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Carbanions 27. Rearrangements of (9-Alkyl-9-fluorenyl)-methyllithium (or Cesium) and 2,2-Diphenyl-3,3-dimethyl-butyllithium[1]

Erling Grovenstein, Jr.*, Jagvir Singh, Bhalchandra B. Patil, and Don VanDerveer

Contribution from the School of Chemistry,
Georgia Institute of Technology, Atlanta, GA 30332

Abstract: A study has been made upon the products from warming various (9-alkyl-9-fluorenyl)methyllithium (or cesium) compounds in THF to near 0 °C followed by carbonation. When the 9-alkyl group is ethyl, the result is chiefly the protonated product (9-alkyl-9-fluorenyl)methane; a similar product evidently is formed when the 9-alkyl group is 1-norbornyl. When the 9-alkyl group is *tert*-butyl, the minor product is 9-neopentylfluorene-9-carboxylic acid from a [1,2]-migration of the *tert*-butyl group while the major product is 9-methylfluorene-9-carboxylic acid from an intramolecular elimination as shown by deuterium labeling. When the 9-alkyl is neopentyl, the major product is 9-neopentyl-9,10-dihydrophenanthrene-9-carboxylic acid along with some 9-neopentylphenanthrene which becomes the major product in diethyl ether solution at 35 °C. 2,2-Diphenyl-3,3-dimethylbutyllithium undergoes predominantly [1,2]-phenyl migration in THF at 0 °C. From an x-ray crystal study upon 9-*tert*-butyl-9-(chloromethyl)fluorene and 9-neopentyl-9-(chloromethyl)fluorene, it is concluded that steric acceleration is responsible for the unusual reactions of (9-alkyl-9-fluorenyl)methyllithiums when the 9-alkyl groups are *tert*-butyl and neopentyl.

INTRODUCTION

[1,2]-Rearrangements of organoalkali metal compounds without hetero atoms save M (eq. 1) are well known where the migrating group (R) is an aryl[2], vinyl[3], alkynyl[4], benzyl[5] or allyl[6] group. While migrations of the first three groups occur as intramolecular [1,2]-sigmatropic shifts (likely by way of bridged intermediates), migration of benzyl and, in part, allyl occur by a cleavage-recombination process (evidently cleavage into an olefin and a carbanion or organoalkali metal compound). Allyl migration also occurs, especially at low temperatures, by an intramolecular [2,3]-sigmatropic shift with allylic inversion[6].

$$R-C-C^{*}M \longrightarrow MC-C^{*}-R \qquad (1)$$

Conspicuously missing from the list of migrating groups, in rearrangements of carbanions containing only carbon and hydrogen, are saturated alkyl groups or hydrogen. According to the rules of orbital symmetry[7], concerted [1,2]-migrations of such groups in carbanions are forbidden as suprafacial-suprafacial processes but are allowed as suprafacial-antarafacial processes[8]. The latter appear unlikely because of steric difficulties; Zimmermann and Zweig[9] concluded that "simple alkyl migration of carbanions...may never be observed except under extreme conditions."

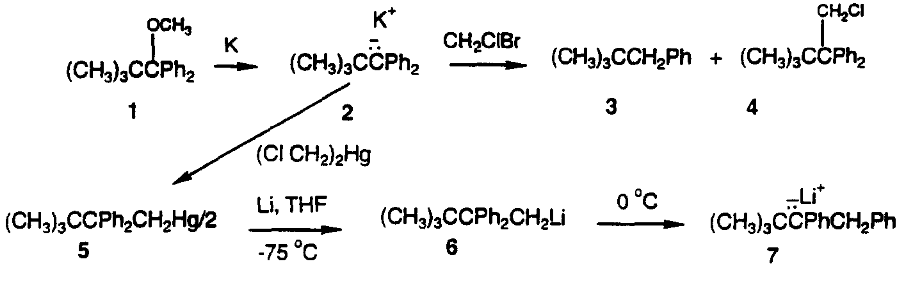
In contrast to all carbon systems, migrations of saturated alkyl groups in carbanions containing heteroatoms are well known[10,11] as in the Wittig ether rearrangement and rearrangement of ylides (Stephens rearrangement, Meisenheimer rearrangement, etc.) These rearrangements are generally considered to occur in a non-concerted fashion by way of dissociation into radical pair intermediates within a solvent cage, followed by recombination of the radicals frequently prior to escape from the cage.[10,11] This mechanism accounts for the migratory aptitudes of alkyl groups which for lithiobenzyl alkyl ethers[12] increase in the order methyl, ethyl, isopropyl, *tert*-butyl (k_{rel} = 1 : 40 : 162 : 2080). The relative rates of formation of alkyl radicals increase in this same order while that of carbanions (organolithium compounds) decrease. Illustrative of the general mechanism lithiobenzyl 1-adamantyl ether undergoes rearrangement while lithiobenzyl 1-norbornyl ether does not in accord with the 1-adamantyl radical being more stable then the 1-norbornyl radical whereas the reverse is true of 1-adamantyl- and 1-norbornyllithium.[13,14]

Since the utility of organoalkali metal compounds in synthesis often rests upon their structural integrity, the question of whether and under what conditions alkyl groups may migrate in carbanions containing only carbon and hydrogen is of both practical and theoretical importance. In view of the fact that tertiary alkyl groups migrate more readily then primary or secondary alkyl groups in carbanions containing heteroatoms, the *tert*-butyl group was selected for study in the present work. The first system examined was 2,2-diphenyl-3,3-dimethylbutyllithium.

RESULTS AND DISCUSSION

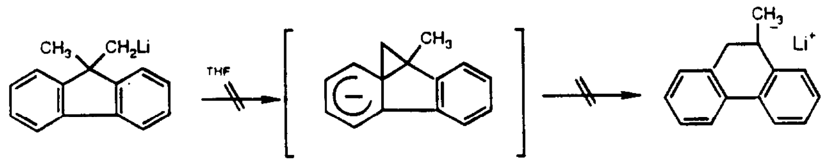
2,2-Diphenyl-3,3-dimethylbutyllithium (6). The synthesis of this compound encountered some experimental difficulties. The usual synthesis by reaction of the corresponding chloride with lithium metal was made impossible by unavailability of the pure chloride. Attempts to make the chloride by reaction of 2,2-dimethyl-1,1-diphenylpropyl anion *(2)* with either dichloromethane or bromochloromethane gave mostly hydrocarbon *(3)* and little of the desired chloride *(4)* (**Scheme 1**). Attempts to separate the chloride from

Scheme 1



the hydrocarbon by-product by chromatography on silica gel were vitiated by decomposition of the chloride (which evidently is activated by steric acceleration and/or phenyl participation). The desired organolithium compound **6** was eventually made by cleavage of the organomercury compound **5** with lithium. The mercury compound was synthesized as shown in **Scheme 1**. Rearrangement of **6** in THF at 0° gave an organolithium compound **7** whose carbonation product had spectroscopic properties (see Experimental Details) in accord with expectations for a product derived from migration of a phenyl rather than a *tert*-butyl group. Thus **6** appears to rearrange like the less methylated analog 2,2-diphenylpropyllithium.[9]

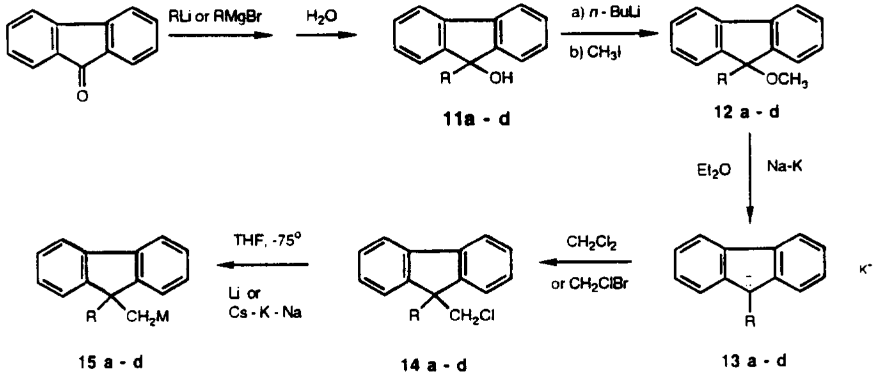
General Method of Preparation of (9-Alkyl-9-fluorenyl)methyllithium (or Cesium) Compounds. Since Eisch and coworkers[15] have found that aryl migration does not occur in fluorene derivatives such as **8** to give **10** (eq. 2), likely because of steric constraints upon formation of the spiro intermediate **9**, other (9-alkyl-9-fluorenyl)methyllithiums were next studied. These compounds were prepared by the general procedure outlined in **Scheme 2**.



8 **9** **10**

(2)

Scheme 2



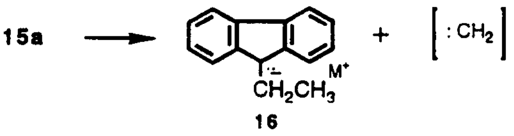
a: R = C_2H_5, **b**: R = $(CH_3)_3C$, **c**: R = $(CH_3)_3CCH_2$, **d**: R = 1-Norbornyl; M = Li or Cs

(9-Ethyl-9-fluorenyl)methyllithium (or Cesium) (15a). Since none of the fluorene derivatives (**15**) studied by Eisch and co-workers contained an R group with β-hydrogens and since such a compound (**15b**) in our hands yielded products different from those of prior workers, we investigated the 9-ethyl compound **15a**. The synthesis of 9-chloromethyl-9-ethyl-fluorene (**14a**) from fluorenone proceeded in a yield of 71% or better in each step of **Scheme 2** or gave an overall yield of some 42%. Pure **14a** was a crystalline compound (mp 43-44 °C). In a prior, somewhat similar synthesis[16], **14a** was obtained as an oil but was likely a little impure according to its elemental analysis.

Reaction of **14a** with excess lithium in THF at -75 °C gave, according to the products of carbonation, 62-73% of the expected organolithium **15a** accompanied by 2-5% of 9-ethyl-9-fluorenyllithium, and 5-13% of 9-ethyl-9-methylfluorene. When the organolithium product was allowed to warm to 0 °C for 3 h prior to carbonation, the yield of **15a** decreased to 17-26% while the yields of 9-ethyl-9-fluorenyllithium and 9-ethyl-9-methylfluorene increased to 9-12% and 30-33% respectively.

Reaction of **14a** with excess of Cs-K-Na alloy in THF at -75 °C for one minute followed by carbonation gave, according to the yields of monocarboxylic acids from carbonation, 2.6% of the organocesium product **15a**, 16.5% of 9-ethyl-9-fluorenylcesium, and 1.4% of 9-ethyl-9-methylfluorene. The low yields are doubtlessly due to further reactions of the initial products with excess Cs-K-Na alloy.

The reaction products demonstrate that (9-ethyl-9-fluorenyl)methyllithium (**15a**) and likely also the corresponding cesium compound do not undergo appreciable intramolecular shifts of either ethyl or aryl moities, in agreement with the observations of Eisch and co-workers[15] upon related compounds. Instead **15a** undergoes slow protonation to give 9-ethyl-9-methylfluorene likely by reaction with solvent THF in conformity with the behavior of simpler organoalkali metal compounds. Also the initial organoalkali metal compound **15a** appears able to lose a methylene group to give the 9-ethyl-9-fluorenyl anion (**16**):



(3)

This reaction can be likened to the formation of dichloromethylene by loss of chloride ion from the trichloromethyl anion during reactions of chloroform with strong bases[17]. Such reaction of **15a** should be facilitated by the comparative stability of the fluorenyl anion **16** and by the change of alkali metal from lithium to cesium. We are, however, unaware of truly comparable reactions in prior literature reports.[18]

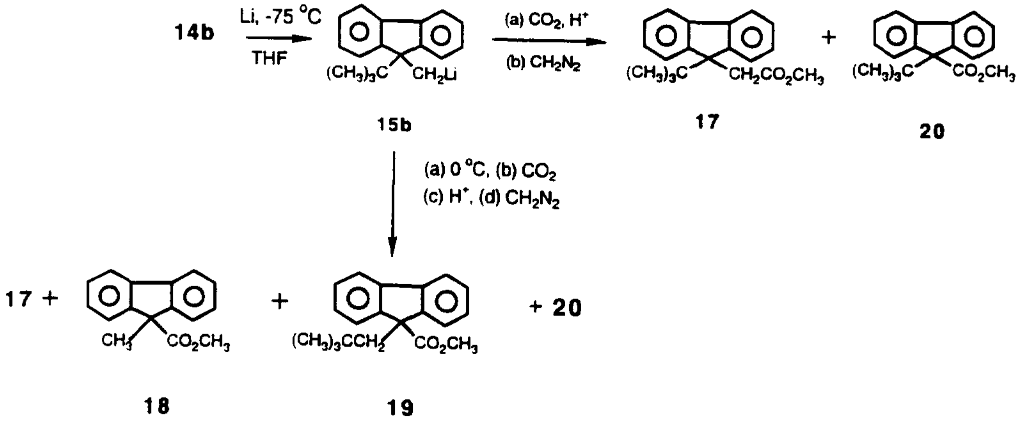
An experiment in which **15a** was warmed to 0 °C in presence of cyclohexene and kept at this temperature for three hours prior to carbonation failed to lead to detectable norcarane (a major product expected from methylene addition to cyclohexene) and gave only the usual products in amounts about as expected in absence of cyclohexene. This result could mean that free methylene was not formed or that it reacted with other substances such as solvent tetrahydrofuran. In some reactions of **15a** carboxylic acids containing one or even two extra methylene groups were present in the products of carbonation as shown by GC-mass spectrometric analysis of the methyl esters. Subsequent experiments, however, showed that these products were artifacts from the excess diazomethane used for esterification. In an experiment in which the starting chloride **14a** was dideuterated on the chloromethylene group, the artifact products contained extra CH_2 groups rather than CD_2 groups.

