about 0.1 mL (0.053 mmol) of 5.3 M dimsyl-d_5 sodium in Me_2SO-d_6 under nitrogen at room temperature. Proton NMR analysis (90 MHz) showed that the anion generated was identical with that from *anti*-9-methyl diene **13**.

Generation of the Fluorenyl Anion (16). Anion **16** was prepared in a manner analogous to that for **4** using a saturated solution of fluorene in 0.5 mL of Me_2SO-d_6 and about 0.2 mL (0.106 mmol) of 5.3 M dimsyl-d_5 sodium in Me_2SO-d_6 under argon at room temperature. The 90-MHz proton NMR is summarized in Table IV. This spectrum was identical with that published by Cox[18] except for slight solvent-induced chemical shift changes.

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Registry No.—5, 65150-14-3; **6,** 26726-28-3; **7,** 65150-15-4; **9,** 65150-16-5; **12,** 65150-17-6; **13,** 65150-18-7; **14,** 65206-89-5; **19,** 65150-19-8; methanesulfonyl chloride, 124-63-0.

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