An alternative source of 9-ethylfluorenyl anion **16** in the present work could be via reduction cleavage of a methyl group from the product 9-ethyl-9-methylfluorene. A phenyl group is reported to be cleaved from 9,9-diphenyl-fluorene[19] by lithium in THF and a benzyl group from 9-benzyl-9-phenylfluorene[20] by 40% sodium amalgam. Electrochemical reduction in dimethylformamide cleaved a benzyl group from 9-benzyl-9-phenylfluorene but failed to cleave 9,9-diphenylfluorene, 9,9-dimethylfluorene, or 9-methyl-9-phenylfluorene, although blue radical anions were produced[21]. 1,1,1-Triphenylethane with Cs-K-Na alloy in THF at 0° underwent cleavage of phenyl.[22] Thus the formation of **16** by alkali metal cleavage of 9-ethyl-9-methylfluorene, while not disproven, appears to be unlikely under the present experimental conditions. Nevertheless the appearance of a little **16** at -75 °C might be attributed to some cleavage of a chloromethyl group from **15a** during initial reaction with alkali metal.

(9-tert-Butyl-9-fluorenyl)methyllithium (or Cesium) (15b). The desired precursor chloride **14b** was made by the general process of **Scheme 2**. Reaction of 9-fluorenone in benzene with a pentane solution of *tert*-butyllithium gave an 81% yield of the desired fluorenol **11b** as assayed by NMR analysis or 48% yield of nearly pure product after recrystallization. Methylation of **11b** to give 9-*tert*-butyl-9-methoxyfluorene (**12b**) proceeded in 91% yield in THF-hexane solution by NMR analysis and gave 52% yield of crystalline product. An attempt to by-pass the isolation of **11b** by reaction of 9-fluorenone with *tert-butyllithium* in THF-pentane solution followed by reaction with methyl iodide gave only 34% yield of **12b** along with four isomeric compounds of which *cis*-3-*tert*-butyl-9a-methyl-3,9a-dihydro-9-fluorenone was characterized by spectroscopic and x-ray crystal analysis. Evidently the addition of *tert*-butyllithium to 9-fluorenone is sensitive in its regioselectivity to solvent composition. Cleavage of **12b** with Na-K and chloromethylation of the resulting carbanion with CH_2ClBr gave 54% yield of the desired crystalline chloride **14b**.

Reaction of chloride **14b** with lithium in THF at -75 °C gave (9-*tert*-butyl-9-fluorenyl)methyllithium (**15b**) in 65-69% yield as determined by the yield of **17** which was produced along with some 8% of **18** and 3% of **20** upon carbonation and esterification (see **Scheme 3**). After 3 hr at 0 °C, the yield of **17** dropped to 3% while that of **18** increased to 65 ± 9% and **20** remained at about 3%; in addition a new product, methyl 9-neopentylfluorene-9-carboxylate (**19**), appeared in some 3% yield.

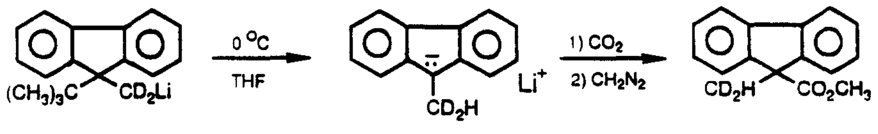
Scheme 3



As a check to see if some of the products ascribed to the organolithium compound **15b** might be due to its mode of preparation from the chloride **14b**, the organolithium compound **15b** was also prepared by lithium cleavage of the mercury compound from reaction of bis(chloromethyl)mercury with 9-*tert*-butyl-9-fluorenylpotassium (*cf.* **Scheme I** for preparation of **6**). The products of this lithium cleavage at -75 °C and after warming to 0 °C were determined by carbonation and proved to be the same and to be formed in about the same ratios as from cleavage of the chloride **14b**, though the yields were reduced, likely because the intermediate mercury compound was not purified prior to cleavage by lithium.

The origin of the major product methyl 9-methylfluorene-9-carboxylate (**18**) from decomposition of (9-*tert*-butyl-9-fluorenyl)methyllithium (**15b**) in THF at 0 °C was investigated by isotopic labeling. 9-*tert*-Butyl-9-(chloromethyl-d_2)fluorene (**14b**-d_2) upon reaction with lithium at -75 °C gave the corresponding organolithium compound **15b**-d_2. Pyrolysis of the latter (see **Scheme 4**) gave 9-(methyl-d_2)fluorenyllithium

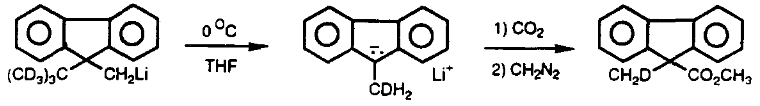
Scheme 4



15b - d_2 **21** - d_2 **18** - d_2

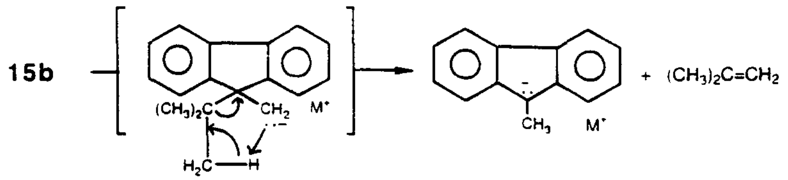
(**21**-d_2) since carbonation and esterification yielded methyl 9-(methyl-d_2)fluorene-9-carboxylate (**18**-d_2). Hence the 9-methyl group of **18** is derived from the lithiomethyl group of **15b** with the lithium ion having been replaced by a proton. The source of the proton was from the *tert*-butyl group of **15b** since 9-(tert-butyl-d_9)-9-(chloromethyl)fluorene (**14b**-d_9) gave the organo-lithium compound **21**-d_1 (see **Scheme 5**) which was characterized by its carbonation product methyl 9-(methyl-d_1)fluorene-9-carboxylate **18**-d_1.

Scheme 5



15b - d_9 **21** - d_1 **18** - d_1

These results are in agreement with a thermal decomposition of the organolithium compound **15b** via the transition state **22** (eq. 4). Further support for this Ei mechanism, which is analogous to that proposed



22 **21** (4)

for decomposition of amino oxides and some ylides,[23] is provided by the slower decomposition of the deuterium compound **15b**-d_9 than the unlabeled compound **15b**. The isotope effect k^H/k^D for this decomposition into **21** or **21**-d_1 is 6 ± 1 at 0 °C. This value is large enough to signify a primary hydrogen isotope effect[24] as expected for cleavage of a C-H bond of the *tert*-butyl group in the rate-determining step of the decomposition. To our knowledge this is the first example of an organolithium compound, without hetero atoms save lithium, decomposing to a large extent by an Ei mechanism via a transition state such as

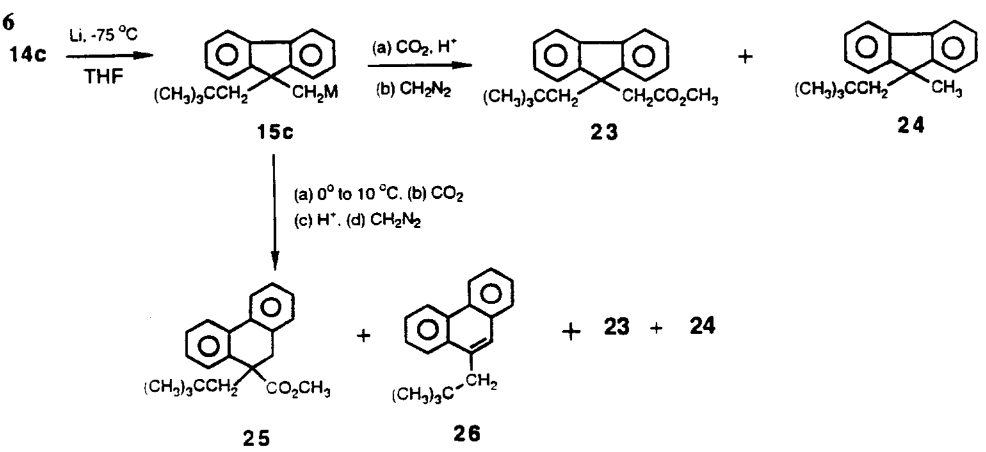
22 which corresponds to a thermally allowed [1,4] suprafacial sigmatropic shift (involving 6 electrons in a stabilized cyclic transition state) in orbital symmetry terms.^{7}

The appearance of a little methyl 9-*tert*-butylfluorene-9-carboxylate (**20**) in the reaction product can be explained by the processes mentioned earlier for the ethyl analog **14a**. Of greater interest is the appearance of methyl 9-neopentyl-9-carboxylate (**19**) in some 3% yield after 3 h at 0 °C. The detailed mechanism of formation of **19** could involve either cleavage of a *tert*-butyl radical or anion from **15b** with readdition to the resulting moiety, 9-methylenefluorene radical anion or 9-methylenefluorene, respectively, to give the organolithium precursor of **19**. The cleavage intermediates are evidently not "free" but exist only momentarily in a solvent cage before collapsing into 9-neopentyl-9-fluorenyllithium. In apparent confirmation an experiment in which the initial organolithium reagent **15b** was allowed to rearrange in presence of preformed benzyllithium gave no detectable benzyl incorporation in products containing the fluorene moiety. This result contrasts with a related case of [1,2] benzyl migration in which external added isopropyllithium or radioactive benzyllithium became incorporated in the final product.^{5b}

Reaction of the chloride **14b** with excess of eutectic Cs-K-Na alloy in THF at -75 °C proceeded very rapidly and was completed in a reaction time of less than three minutes. The volatile products from the most successful reaction (that involving the smallest ratio of cesium to halide) were 33% of **18**, 5% of **20**, 1% of **17**, 8% of 9-methylfluorene, 8% of 9-methyl-9-*tert*-butyl-fluorene, and 1% of 9-*tert*--butylfluorene. The products are, therefore, similar to those with lithium except that none of the product of 1,2-migration of *tert*-butyl was observed. The putative organocesium intermediate **15b** (M$^+$ = Cs$^+$) evidently decomposes more readily at -75 °C than does the organolithium product (**15b**, M$^+$ = Li$^+$) at 0 °C. In both cases the major organometallic product is the fragmentation product **21**.

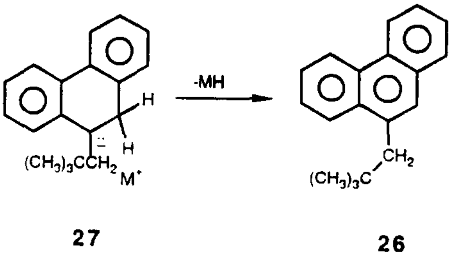
(9-Neopentyl-9-fluorenyl)methyllithium (or Cesium) (15c). The desired 9-(chloro-methyl)-9-neopentylfluorene (**14c**) was made in about 50% overall yield from 9-fluorenone by the process of Scheme 2 (but without protonation and isolation of **11c**). Reaction of **14c** with lithium in THF at -75 °C gave the desired organolithium compound **15c** in some 60% yield as inferred from the yield of the expected carbonation product **23** which was produced along with 8% of the non-rearranged hydrocarbon **24** (see Scheme 6). In three runs in which the organolithium product **15c** was held at 0° to 10 °C for 1 h before

Scheme 6



carbonation the yield of **23** dropped to about 30% while some 20% of a new carbonation product **25** was formed along with some 30% of non-rearranged hydrocarbon **24** and 5% of 9-neopentylphenanthrene (**26**). The structure of **26** was deduced by comparison with a synthetic sample of **26**. The structure of **25** is believed to be that of the methyl ester of 9-neopentyl-9,10-dihydrophenanthrene-9-carboxylic acid based on its ^{1}H and ^{13}C NMR and mass spectrum. Compound **25** was shown *not* to be the product from [1,2]-migration of the neopentyl group since it was distinctly different from the synthetic product methyl 9-(3,3-dimethylbutyl)fluorene-9-carboxylate. The structure assigned to **25** is that of a product expected from [1,2]-migration of an aryl group of the fluorene ring system of **15c**.

Reaction of the chloride **14c** with lithium in the solvent diethyl ether was slow at 15 °C and after 2 h only some 5% of non-rearranged organolithium product **15c** was present according to the yield of its carbonation product **23** which was formed along with some 0.6% of rearranged product **25** and the hydrocarbons **24** and **26** in 7% and 9% yields respectively in addition to 40% of unreacted chloride **14c**. When the reaction temperature was held at 35 °C for three more hr, the yield of **15c** dropped to 1.3%, that of **25** remained about constant at 0.5% while the yields of the hydrocarbons **24** and **26** increased to 14 and 34% respectively. The lower yield of **25** and the higher yield of 9-neopentylphenanthrene (**26**) in diethyl ether than in THF is notable. While some **26** could result from α-elimination upon the starting chloride **14c** by the initially formed organolithium reagent **15c**, this mechanism requires the production of one **24** for every molecule of **26** formed when instead the amount of **26** exceeds **24** by 2.4 fold. A more likely route to **26**, and one which explains the low yield of **25**, is that the carbanionic precursor (**27**, M=Li) of **25** loses the elements of LiH to form the more fully aromatic **26**:



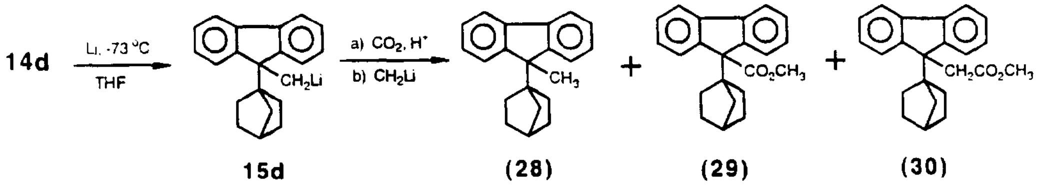
(5)

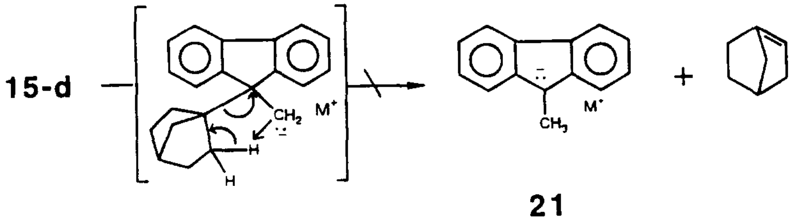
Ample precedent for such a reaction is the aromatization of 1,4-dihydrodibenzofuran and of 1,4-dihydronaphthalene by metalation with phenyllithium and subsequent loss of lithium hydride in diethyl ether solution at reflux.[26]

Reaction of **14c** with finely divided Cs-K-Na eutectic alloy (containing slightly less than the theoretical amount of Cs) in THF at -75 °C proceeded readily. Carbonation after 15 minutes of reaction time gave low yields carboxylic acids (0.2% of **23** and 5% of **25**) but high yields of neutral hydrocarbons (45% of **24** and 40% of the rearranged hydrocarbon **26**). Thus while the organocesium compound **15c** (M=Cs) evidently undergoes [1,2]-migration of an aryl group at -75 °C much more readily than the corresponding organolithium compound, the aromatization of **27** to **26** also occurs much more readily when M=Cs rather than Li.[27]

[9-(1-Norbornyl)-9-fluorenyl]methyllithium (15d). The desired 9-(chloromethyl)-9-(1-norbornyl)fluorene (**14d**) was prepared from 1-chloronorbornone by the general procedure of **Scheme 2**. Only a preliminary semi-quantitative study has been made of the reaction of **14d** with lithium in THF at -73 °C and of its subsequent products upon warming to 0 °C. The reaction with lithium at low temperatures appears to proceed normally (see **Scheme 7**). The assumed structures of **28**, **29**, and **30** are in agreement with their mass spectra and with the general expectations for such a reaction. Upon warming to 0 °C for two hr the yield of ester **30** decreased some threefold while the yield of hydrocarbon **28** rose. Gas chromatographic and mass spectrometric analysis failed to reveal additional components upon warming to 0 °C; in particular if any fragmentation product **18** was produced as from the *tert*-butyl analog **15b** its amount must have been less than 1%. Such a low yield of **18** was to be expected if the fragmentation took place by a mechanism like that proposed for the *tert*-butyl compound as shown in eq. (4) since the fragmentation would involve formation of a highly strained double bond at a bridgehead position (see eq. 6) in violation of Bredt's rule.[28] Furthermore the failure to detect a product of [1,2]-migration of the norbornyl group is in agreement with the expected difficulty of dissociation of **15-d** into the radical pair, 1-norbornyl radical and 9-methylenefluorene radical anion, as presumed form the reluctance of formation of 1-adamantyl radical in the Wittig ether rearrangement.[13] Thus the present work provides some evidence in favor of the migration in **15b** of *tert*-butyl radical rather than a *tert*-butyl anion, since were fragmentation by way of a *tert*-alkyl anion enhanced migration of *tert*-alkyl in **15-d** would have been expected since 1-norbornyllithium is much more stable than *tert*-butyllithium.[29] This argument is tentative in absence of suitable reference compounds for comparison with the products from **15d**.

Scheme 7





(6)

X-Ray Structures of 14b and 14c. In view of the discovery that of the (9-alkyl-9-fluorenyl)methyllithium (or cesium) compounds **8** and **15a-d**, the 9-*tert*-butyl and 9-neopentyl compounds (**15b** and **15c** respectively) undergo reactions not shown by the 9-methyl (**8**), 9-ethyl (**15a**), nor apparently the 9-(1-norbornyl) (**15d**) analogs, an x-ray crystallographic study was made upon the 9-*tert*-butyl and 9-neopentyl precursor chlorides **14b** and **14c** in order to attempt to understand the unusual behavior of **15b** and **15c**. The ORTEP structures determined for **14b** and **14c** are shown in Fig. 1 and 2 respectively.

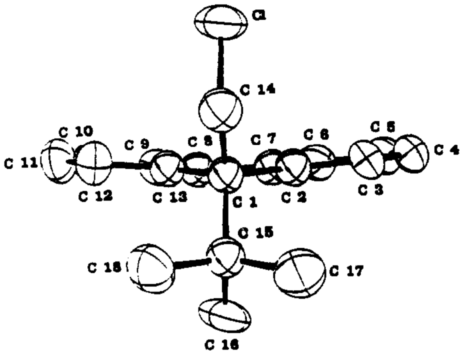


Fig. 1 ORTEP structure of **14b**

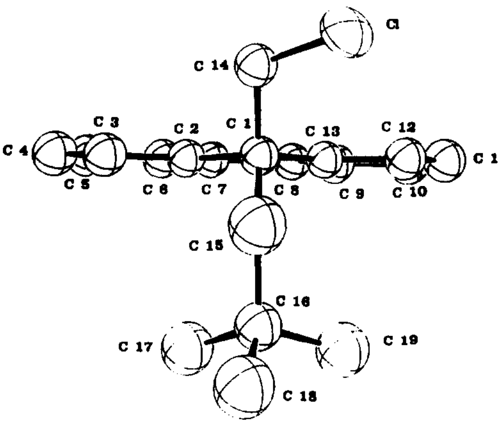


Fig. 2 ORTEP structure of **14c**

For **14b** the most obvious peculiarity revealed in Fig. 1 is the non-coplanarity of the two benzenoid rings of the fluorene nucleus. The acute angle between the rings is 10.6° rather than 0° as expected. This deviation from coplanarity is evidently due to steric interaction of the benzenoid rings with the *tert*-butyl group. This interaction is also responsible for stretching the C1-C15 bond (which joins the *tert-butyl* group to the fluorene nucleus to 1.605 Å rather than the usual 1.54 Å value expected for an ordinary single bond. Even with these deviations from normal geometry, the *tert*-butyl group in **14b** presses tightly upon the fluorene nucleus as revealed by the following internuclear distances: C16 to C2 and C13, 3.03 and 2.94 Å respectively; C17 to C2, 3.07 Å; C18 to C13, 3.15 Å. These may be compared to 3.70 Å as expected from Pauling's Van der Waals radius of a methyl group and half-thickness of an aromatic molecule.[30] Since a rather similar geometry is anticipated for the corresponding organolithium compound **15b**, the strained nature of **15b** likely accounts for its high reactivity. In particular cleavage of the already lengthened C_1-C_{15} bond joining *tert*-butyl to the fluorene nucleus should relieve the steric compression in **15b** and such cleavage accompanied the major reactions of **15b** in the present work. This cleavage is aided by loss of a proton from the *tert*-butyl group (see eq 4) with the result that isobutylene and 9-methylfluorenyl anion (**21**) are the major products. The minor product **19** from *tert*-butyl migration evidently results from complete cleavage of *tert*-butyl likely as *tert*-butyl radical in a solvent cage along with 9-methylenefluorene radical anion as discussed earlier.

For **14c** the structure shown in Fig. 2 may seem normal in that the fluorenyl ring system is essentially planar. Detailed examination of the x-ray data reveals a somewhat complex crystal with four crystallographically unique molecules of **14c** in the unit cell. Although the four orientations of **14c** are crystallographically distinct, their geometries are nearly the same and so internuclear distances are averaged in the present discussion. The angle C1-C15-C16 is expanded to 122.5 ± 0.4° rather than the usual tetrahedral value of 109.5° but the angle C14-C1-C15 is about normal at 108.7 ± 0.3°. While the methylene group (C15) in **14c** imparts additional flexibility to **14c** over that of **14b**, the *tert*-butyl group of **14c** still impacts the fluorene ring as revealed by the internuclear distances (Å): C1-C17, 3.25 ± 0.04; C2-C17, 3.16

± 0.05; C3-C17, 3.42 ± 0.07; C1-C19, 3.28 ± 0.05; C13-C19, 3.20 ± 0.06; C12-C19, 3.35 ± 0.04. Hence **14c** and likely its corresponding organolithium compound **15c** suffer steric strain. During aryl migration bonding of the lithiomethyl group to the aryl ring (in Fig. 2, suitably C14 to C2) forces the newly bound carbon of the aryl ring to move away from the nearest methyl of the *tert*-butyl group. Evidently the accompanying release of steric compression overcomes the normal reluctance of this fluorenyl system for formation of the necessary spiro intermediate for aryl migration (*cf.* **9** from **8**).

The alternative reactions which **15b** undergoes appear inappropriate for **15c**. Thus cleavage of **15c** by the Ei mechanism is blocked by absence of suitable hydrogens for an olefin-elimination process. The absence of measurable [1,2]-migration of neopentyl argues in favor of [1,2]-alkyl migration occurring in carbanions containing only carbon and hydrogen by cleavage of an alkyl radical, rather than an alkyl anion, in agreement with prior conclusions for related migrations in Wittig ether rearrangements and rearrangements of ylides.[10-14] On this basis the reluctance of migration of neopentyl versus *tert*-butyl is rational (*cf.* the 52 fold greater rate of migration of *tert*-butyl compared to ethyl in lithiobenzyl alkyl ethers[12]) and concurs with the tentative conclusions upon [9-(1-norbornyl)-9-fluorenyl]methyl-lithium (**15d**).

Conclusions. 2,2-Diphenyl-3,3-dimethylbutyllithium (**6**), (9-ethyl-9-fluorenyl)methyllithium (**15a**), (9-neopentyl-9-fluorenyl)methyllithium (**15c**), and [9-(1-norbornyl)-9-fluorenyl]methyllithium (**15d**), and their cesium analogs, as far as studied, do not undergo [1,2]-migration of alkyl groups in THF in accordance with the rules of orbital symmetry which prohibit such processes as concerted suprafacial-suprafacial reactions. Nevertheless (9-*tert*-butyl-9-fluorenyl)methyllithium (**15b**) undergoes a non-concerted [1,2]-migration of *tert*-butyl as a minor reaction and fragmentation into isobutylene and 9-methylfluorenyllithium (**21**) by an Ei mechanism as a major reaction; these unusual reactions for organoalkali compounds without heteroatoms appear to owe their origins to steric acceleration. (9-Ethyl-9-fluorenylmethyllithium (**15a**) and, evidently [9-(1-norbornyl)-9-fluorenyl]methyllithium (**15d**) also do not undergo [1,2]-aryl migration evidently because of steric constraint which is lacking in 2,2-diphenyl-3,3-dimethylbutyllithium (**6**), 2,2,2-triphenylethyllithium and similar compounds which undergo phenyl migration by a concerted suprafacial-antarafacial process. Nevertheless (9-neopentyl-9-fluorenyl)methyllithium or cesium (**15c**) undergoes [1,2]-migration of an aryl group (*o*-phenylene group) evidently because of steric acceleration (release of steric compression).

EXPERIMENTAL SECTION

General Procedures. All organoalkali metal reactions were run under nitrogen in a Morton high-speed stirring apparatus[31] which, for safety, was enclosed in a glove box filled with nitrogen and/or carbon dioxide from the dry ice cooled bath. Detailed procedures for conducting these reactions are given elsewhere[3]

^{1}H NMR spectra were determined at 60 MHz with a Varian model T-60A spectrometer or at 300 MHz with a Bruker model WM-300 spectrometer. ^{13}C NMR spectra were determined at 75 MHz with a Bruker model WM-300 spectrometer; the multiplicity of the ^{13}C spectra was determined by off-resonance decoupling or by distortionless enhancement of population transfer. The spectra are reported in parts per million (δ) downfield from tetramethylsilane as an internal standard. Mass spectra were run on a Varian MAT 1125 (with SS 200 data system) mass spectrometer interfaced to a Varian 3700 gas chromatograph equipped with fused silica capillary columns coated with polydimethylsiloxane (SP 2100, 50 m x 0.2 mm), OV-1 (30 m x 0.25 mm), or polymethylphenylsiloxane (OV-17, 25 m x 0.1 mm).

Routine gas chromatographic work was done on a Perkin Elmer gas chromatograph (model 881) which had a hydrogen-flame ionization detector. The columns were a 6′ x ⅛" column packed with 3% SE-30 on 100-120 mesh Chromosorb (AW, DMCS); a 12′ x ¼" column packed with 10% Carbowax 20-M on Chromosorb (AW, DMCS), and a 12′ x ⅛" column packed with 15% FFAP on 100-200 mesh Chromosorb-W (AW, DMCS). Qualitative and quantitative gas chromatographic analyses were done on methyl esters (prepared by reaction of the acids from carbonation with diazomethane) with use of internal standards and calibrations based on authentic samples except where indicated otherwise. These analyses were confirmed by relative retention times on several columns, gas chromatographic-mass spectral fragmentation patterns, and ^{1}H/^{13}C NMR analysis. Melting points are corrected while boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Attempted Preparation of 1-Chloro-3,3-dimethyl-2,2-diphenylbutane[32] *(4).* The methyl ether (**1**) of *tert*-butyldiphenylcarbinol was prepared in 70% yield of recrystallized product [mp 42-44 °C, *cf.* lit[33] 45 °C; ^{1}H NMR (60 MHz, CCl_4) δ 1.04 (9 H, s), 2.97 (3 H, s), 7.2-7.7 (10 H, m)] by reaction of phenyllithium[34] in THF-hexane at -75°C and then at room temperature for 30 minutes before addition of methyl iodide, an eight-fold excess, added over a period of five days to the reaction mixture at reflux temperature. Cleavage of the methyl ether (5.1 g, 0.020 mole) with eutectic Na-K alloy (6.7 g of K, 0.17 mmol) in diethyl ether at reflux temperature for 2 h gave a blood red solution of the expected organopotassium compound which, after amalgamation of the excess Na-K with 5 mL of mercury, was then slowly forced into 500 mL of CH_2ClBr. Analysis of the crude product by ^{1}H NMR and IR spectroscopy indicated that the product was primarily hydrocarbon containing only some 15-20% of the chloride (**4**). A repeat cleavage of the methyl ether (5.6 g, 0.022 mole) with molten potassium (1.9 g, 0.049 mmol) in THF by dropwise addition of the methyl ether in THF to the finely divided potassium metal in refluxing THF, deactivation of remaining K by addition of mercury, and then forcing the cooled solution into 300 mL of CH_2ClBr at -70 °C gave a product containing only some 10-15% of the chloride (**4**) even though this ether cleavage technique[35] was shown by carbonation to give 95% yield of 3,3-dimethyl-2,2-diphenylbutanoic acid.

Preparation and Rearrangement of 3,3-Dimethyl-2,2-diphenylbutyllithium (**6**). Cleavage of 5.10 g (20 mmol) of the methyl ether (**1**) with 3.1 g of eutectic Na-K alloy (2.4 g, 62 mmol of K) in 350 mL of diethyl ether gave the red organopotassium compound **2**. The excess Na-K alloy was deactivated by dropwise addition of 5 mL of mercury and then the red solution was transferred by cannula into a stirred solution of 6.1 g (22.5 mmol) of bis(chloromethyl)mercury[36] (^{1}H NMR in CCl_4, single peak at δ 3.50) in 200 mL of anhydrous ether at -75 °C. The reaction mixture was allowed to warm to rt and left overnight. The ethereal solution was filtered through a sintered glass frit. Removal of diethyl ether left 4.9 g of crude organomercurial (**5**) which was dissolved in 25 mL of THF. Finely divided lithium sand was prepared from 4.8 g (0.69 mmol) of lithium and 0.050 g of Na under dodecane at reflux in the usual high-speed stirring apparatus. The lithium sand, after removal of dodecone via a cannula and rinsing with anhydrous THF, was suspended in 250 mL of THF and activated by treatment with 0.2 mL of methyl iodide. Addition of 5% of the THF solution of **5** to the well stirred lithium sand gave almost instantly a red color. The reaction mixture was then cooled to -75 °C and the solution of **5** was added dropwise over a period of 20 min with vigorous stirring continued for 2.5 h before carbonation of about one-third of the reaction mixture with solid carbon dioxide (aliquot A). The remaining reaction mixture was then warmed to 0 ±5 °C for 2 h before carbonation (aliquot B). The usual work-up with separation of neutral materials from carboxylic acids gave 0.27 g of crude acid from aliquot A and 0.51 g of acid from aliquot B. The acid of aliquot A had ^{1}H NMR (60 MHz, CCl_4) at δ 1.08 (9 H, s), 3.21 (2 H, s), 7.0-7.5 (10 H, m), 11.12 (1 H, s). This acid failed to crystallize for us. Its methyl ether had ^{1}H NMR (CCl_4) at δ 1.09 (9 H, s), 3.17 and 3.21 (5 H, overlapping s due to OCH_3 and CH_2), 7.0-7.4 (10 H, m); MS *m/e* (relative intensity) 240 (100), 208 (97), 181 (19), 180 (18), 179 (45), 178 (36), 162 (81). The crude acid of aliquot B had mp 148-149 °C; after sublimation *in vacuo* and recrystallization from hexane it had mp 156.5-157.0 °C: ^{1}H NMR (60 MHz, CCl_4) δ 1.06 (9 H, s), 3.60 (2 H, s), 6.9-7.7 (10 H, m), 12.0 (1 H, s); MS *m/e* (relative intensity) 226 (69), 208 (39), 148 (100); MS *m/e* (chemical ionization) 283 (36, M + 1), 227 (100), 226 (36), 181 (21). Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.55; H, 7.52. From their method of synthesis and their spectroscopic properties the acids of aliquots A and B are assigned the structures of 4,4-dimethyl-3,3-diphenylpentanoic acid and 2-benzyl-3,3-dimethyl-2-phenylbutanoic acid respectively; neither A nor B could be 4,4-dimethyl-2,2-diphenylpentanoic acid (product of *tert*-butyl migration).

9-Ethyl-9-methoxyfluorene **12a**. To 9-ethyl-9-fluorenol (133 g, 0.633 mole) in 400 mL of THF at -75 °C was added dropwise over 0.5 h 0.65 mol of *n*-butyllithium (1.7 *M* solution in hexane) with stirring under a nitrogen atmosphere. The reaction mixture was allowed to warm to rt, 60 mL (0.96 mol) of methyl iodide was added, and then the reaction mixture was kept at reflux for three days. The cold reaction mixture was extracted with three 200 mL portions of saturated aqueous NaCl, dried over anhyd $MgSO_4$; solvent was then removed and the product distilled through a Hickmann still at 100-110 °C at 0.05 mm Hg. The product, 115 g (81%), crystallized upon standing in a refrigerator and had mp 38-39 °C; ^{1}H NMR (CCl_4) at δ 0.51 (3 H, t, J = 7.5 Hz), 2.04 (2 H, q, J = 7.5 Hz), 2.67 (3 H, s), 7.7-7.0 (8 H, m). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.51; H, 7.24.

9-Chloromethyl-9-ethylfluorene **14a**. To 21.8 g of eutectic Na-K alloy (0.435 mol of K), which was finely divided and vigorously stirred in 400 mL of diethyl ether at reflux temp was added dropwise 36.4 g (0.162 mol) of **12a** dissolved in 70 mL of diethyl ether. After 35 min the addition was completed and 20 mL of mercury was added in tiny droplets to amalgamate the excess alkali metal. The dark red solution, containing some solid red organoalkali product, was cooled to -20 °C and then 125 mL of CH_2Cl_2 diluted with 100 mL of diethyl ether was added by cannula with continued stirring. The reaction mixture was allowed to warm slowly to 0 °C over a period of 1 h and then to 15 °C, by which temperature the red color was completely discharged. The next day the reaction mixture was filtered through a fritted-glass filter covered with a mixture of anhyd $MgSO_4$ and Celite (filter aid). The ethereal solution was washed with saturated aqueous NaCl solution and dried over anhyd $MgSO_4$. The solvents were removed *in vacuo* and the product distilled through a Hickmann still at a bath temp of 120-130 °C at 0.11 mm Hg. The product amounted to 28.6 g (73% yield) of liquid which crystallized in the cold from *n*-pentane to give 22.6 g (57.5% yield) of white crystals of mp 43-44 °C; ^{1}H NMR (CCl_4) at δ 0.36 (3 H, t, J = 7 Hz), 2.18 (2 H, q, J = 7 Hz), 3.62 (2 H, s), 7.0-7.7 (8 H, m). Anal. calcd for $C_{16}H_{15}Cl$: C, 79.17; H, 6.23; Cl, 14.61. Found 79.10; H, 6.29; Cl, 14.60.

9-(Chloromethyl-d_2)-9-ethylfluorene was prepared in the same way in similar yield as the unlabeled **14a** except for use of CD_2Cl_2 (100% molar excess over carbanion) in place of CH_2Cl_2; ^{1}H NMR (CCl_4) at

δ 0.33 (3 H, t, J = 7 Hz), 2.18 (2 H, q, J = 7 Hz), 6.9-7.7 (8 H, m); MS *m/e* (relative intensity) 246 (6.9), 244 (19.9), 215 (11), 193 (100).

9-Ethyl-9-methylfluorene was prepared by methylation of 9-ethyl-9-fluorenylpotassium (prepared as in preparation of **14a**) with CH_3I. The most highly purified sample (crystallized from *n*-pentane and then sublimed *in vacuo*) had mp 61.5-62.5 °C (lit.[16] mp 61-62 °C); ^1H NMR (CCl_4) at δ 0.32 (3 H, t, J = 7.5 Hz), 1.41 (3 H, s), 1.95 (2 H, q, J = 7.5 Hz), 6.9-7.8 (8 H, m); MS *m/e* (relative intensity) 208 (29), 194 (1.6), 193 (7), 179 (100).

Methyl 9-ethyl-9-fluorenecarboxylate was prepared by carbonation of 9-ethyl-9-fluorenylpotassium (prepared as previously) and esterification of the carboxylic acid with diazomethane; *mp* 81-82 °C (lit.[37] 81.5-82.0 °C); ^1H NMR ($CDCl_3$) at δ 0.43 (3 H, t, J = 7 Hz), 2.38 (2 H, q, J = 7 Hz), 3.54 (3 H, s), 7.1-7.8 (8 H, m); MS *m/e* (relative intensity) 252 (32), 224 (0.8), 223 (3), 193 (100).

Methyl 9-n-propyl-9-fluorenecarboxylate was prepared by carbonation of 9-*n*-propyl-9-fluorenylpotassium (from cleavage of 9-*n*-propyl-9-methoxyfluorene with NaK) and esterification of the carboxylic acid with diazomethane; the crystals from pentane had mp 84.0-85.5 °C (lit.[37] mp 85.0-85.5 °C); ^1H NMR (CCl_4) at δ 0.73 (5 H, m), 2.24 (2 H, m), 3.45 (3 H, s), 7.0-7.7 (8 H, m); MS *m/e* (relative intensity) 266 (54), 224 (4), 223 (5), 207 (100).

Reactions of 14a. A. With Lithium at -75 °C. Finely divided lithium sand (3.60 g Li, 0.52 mol) containing 0.057 g of sodium (2.5 mmol) was stirred vigorously at -10 °C and was activated by addition of 0.22 g (1.2 mmol) of CH_2BrCH_2Br. Addition of 5 mL of a solution of 4.16 g (17.1 mmol) of **14a** in 60 mL of THF over a 10 min period gave an initial light reddish color which changed to dark blue green upon stirring another 10 min. The solution was cooled to -75 °C and the remainder of the solution of **14a** was added dropwise over a period of 30 min with additional stirring for 10 min more before forcing the green solution onto crushed solid carbon dioxide. The usual acid-base work up (separation of neutral product) yielded 4.3 g of crude carboxylic acid. Extraction of the crude acid with 125 mL of benzene containing 10 mL of *n*-hexane gave 3.65 g of soluble product which after two recrystallizations from aqueous ethanol afforded 1.43 g of crystals of mp 108-110 °C. Recrystallization from cyclohexane and then distillation in a Hickmann still (bath at 110 °C, 0.11 mm Hg) gave 0.25 g of white crystals of mp 115.5-116.5 °C whose properties agreed with those expected for (9-ethyl-9-fluorenyl)acetic acid: ^1H NMR ($CDCl_3$) at δ 0.28 (3 H, t, J = 7 Hz), 2.12 (2 H, q, J = 7 Hz), 2.81 (2 H, s), 6.9-7.8 (8 H, m), 10.5 (1 H, s). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.81; H, 6.42. MS of methyl ester *m/e* (relative intensity) 266 (57, M^+), 237 (49), 206 (14), 195 (84), 193 (62), 191 (13), 178 (100), 177 (14), 176 (13), 165 (12), 152 (12).

In a repeat run with 2.00 g (8.24 mmol) of **14a** and lithium sand (1.73 g or 0.249 mol of Li and 0.035 g of Na) in THF as previously at -75 °C, except that 10 mL of mercury was added in tiny droplets prior to carbonation. The yield was 1.80 g of crude acids which, by quantitative GC analysis as methyl esters at 180 °C on a 10% silicone (SE 30) column (8′ x 1/8") packed with 100-120 mesh Chromosorb Q (AW, DMCS) with fluorene as internal standard, contained 1.61 g (73%) of methyl (9-ethyl-9-fluorenyl)acetate and 0.048

g (2.3%) of methyl 9-ethylfluorene-9-carboxylate. The neutral material by quantitative analysis on the FFAP column at 220 °C contained 0.16 g (9.4%) of 9-ethyl-9-methylfluorene.

B. With Lithium at -75 °C and then 0 °C. Reaction of 30 min. duration between 2.18 g (8.97 mmol) of **14a** and lithium sand (2.00 g, 0.288 mol, of Li and 0.62 g of Na), which had been activated with 0.87 g (4.5 mmol) of CH_2BrCH_2Br, was conducted as in the prior run at -75 °C in 300 mol of THF. Cyclohexene (1.47 g, 17.9 mmol) and finely divided mercury (8.0 mL) were then added to the bluish-green solution which was stirred vigorously at -75 °C for 30 min before carbonation of half of the reaction mixture (aliquot A). The remainder of the reaction mixture was then kept for 3 h at 0 ± 5 °C before carbonation of the remaining now pale red solution (aliquot B). Since 30 mL aliquots of the reaction solution were removed before each carbonation for GC analysis (after protonation) for norcarane on the FFAP column at 70 °C, the yields of products from aliquots A and B are calculated on the basis of reaction of 7.18 mmol of **14a**. According to quantitative GC analysis, aliquot A contained 0.023 g (2.5%) of methyl 9-ethylfluorene-9-carboxylate, 0.60 g (62%) of methyl (9-ethyl-9-fluorenyl)acetate, and 0.098 g (13%) of 9-ethyl-9-methylfluorene. Aliquot B contained 0.082 g (9.1%) of methyl 9-ethylfluorene-9-carboxylate, 0.160 g (16.7%) of methyl (9-ethyl-9-fluorenyl)acetate, 0.247 g (33%) of 9-ethyl-9-methylfluorene, and 0.07 (6%) of an unknown methyl ether which is likely an artifact from reaction with excess of diazomethane.

In another reaction which was run exactly as in the prior reaction but without cyclohexene and with the deuterated chloride 9-(chloromethyl-d_2)-9-ethylfluorene (2.04 g, 8.32 mmol) and lithium (1.74 g containing 0.062 g of Na), aliquot A contained 0.059 g (5.6%) of methyl 9-ethylfluorene-9-carboxylate, 0.67 g (60%) of methyl (9-ethyl-9-fluorenyl)acetate-d_2, 0.049 g (5.6%) of 9-ethyl-9-methylfluorene-d_2, and 0.139 g (12%) of a product of MW 282 (which corresponds to $C_{19}H_{18}D_2O_2$) via GC/MS. The product of MW 282 is evidently an artifact from reaction of excess diazomethane with methyl 9-ethyl-9-fluorenylacetate. Aliquot B contained 0.121 (11.5%) of methyl 9-ethylfluorene-9-carboxylate, 0.231 g (20.7%) of methyl (9-ethyl-9-fluorenyl)acetate-d_2, 0.262 g (30%) of 9-ethyl-9-methylfluorene-d_2, 0.034 g (2.9%) of the product of MW 282, and 0.03 g (2%) of a product of MW 296 (GC/MS) which corresponds to incorporation of two extra CH_2 groups.

C. With Cs-K-Na Alloy at -75 °C. To finely divide Cs-K-Na alloy (2.33 g of Cs, 0.83 g of K, 0.118 g of Na) vigorously stirred in 250 mL of THF at -75 °C was added 0.659 g (2.72 mmol) of **14a** dissolved in 15 mL of THF. The blue solution changed rapidly to red during the 10 sec addition time of **14a**; after another 9 sec the solution was greenish blue whereupon the reaction mixture was force onto crushed solid carbon dioxide during a 36 sec interval. The usual acid-base work-up gave 0.54 g of crude acids and 0.17 g of crude neutral material. Quantitative GC analysis (after esterification with diazomethane) gave 0.113 g (16.5%) of methyl 9-ethylfluorene-9-carboxylate, 0.019 g (2.6% of methyl (9-ethyl-9-fluorenyl)acetate, 0.0082 g (1.4% of 9-ethyl-9-methylfluorene, and unidentified esters of higher mol wt.

9-tert-Butylfluoren-9-ol (**11b**). This compound has been previously prepared in low yield by reaction of *tert*-BuMgCl with 9-fluorenone[38]. To 9-fluorenone (67.6 g, 375 mmol) in 450 mL of benzene was added at 0 °C 196 mL of a solution of *tert*-butyllithium (412 mmol) in pentane over a period of 40 min with stirring for 4 h before decomposition with ice water. The yield of crude product was 88 g; however, the ^{1}H NMR spectrum of this material showed that it contained only an 81% yield of the expected fluorenol.

Recrystallization from pentane gave 43 g (48% yield) of product which was 94% pure by NMR; another recrystallization from this solvent gave 24 g (27% yield) of pure product of mp 92-93 °C (lit.[38] 96 °C); ^{1}H NMR (CCl_4) at δ 0.93 (9 H, s), 7.0-7.6 (8 H, m).

9-tert-Butyl-9-methoxyfluorene **(12b).** To 43.6 g (183 mmol) of 9-*tert*-butylfluoren-9-ol in 400 mL of THF under nitrogen was added with stirring at -75 °C *n*-butyllithium (211 mmol in 122 mL of hexane). To the mixture after stirring for 1 h at -75 °C was added methyl iodide (60 g, 422 mmol); the mixture was allowed to warm to rt and stirred overnight. Since ^{1}H NMR analysis indicated that methylation was only one-third complete, more methyl iodide (60 g) was added and reaction allowed to proceed for 48 h more. The crude product (91% yield by NMR) after recrystallization from diethyl ether gave 24 g (52%) of pure crystals (**12b**), mp 83-84 °C; ^{1}H NMR (300 MHz, $CDCl_3$).[39] δ 0.95 (9 H, s), 2.82 (3 H, s), 7.21 (2 H, dt, J = 7.4 and 1.1 Hz), 7.32 (2 H, dt, J = 7.4 and 0.7 Hz), 7.60 (2 H, m, J = 7.4 and 0.7 Hz); ^{13}C NMR ($CDCl_3$) δ 25.5 (q), 38.2 (s), 51.8 (q), 93.7 (s), 118.9 (d), 125.3 (d), 125.5 (d), 127.7 (d), 141 (s), 144.6 (s); MS *m/e* (relative intensity) 252 (3, M^+), 195 (100), 180 (18), 165 (4). The analytical sample was sublimed at a bath temp of 50-80 °C (50 μ). Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.62; H, 7.99.

In an attempt to abbreviate the synthesis of **12b** from fluorenone to a one-flask reaction, 9-fluorenone (45.0 g, 250 mmol) in 250 mL of THF was allowed to react at -75 °C with *tert*-butyllithium (256 mmol in 122 mL of pentane) for 5 h at -75 °C; methyl iodide (77.5 g, 546 mmol) was then added and the mixture allowed to warm to rt and stirred overnight. Additional methyl iodide (37.5 g) was then added and the solution held at reflux for 24 h. Since ^{1}H NMR analysis indicated that methylation was still incomplete, pentane was removed via distillation, more methyl iodide (37.5 g, 264 mmol) was added and the solution was held at reflux for 30 h. After removal of most of the solvent *in vacuo*, addition of saturated aq NaCl solution, and ether extraction, the crude product was found to contain (by ^{1}H NMR analysis) only 34% yield of **12b**; the remainder of the product according to GC MS was a mixture of four additional isomers of *m/e* 252. The ethereal solution of product after concentration on a rotovac deposited 13.4 g (22% yield) of crystals which upon two recrystallizations from *n*-hexane gave 4.5 g of pure **A**, mp 125-126 °C; IR (CCl_4), 1731 cm^{-1} (>C=O); UV (95% EtOH) λ max (ε) 234 (19,190) and 328 nm (1460); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (9 H, s), 1.35 (3 H, s); 2.82 (1 H_C, ca dt, $J_{BC} \cong J_{DC}$ = 4.8 Hz, J_{AC} = 1.5 Hz), 5.89 (1H_B, ddd, J_{AB} = 9.9 Hz, J_{BD} = 1.5 Hz), 6.25 and 6.27 (2 H, m, H_D and H_A), 7.38 (1 H, dt, J = 7.4 and 1.1 Hz), 7.60 (1 H, dt, J = 7.4 and 1.3 Hz), 7.68 (1 H, br d, J = 7.5 Hz), 7.77 (1 H, br d, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) 28.2 (q, $C(CH_3)_3$ and CH_3), 35.0 (s), 50.4 (s), 50.9 (d), 120.7 (d), 121.2 (d), 124.5 (d), 127.3 (d, 2 C's), 127.6 (d), 132.1 (s), 134.0 (d), 140.3 (s), 147.1 (s), 203.8 (s); MS *m/e* (relative intensity) 252 (2, M^+), 195 (100), 181 (9), 180 (3), 178 (3), 167 (21), 165 (35), 152 (23). Anal Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.65; H, 8.33. This data is in agreement with the structure of **A** being *cis*-3-*tert*-butyl-9a-methyl-3,9a-dihydro-9-fluorenone as confirmed by x-ray diffraction (see *X-Ray Crystallographic Data*). The residual material from the recrystallization of **A** after storage for one month was distilled in a Hickman still at 50 μ. After collection of fractions rich in **12b** and then **A**, a fraction was obtained which after recrystallization from hexane and sublimation at 140-150 °C (90 μ) amounted to 0.23 g of a material **B** of mp 175-176 °C; IR (benzene), 1703 and 3560 cm^{-1} (-CO_2H); UV_{max} (95% EtOH) 268 nm (ε 5840); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (9 H, s), 1.99 (3 H, s), 6.53 (1 H, s), 6.97 (1 H, s), 7.25 (2 H, m), 7.40 (1 H, dt, J = 7.5 and 1.4 Hz), 7.54 (1 H, dt, J = 7.5 and 1.4 Hz), 8.02 (1 H, dd, J = 7.5 and 0.9 Hz); ^{13}C NMR ($CDCl_3$ + CD_3COCD_3) δ 19.3 (q), 29.5 (q), 34.2 (s), 117.1 (d), 126.1 (d), 127.0 (d), 129.5 (d), 130.5

(s), 130.7 (d), 131.2 (d), 131.6 (s), 132.3 (s), 133.1 (s), 142.6 (s), 153.7 (s), 169.6 (s); MS *m/e* (relative intensity) 284 (40, M^+), 269 (100), 251 (8), 233 (6), 223 (15), 211 (10), 209 (44). Anal. calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.99; H, 7.12. This data is in agreement with **B** being 2-(5-*tert*-butyl-4-hydroxy-2-methylphenyl)benzoic acid as confirmed by x-ray diffraction (see *X-Ray Crystallographic Data*).

9-tert-Butyl-9-(chloromethyl)fluorene (14b). The methyl ether **12b** (20.1 g, 80 mmol) in 100 mL of diethyl ether was added dropwise over a 20 min period to eutectic Na-K alloy (2.93 g of Na and 10.2 g of K) which was kept finely dispersed by high-speed stirring in 250 mL of ether at reflux temperature under a nitrogen atmosphere. The rate of the exothermal reaction was regulated by the rate of addition which was maintained so as not to exceed the capacity of the condenser. Stirring of the orange-brown reaction mixture was continued for 1 h and then the excess alkali metal was deactivated by cautious addition of 10 mL of tiny droplets of mercury (235 g). The reaction mixture was transferred by a siphon into 40 mL (615 mmol) of bromochloromethane in 100 mL of ether maintained at -10 °C. The reaction mixture was then allowed to warm to room temperature (greyish green solution after 2 h) and stirred over night. The mixture was worked up according to the procedure for **14a**. Concentration of the ethereal solution gave 11.7 g (54% yield) of product of MP 145-146.5 °C (**14b**). The analytical sample after two sublimations at 90 μ (bath at 100-110 °C) had MP 146.0-147.0 °C; ^1H NMR (CCl_4) δ 0.89 (9 H, s), 4.22 (2 H, s), 7.0-7.7 (8 H, m); ^{13}C NMR ($CDCl_3$) δ 26.8 (q), 37.4 (s), 46.7 (t), 61.8 (s), 119.0 (d), 124.1 (d), 125.6 (d), 126.9 (d), 141.5 (s), 146.0 (s); MS *m/e* (relative intensity) 272 (0.44, M^+, ^{37}Cl), 270 (1.5, M^+, ^{35}Cl), 219 (1.3), 216 (0.8), 215 (1.4), 214 (2.6), 213 (2.6), 191 (3.0), 178 (100). Anal. calcd for $C_{18}H_{19}Cl$: C, 79.83; H, 7.07; Cl, 13.10. Found: C, 79.89; H, 7.09; Cl, 12.95.

9-Neopentylfluorene-9-carboxylic Acid. To 4.26 g (23.9 mmol) of freshly prepared 9-methylenefluorene[40] [^1H NMR (CCl_4) δ 5.98 (2 H, s); 7.0-7.8 (8 H, m)] in 40 mL of THF at -75 °C was added with stirring 20 mL (42 mmol) of *tert*-butyllithium in pentane. After 2 h at -75 °C the reaction mixture was forced onto crushed solid carbon dioxide. The usual acid-base work-up yielded 4.5 g of carboxylic acid, MP 164-165 °C. Anal. calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.48; H, 7.28. Methyl ether (**19**) (from reaction with diazomethane) had ^1H NMR (CCl_4) at δ 0.36 (9 H, s), 2.56 (2 H, s), 3.40 (3 H, s), 7.36 (8 H, m); MS *m/e* (relative intensity) 294 (26, M^+), 235 (16), 224 (49), 180 (27), 179 (100). MS *m/e* (chemical ionization) 295 (100, $M^+ + H^+$), 294 (15), 235 (29), 221 (7), 180 (2), 179 (10).

Methyl 9-tert-Butylfluorene-9-carboxylate (20) was prepared by carbonation of the anion from cleavage of **12b** and esterification of the free acid with diazomethane; MP 113-114 °C (lit.[41] 113 °C); ^1H NMR ($CDCl_3$) δ 0.97 (9 H, s), 3.65 (3 H, s), 7.1-8.0 (8 H, m); MS *m/e* (relative intensity) 280 (1.5, M^+), 224 (100), 192 (23), 165 (76); MS *m/e* (chemical ionization) 281 (100, $M^+ + H^+$), 267 (8), 225 (34), 224 (29), 221 (18), 165 (6).

Methyl 9-Methylfluorene-9-carboxylate[41] (**18**) was prepared by carbonation of the anion from cleavage of 9-methyl-9-methoxyfluorene by NaK alloy in ether and esterification of the free acid with diazomethane; ^1H NMR (CCl_4) δ 1.69 (3 H, s), 3.40 (3 H, s), 7.0-7.8 (8 H, m); MS *m/e* (relative intensity) 238 (22, M^+), 179 (100), 178 (33); MS *m/e* (chemical ionization) 239 (100, M^+ + H^+), 238 (41), 221 (22), 219 (16), 179 (94), 178 (7).

9-tert-Butylfluorene was prepared by protonation of the anion from cleavage of **12b** by NaK; ^{1}H NMR (CCl_4) δ 0.96 (9 H, s), 3.65 (1 H, s); 7.0-7.8 (8 H, m); MS (relative intensity) 222 (24, M^+), 207 (5), 192 (8), 191 (6), 181 (6), 166 (100), 165 (82).

9-tert-Butyl-9-methylfluorene was prepared by reaction of iodomethane with the anion from cleavage of **12b** with NaK; ^{1}H NMR (CCl_4) δ 0.72 (9 H, s), 1.35 (3 H, s), 7.0-7.8 (8 H, m); MS *m/e* (relative intensity) 236 (13, M^+), 221 (2), 206 (3), 195 (16), 191 (6), 180 (51), 179 (100), 178 (48), 165 (25).

Reactions of 14b. A. with Lithium at -75 °C and then 0 °C. To finely divided lithium sand [3.5 g (0.50 mol) of Li and 0.074 g of Na] vigorously stirred in 300 mL of THF at -5 °C was added 1.7 g (9.1 mmol) of 1,2-dibromoethane for activation of the lithium sand. Then 3 mL of a solution of 4.07 g (15.0 mmol) of **14b** in 50 mL of THF was added. After about 8 min of vigorous stirring the color changed to brick red and then green (the colors indicate that the reaction has been satisfactorily initiated); the temperature was lowered to -75 °C (dry ice-isopropyl alcohol bath) and then the remainder of the solution of **14b** was added dropwise over a 39 min period. The color of the solution changed to orange and then a final dark green color. Vigorous stirring was continued for 3 h and then the excess lithium was amalgamated by addition of very finely divided mercury (20 mL) with continued stirring over a 20 min period. Approximately 38% of the solution was carbonated (aliquot A) and then the solution was allowed to warm to 0 °C ±5 °C and stirred at this temperature for 1.8 h before carbonation of the remainder of the reaction mixture (aliquot B). The usual work-up with separation of neutral materials from carboxylic acids gave 1.66 g of crude acids from aliquot A and 2.12 g from aliquot B. The acids after esterification with ethereal diazomethane were analyzed quantitatively on the 3% SE-30 column at 160 °C. Aliquot A contained 0.054 g (4.0%) of **18**, 0.070 g (4.4%) of **20**, and 1.15 g (69%) of **17**. Aliquot B contained 1.34 g (60%) of **18**, 0.15 g (5.5%) of **19**, 0.11 g (4.4%) of **20**, and 0.19 g (7.1%) of **17**.

In a repetitive run with 2.05 g (7.56 mmol) of **14b** and half the previous quantity of lithium (but with omission of the amalgamation procedure), the aliquots for carbonation were of equal size. Aliquot A (-75 °C) contained 0.057 g (6.3%) of **18** and 0.75 g (68%) of **17**. Aliquot B (3.5 h at 0 °C) contained 0.50 g (56%) of **18**, 0.011 g (1.0%) of **19**, 0.010 g (0.9%) of **20**, and no detectable **17**.

A 0.98 g sample of carboxylic acid from the above aliquots A (-75 °C) was subjected to chromatography on a column (3 cm in diameter) packed with 50 g of silica gel (ICN Silica 32/63) with elution by 80:20 (by volume) of hexane:diethyl ether. The major component, after two recrystallizations from *n*-hexane, amounted to 0.21 g of white crystals of (9-*tert*-butylfluoren-9-yl)acetic acid which after sublimation *in vacuo* (90 μ, 100-110 °C) had MP 180.5-181.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.83 (9 H, s), 3.13 (2 H, s), 7.0-7.6 (8 H, m), 8.5 (1 H, bd s). Anal. calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.42; H, 7.20. Reaction of this carboxylic acid with ethereal diazomethane gave the corresponding methyl ester **17**; MS *m/e* (relative intensity) 294 (1.5 M^+), 238 (35), 221 (4), 205 (4), 195 (26), 191 (3), 178 (100), 177 (7), 176 (6), 165 (10); MS *m/e* (chemical ionization) 295 (94, M^+ + 1), 277 (14), 263 (97), 261 (11), 238 (47), 221 (100), 178 (14).

In a further run the organolithium compound **15b** was prepared from 2.06 g (7.61 mmol) of **14b** and excess lithium sand (1.75 g of Li, 0.033 g of Na) in 300 mL of THF at -75 °C as in the previous runs, with amalgamation of the excess lithium with 10 mL of finely divided mercury. To this solution was added at -75 °C benzyllithium prepared[42] by cleavage of benzyl methyl ether (2.46 g, 20.2 mmol) with lithium sand (2.8 g of Li, 0.042 g Na) in 200 mL of THF. Stirring was continued while the solution was allowed to warm to 0 °C and kept at this temperature (±5 °C) for 3 h prior to carbonation. The usual quantitative analysis of the products after esterification with diazomethane gave 1.44 g (79%) of **18**, 0.082 g (3.7%) of **19**, 0.093 g (4.3%) of **20**, and 0.067 g (3.0%) of **17** with no detectable incorporation of the benzyl moiety in any of the products according to GC-MS analysis.

In a final run 1.209 g (4.46 mmol) of **14b** was allowed to react with excess lithium sand (1.75 g of Li and 0.04 g of Na) in 365 mL of THF at -69 °C as in prior runs with amalgamation of the excess lithium with 6 mL of mercury. The solution was then warmed to -10 °C within 30 min whereupon a 156 mL portion (aliquot A) was carbonated and then the remainder of the solution was warmed within a few minutes to 0 °C ±0.2 °C. After 60 min the remaining solution was rapidly carbonated (aliquot B). The usual quantitative analysis gave for aliquot A: 0.058 g (12.6%) of **18**, 0.011 g (2.1%) of **20**, 0.367 g (65.4%) of **17**, 0.043 g (9.4%) of 9-*tert*-butyl-9-methylfluorene, and 0.10 g (2%) of 9-*tert*-butylfluorene; for aliquot B: 0.199 g (32.7%) of **18**, 0.27 g (3.5%) of **19**, 0.033 g (4.6%) of **20**, 0.185 g (24.6% of **17**, 0.12 g (20%) of 9-*tert*-butyl-9-methylfluorene, 0.005 g (0.8%) of 9-*tert*-butylfluorene. From the results of the two carbonated aliquots the first order decomposition of the organolithium reagent **15b** into the anionic precursor of **18** is calculated to be 0.48 h^{-1} at 0 °C.

B. With Cs-K-Na Alloy at -75 °C. To 7.1 g of finely divided eutectic[43] Cs-K-Na alloy (0.038 g atom of Cs) vigorously stirred in 250 mL of THF at -75 °C was added 0.888 g (3.28 mmol) of **14b** in 15 mL of THF over a period of 1 min. The reaction mixture changed in color from blue to brown to black during this addition. Stirring was continued for 1 min and then the reaction mixture was forced in 1 min onto crushed solid carbon dioxide. Methanol (20 mL) was added to destroy any unreacted alloy. The usual work-up and quantitative GC analysis of the 0.95 g of crude acids gave 0.208 g (27%) of **18** and 0.052 g (5.5%) of **20**.

Another run was made under conditions like the first except that 0.712 g (2.63 mmol) of **14b** was added to 6.3 g of eutectic Cs-K-Na alloy (0.040 g atom of Cs) over a period of 8 s with stirring for 15 s before carbonation, over a 30 s interval. The yield was 0.88 g of crude acids which contained 0.192 g (31%) of **18** and 0.015 g (2.0%) of **20**.

A final repetitive run was made like the first run except that 1.85 g (6.83 mmol) of **14b** was added to 7.12 g of eutectic Cs-K-Na alloy (0.038 g atom of Cs) over 40 s and then stirring for 1 min and carbonation completed after an additional minute. The usual work-up gave 2.13 g of crude acids and 0.30 g of neutral materials which contained 0.537 g (33%) of **18**, 0.100 g (5.1%) of **20**, 0.020 g (1.0%) of **17**, 0.099 g (7.9%) of 9-methylfluorene, 0.124 g (7.6%) of 9-*tert*-butyl-9-methylfluorene, and 0.020 g (1.3%) of 9-*tert*-butylfluorene.

Rearrangement of 15b Formed from the Corresponding Organomercury Derivative. The methyl ether **12b** (4.00 g, 15.9 mmol) was cleaved with Na-K alloy (0.75 g of Na and 1.75 g of K) in 250 mL of diethyl ether exactly as described under the preparation of **14b**. After amalgamation of the excess Na-K alloy the carbanion **13b** was transferred via a cannula to a solution containing 2.38 g (7.96 mmol) of $(ClCH_2)_2Hg$ in

50 mL of diethyl ether at -30 °C. The solution was allowed to warm up to rt and held at this temperature for 2 h during which time the red solution slowly turned grey. The solution was filtered through 10 g of anhyd $MgSO_4$ on a course sintered glass frit; removal of solvent under reduced pressure gave 4.0 g of crude mercury compound which was used for the next reaction without further purification. A solution of 3.0 g (4.5 mmol) of this mercury compound in 60 mL of THF-diethyl ether (1:1 by volume) was added dropwise to finely divided lithium sand (0.80 g of Li and 0.015 g of Na) in 200 mL of THF at -75 °C over a 30 min period with vigorous stirring and stirring continued for 3 h at -75 °C before carbonation of 42% of the solution (aliquot A). The remainder of the solution was allowed to warm to 0 °C over a 1 h period and then kept at 0 ° ±5 °C for 2 h prior to carbonation (aliquot B). The usual work-up and quantitative GC analysis gave for aliquot (A) 0.0083 g (0.9%) of **18**, 0.040 g (3.8%) of **20**, and 0.238 g (21.4%) of **17**; for aliquot (B) 0.248 g (20.2%) of **18**, 0.017 g (1.1%) of **19**, 0.019 g (1.3%) of **20**, and 0.051 g (3.3%) of **17**.

*9-tert-Butyl-9-(chloromethyl-d_2)fluorene (**14b-d_2**).* This compound was prepared from the methyl ether **12b** (14.53 g, 57.7 mmol) by the general procedure for the unlabeled compound except that the organopotassium intermediate **13b** was allowed to react with CD_2Cl_2 (10.0 g, 115 mmol, 99.5% D) in diethyl ether solution (600 mL) with stirring for 14 d at room temperature (rather than with $ClCH_2Br$). Since the orange-brown color of the carbanion was still not discharged, 300 mL of THF was added and stirring continued for 6 more days before the color changed to grey. The usual work-up gave 10.3 g of crude product which after recrystallization from pentane amounted to 5.7 g (36% yield). Sublimation *in vacuo* gave 3.2 g (20% yield) of colorless crystals of mp 145.0-146.0 °C; ^1H NMR ($CDCl_3$, 300 MHz), δ 0.93 (9 H, s), 7.27 (2 H, dt, J = 7.5 and 1.3 Hz), 7.36 (2 H, dt, J = 7.5 and 1.3 Hz), 7.48 (2 H, br d, J = 7.7 Hz), 7.70 (2 H, br d, J = 7.7 Hz); MS *m/e* (relative intensity) 274 (2.9, M^+, ^{37}Cl), 272 (8.5, M^+, ^{35}Cl), 235 (4), 220 (7.2), 218 (1.9), 217 (1.8), 216 (4.7), 215 (4.2), 191 (2.7), 180 (100).

*Reaction of **14b-d_2** with Lithium at -75 °C and then 0 °C.* Reaction of **14b-d_2** (1.63 g, 5.99 mmol) with excess lithium (1.30 g of Li and 0.025 g of Na) in 300 mL of THF was conducted at -75 °C for 1 h according to the general procedure for unlabeled **14b**. After amalgamation of the excess of lithium sand with mercury (8 mL) 36% of the solution was carbonated (aliquot A) and the remainder held at 0 ±5 °C for 3 h prior to carbonation (aliquot B). Quantitative GC analysis gave for aliquot A: 0.053 g (10%) of **18-d_2**, 0.016 g (2.7%) of **20**, and 0.40 g (62%) of **17-d_2**; for aliquot B: 0.549 g (60%) of **18-d_2**, 0.032 g (2.9%) of **19-d_2**, 0.064 g (6.0%) of **20**, and 0.072 g (6.4%) of **17-d_2**. The isotopic composition of the aliquot B methyl esters was assayed by GC MS *m/e* (relative intensity): for **18-d_2** 240 (27, M^+), 181 (100), 180 (30), 179 (10). MS *m/e* by chemical ionization: for **18-d_2** 241 (100, $M^+ + H^+$), 240 (32), 223 (13), 221 (10), 181 (63), 180 (6), 179 (2); for **19-d_2** 297 (100, $M^+ + H$), 296 (17), 237 (29), 223 (7), 181 (63), 180 (2); for **20** 281 (100, $M^+ + H^+$), 280 (0.1), 267 (10), 225 (69), 224 (46), 221 (39), 165 (14); for **17-d_2** 297 (69, $M + H^+$), 296 (3), 277 (9), 265 (70), 264 (11), 263 (32), 261 (81), 240 (48), 221 (100), 180 (18).

*9-(tert-Butyl-d_9)-9-fluorenol)(**11b-d_9**).* *tert*-Butyl-d_9-lithium was prepared in 92% yield by reaction of 10.0 g (98 mmol) of *tert*-butyl-d_9 chloride (Aldrich, 99.0 atom % D) with lithium sand [5.0 g (0.72 mol) of Li and 0.070 g of Na] in 200 mL of pentane at reflux temperature.[44] The excess of lithium was amalgamated by addition of 8 mL of finely divided mercury at 0 °C. The organolithium reagent was then added via a cannula to a solution of 15.4 g (86 mmol) of fluorenone in 200 mL of benzene at 0 °C. The usual work-up gave 22 g of crude **11-b-d_9** which was used without further purification in the following reaction.

9-(tert-Butyl-d_9)-9-methoxyfluorene (12b-d_9). The 22 g of crude **11-b-d_9** from the prior reaction was converted to the methyl ether by the procedure for the unlabeled compound **12b**. The crude product was purified by chromatography over 450 g of silica gel (0.2-0.5 mm, EM reagents) on a column 5.0 cm in diameter with elution by cyclohexane. The yield was 7.8 g (37% yield based on fluorenone) of crystals of mp 82-83 °C; ^{1}H NMR (CDCl$_3$) δ 0.95 (<0.4 H), 2.82 (3 H, s), 7.0-7.7 (8.0 H, m).

9-(tert-Butyl-d_9)-9-(chloromethyl)fluorene (14b-d_9). This compound was prepared from **12b-d_9** by the procedure used for the unlabeled compound; ^{1}H NMR (CDCl$_3$) δ 0.9 (< 0.2 H), 4.27 (2 H, s), 7.0-7.7 (8 H, m); MS *m/e* (relative intensity) 281 (0.51, M$^+$, ^{37}Cl), 279 (1.6, M$^+$, ^{35}Cl), 225 (2.0), 217 (0.4), 215 (2.3), 213 (3.2), 194 (3.0), 178 (100).

Reaction of 14b-d_9 with Lithium at -75 °C and then at 0 °C. Reaction of **14b-d_9** (0.95 g, 3.43 mmol) with lithium sand (1.34 g of Li, 0.049 g of Na) in 300 mL of at -75 °C was conducted over a period of 2 h in the manner described for unlabeled **14b**. After amalgamation of the excess lithium with mercury (8 mL), an 80 mL portion (aliquot A) was carbonated. The solution was warmed to 0° ±5 °C over a 30 min period and kept at this temperature for 3.0 h prior to carbonation (aliquot B). Quantitative GC analysis gave for aliquot A: 0.0009 g (0.4%) of **18-d_0**, 0.0020 g (0.8%) of **20-d_9**, 0.187 g (67.3%) of **17-d_9**, 0.015 g (6.7%) of 9-(*tert*-butyl-d_9)-9-methylfluorene, and 0.0019 g (0.9%) of 9-(*tert*-butyl-d_9)fluorene. Aliquot B contained 0.067 g (11.1%) of **18-d_1**, 0.024 g (3.1%) of **17-d_9**, 0.034 g (4.7%) of **20-d_9**, 0.241 g (31.6%) of **17-d_9**, 0.159 g (25.7%) of 9-(*tert*-butyl-d_9)-9-methylfluorene, and 0.0075 g (1.3%) of 9-(*tert*-butyl-d_9)-fluorene. From the results of the two carbonated aliquots the first order decompositions of the organolithium reagent **15b-d_9** into **21-d_1** (the anionic precursor of **18-d_1**) is estimated to be 0.076 h^{-1} at 0 °C. In conjunction with the corresponding data for the protium compound at a similar percentage of reaction, the isotope effect k_H/k_D for this decomposition is 0.48/0.076 or 6.3 ± 1 at 0 °C. The isotopic composition of the aliquot B methyl esters was assayed by GC MS *m/e* (relative intensity): for **18-d_1** 239 (20, M$^+$), 238 (3.4), 180 (100), 179 (51); **19-d_9** 303 (6.3, M$^+$), 302 (0.8)...(contamination of GC peak with **20-d_9**); **17-d_9** 303 (2.7, M$^+$), 239 (70), 238 (2.7), 237 (12), 195 (44), 179 (100), 178 (65). The aliquot A methyl esters by similar analysis gave: for **18-d_0** 239 (3.9), 238 (19.3, M$^+$), 180 (19), 179 (100) as expected if no appreciable deuterium is present; for **20-d_9** 289 (0.6, M$^+$), 230 (2.9), 225 (100); for **17-d_9** same as aliquot B.

9-Methoxy-9-neopentylfluorene (12c). Neopentyllithium was prepared in 79% yield (according to titration[45]) by reaction of neopentyl chloride (40.0 g, 0.375 mol) with lithium sand (7.8 g, 1.12 g. at., activated with 0.10 g Na) in 300 mL of THF at -75 °C. The excess of lithium was amalgamated by addition of 8.0 mL of finely divided mercury. The solution of neopentyllithium was added by cannula to 9-fluorenone (49.8 g, 0.276 mol) in 200 mL of THF at -40 °C. The stirred solution was allowed to warm to -10 °C over a 45 min period and then iodomethane (160 g, 1.14 mol) was added and the solution stirred for 132 h at rt. After the usual work-up, the residual oil was recrystallized from pentane to give 48.8 g (66% yield) of product of mp 85-87 °C. Recrystallization from diethyl ether gave pure **12c** as white crystals, mp 86-87 °C; ^{1}H NMR (CDCl$_3$) δ 0.37 (9 H, s), 2.37 (2 H, s), 2.63 (3 H, s), 7.0-7.8 (8 H, m). Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.68; H, 8.37.

9-(Chloromethyl)-9-neopentylfluorene (14c). The methyl ether **12c** (15.1 g, 56.8 mmol) was allowed to react with 8.2 g of eutectic Na-K alloy (6.4 g K) in 375 mL of diethyl ether according to the general procedure (see **14a**). After amalgamation of the excess alloy with 8 mL of mercury, the red solution was forced into 66 g of methylene chloride in 100 mL of diethyl ether at -20 °C. The solution, upon warming to rt, lost its red color after 1 h. The next day, the usual work-up of product yielded, after recrystallization from diethyl ether, 12.2 g (75% yield) of **14c**: mp 69.5-70.5 °C; ^{1}H NMR (CCl_4) at δ 0.36 (9 H, s), 2.36 (2 H, s), 3.47 (2 H, s), 7.0-7.7 (8 H, m); MS *m/e* (relative intensity) 286 (4.6, M^+ for ^{37}Cl), 284 (14.5, M^+ for ^{35}Cl), 235 (12), 213 (10), 192 (8), 191 (10), 179 (74), 178 (53), 177 (10), 176 (8), 165 (4),... 57 (100). Anal. Calcd for $C_{19}H_{21}Cl$: C, 80.12; H, 7.43; Cl, 12.45. Found: C, 80.21; H, 7.45, Cl, 12.48.

9-(3,3-Dimethylbutyl)fluorene-9-carboxylic Acid. Freshly prepared 9-methylenefluorene[40] (1.80 g, 10.1 mmol) in 40 mL of THF was added dropwise to an excess of neopentyllithium (prepared in 70% yield at -75 °C from reaction of 4.8 g, 45 mmol, of neopentyl chloride with 5.1 g, 0.73 mole of lithium sand and then amalgamation of the excess lithium with 8 mL of mercury) in 230 mL of THF at -20 °C. After continued stirring at 0 °C for 2 h the mixture was carbonated. The usual acid-base work-up yielded 2.87 g of crude acid, mp 161-162 °C, which after recrystallization from ethyl alcohol gave 0.80 g of crystals of mp 163-165 °C. After three sublimations *in vacuo* at 170°, the analytical sample had mp 167-168 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.63 (2 H, m, part of AA'XX'), 0.70 (9 H, s), 2.31 (2 H, m, other part of AA'XX'), 7.28 (2 H, dt, J = 7.4 and 1.3 Hz), 7.35 (2 H, dt, J = 7.4 and 1.3 Hz), 7.54 (2 H, m), 7.68 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 29.1 (q), 29.9 (s), 32.2 (t), 37.0 (t), 61.2 (s), 119.9 (d), 124.8 (d), 127.4 (d), 128.2 (d), 141.2 (s), 144.7 (s), 180.1 (s); MS of methyl ester *m/e* (relative intensity) 308 (33, M^+), 249 (37), 233 (6), 224 (18), 223 (6) ... 165 (100). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.47; H, 7.54.

9-Neopentylphenanthrene (26). To 9-cyanophenanthrene (10.2 g, 50.4 mmol) dissolved in 200 mL of benzene at 0 ±5 °C was added *tert*-butyllithium (59 mmol) in 205 mL of pentane and the mixture held at this temperature with stirring for 3 h before decomposition with ice-cold 5% hydrochloric acid. The reaction mixture was stirred for 48 h to complete hydrolysis. After removal of solvents the crude ketone was purified by chromatography two times over silica gel with elution by hexane-diethyl ether. The crude viscous ketone (7.6 g, 29 mmol) was reduced to hydrocarbon by the Huang-Minlon[46] modification of the Wolff-Kishner reaction by use of 3.9 mL of hydrazine hydrate and 3.4 g of KOH in 40 mL of diethylene glycol. The yield was 4.4 g (35% overall yield) of crude hydrocarbon which after chromatography over silica gel, distillation *in vacuo*, and recrystallization from pentane gave crystals of **26**: mp 64.0-65.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.93 (9 H, s), 2.97 (2 H, s), 6.8-8.9 (9 H, m); MS *m/e* (relative intensity) 248 (23), 233 (3), 215 (3), 202 (4), 192 (100), 191 (98), 190 (11), 189 (21), 176 (3), 165 (15). Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.69; H, 8.30.

Reactions of 14c A. With Lithium at -75 °C and then 0 °C. These reactions were conducted, unless otherwise specified, according to the first procedure described for **14b**. Reaction of **14c** (4.14 g, 14.5 mmol) with lithium sand (2.14 g of Li and 0.05 g of Na) in 275 mL of THF was carried out at -75 °C for 0.8 h before deactivation of the excess lithium with mercury (8.0 mL) and then carbonation of 75% of the solution (aliquot A) with the remainder stored at 7±4 °C for 1 h before carbonation (aliquot B). The crude acids of aliquot A (2.8 g) and B (1.1 g) were analyzed after esterification along with the neutral fractions by quantitative GC on a 10% SE-30 column at 180 °C or 170 °C (for neutral fractions). Aliquot A contained 0.015 g (0.5%) of methyl 9-neopentylfluorene-9-carboxylate, 2.04 g (60.6%) of **23**, 0.21 g (7.7%) of **24**, and 0.038 g (1.4%) of **26**. Aliquot B contained 0.015 g (1.4%) of methyl 9-neopentylfluorene-9-carboxylate, 0.45 g (40%) of **23**, 0.38 g (35%) of **25**, 0.17 g (19%) of **24**, and 0.43 g (4.8%) of **26**.

In run 2, **14c** (3.08 g, 10.8 mmol) was allowed to react with excess lithium sand (2.08 g of Li, 0.06 g of Na) in 245 mL of THF at -75 °C over a period of 1 h at which time the solution was green (presence of radical anion) and withdrawal of an aliquot (6 mL, which was protonated) and analysis (by ^{1}H NMR) showed completion of reaction (absence of NMR peak for CH$_2$Cl). The excess of lithium was deactivated by addition of 8.0 mL of finely divided mercury and stirring while the solution was allowed to warm (color changed from green to red at -20 °C due to loss of radical anion) and was held at 2 ± 2 °C for 1 h before carbonation. The usual analysis gave 0.037 g (1.2%) of methyl 9-neopentylfluorene-9-carboxylate, 1.14 g (34%) of **23**, 0.27 g (8.1%) of **25**, and 0.79 g (29%) of **24**.

In run 3, which was conducted as in run 2 from 3.72 g (13.07 mmol) of **14c** and 2.69 g of lithium sand (containing 0.12 g of Na) in 290 mL of THF at -75 °C and then at 5 ± 2 °C for 1 h before carbonation. Analysis gave 0.009 g (0.2%) of methyl 9-neopentylfluorene-9-carboxylate, 0.48 g (11.9%) of **23**, 0.69 g (17%) of **25**, 1.30 g (40%) of **24**, and 0.15 g (4.6%) of **26**.

Run 4 was conducted with 1.41 g (4.96 mmol) of **14c** and 0.904 g of Li sand (130 mmol containing 0.03 g of Na) in 300 mL of diethyl ether. Reaction was first attempted at 4 °C; however, even though the lithium sand had been activated in the usual manner (for THF solutions) with 1,2-dibromoethane (0.5 mL), analysis by ^{1}H NMR of a small aliquot showed that 95% of the halide was unreacted. The solution was thereupon warmed to 15 ± 2 °C and stirred for 2 h before carbonation of half of the solution (aliquot A). The remaining solution was then stirred at reflux temperature (35 °C) for 3 h before carbonation (aliquot B). The usual analysis gave for aliquot A 0.0025 g (0.33%) of methyl 9-neopentylfluorene-9-carboxylate, 0.040 g (5.2%) of **23**, 0.0045 g (0.59%) of **25**, 0.045 g (7.2%) of **24**, 0.056 g (9.0%) of **26**, and 0.28 g (40%) of unreacted **14c**; for aliquot B 0.0018 g (0.25%) of methyl 9-neopentylfluorene-9-carboxylate, 0.0099 g (1.3%) of **23**, 0.0035 g (0.46%) of **25**, 0.086 g (14%) of **24**, 0.212 g (34%) of **26**, and 0.055 g (7.9%) of **14c**.

(9-Neopentyl-9-fluorenyl)ethanoic Acid. A 0.53 g portion of the crude acid from aliquot A of the first reaction of **14c** with lithium (see above) at -75 °C was purified by chromatography over silica gel (32-63 μm) with elution with hexane-diethyl ether. The major fraction (0.26 g) after two sublimations *in vacuo* at 140 °C amounted to 0.12 g of white crystals of (9-neopentyl-9-fluorenyl)ethanoic acid: mp 141-142 °C; ^{1}H NMR (CDCl$_3$) δ 0.31 (9 H, s), 2.28 (2 H, s), 2.71 (2 H, s), 7.0-7.8 (8 H, m), 9.0 (1 H, s); methyl ester (**23**), MS *m/e* (relative intensity) 308 (39, M$^+$), 238 (35), 237 (49), 235 (7.6), 195 (58), 191 (15), 178 (100), 177 (8), 176 (10), 165 (11). Anal. Calcd for C$_{20}$H$_{22}$O$_2$: C, 81.60; H, 7.53. Found: C, 81.54; H, 7.55.

B. With Cs-K-Na Alloy. These reactions were run like the corresponding reactions of **14b** except where indicated below. To 3.49 g of finely divided eutectic Cs-K-Na alloy (0.0189 g atom of Cs) vigorously stirred in 225 mL of THF at -75 °C was rapidly added 2.09 g (7.35 mmol) of **14c** dissolved in 20 mL of THF and the solution stirred for 3 min. To the dark blue-green solution was next added 3.5 mL of finely divided mercury with stirring continued for 20 min at -75 °C before warming to -25 °C and stirring for 1 h. The light green solution was then carbonated. The usual analysis gave 1.5 mg (0.07%) of methyl 9-neopentylfluorene-9 carboxylate, 3.5 mg (0.15%) of **23**, 30 mg (1.3%) of **25**, 0.695 g (38%) of **24**, and 0.58 g (32%) of **26**.

In a second run 4.49 g (15.8 mmol) of **14c** dissolved in 32 mL of THF was added over a 15 min period to 2.59 g of finely divided eutectic Cs-K-Na alloy (13.9 mg atoms of Cs) vigorously stirred in 225 mL of THF at -75 °C before carbonation of the pale green solution. The usual analysis gave 10.5 mg (0.22%) of **23**, 0.23 g (4.6%) of **25**, 1.78 g (45%) of **24**, and 1.57 g (40%) of **26**.

In a final run 1.039 g (3.65 mmol) of **14c** dissolved in 20 mL of THF was added very slowly over a period of 2.3 h to 3.88 g of finely divided eutectic Cs-K-Na alloy (21 mg atom of Cs) in 225 mL of THF at -75 °C. Next 6.0 mL of finely divided mercury was added and the solution warmed to -30 °C and stirred for 30 min before carbonation. The usual analysis gave 2.3 mg (0.20%) of **23**, 0.093 g (8.3%) of **25**, 0.51 g (55%) of **24**, and 0.122 g (13.5%) of **26**.

9-Neopentyl-9,10-dihydrophenanthrene-9-carboxylic Acid. The crude acids (0.52 g) from carbonation of the second run (above) of the reactions of **14c** with Cs-K-Na alloy was chromatographed over 89 g of Silica Gel-60 (30-70 mesh) in a column whose packed section was 33 cm in height with elution by 80:20 (by vol.) of hexane:diethyl ether. The yield was 0.191 g of carboxylic acid which after two sublimations *in vacuo* at a bath temp of 130-140 °C had mp 154-155 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (9 H, s), 1.65 (1 H, d, J = 14.7 Hz), 2.14 (1 H, d, J = 14.7 Hz), 3.12 (1 H, d, J = 15.5 Hz), 3.56 (1 H, d, J = 15.5 Hz), 7.2-7.8 (8 H, m); ^{13}C NMR ($CDCl_3$) δ 31.0 (q), 31.9 (s), 37.7 (t), 47.6 (t), 50.3 (s), 123.4 (d), 124.5 (d), 126.4 (d), 127.0 (d), 127.68 (d), 127.73 (d, 2 CH), 129.1 (d), 133.2 (s), 133.4 (s), 134.4 (s), 138.2 (s), 181.6 (s); MS of methyl ester **25** *m/e* (relative intensity) 308 (19, M^+), 249 (17), 237 (13), 205 (17), 193 (54), 192 (18), 191 (18), 179 (28), 178 (50), 177 (12) ... 71 (100).

9-Methyl-9-neopentylfluorene (24). The neutral material of the final run from the reaction of **14c** with Cs-K-Na alloy, after correction for the minor amount of **26** present had ^{1}H NMR absorption ($CDCl_3$) at δ 0.32 (9 H, s), 2.16 (3 H, s), 6.9-7.8 (8 H, m); GC MS *m/e* (relative intensity) 250 (20, M^+), 194 (2.4), 193 (3.0), 192 (2.0), 191 (1.9), 179 (100), 178 (48).

9-(1-Norbornyl)-9-fluorenol (11d). The necessary 1-chloronorbornane (or 1-chlorobicyclo[2.2.1]heptane) was prepared from norcamphor by a published procedure[47]. Reaction of 1-chloronorbornane (7.23 g, 0.0554 mol) with lithium sand (3.24 g, 0.46 mol, of Li plus 0.036 g of Na) in 200 mL of pentane at reflux gave, after 1 h, a 74% yield of 1-norbornylithium according to titration[45]. This organolithium reagent was transferred via cannula to 6.50 g (36.0 mmol) of 9-fluorenone dissolved in 250 mL of anhydrous toluene at 0 °C with magnetic stirring continued for 30 min before warming to rt and protonation with ice water. Analysis by GC of the crude product (10.6 g) showed that it contained some 70 area % of the desired fluorenol. This product was combined with 5.6 g of crude product from a similar run and chromatographed over 385 g of silica gel with elution by hexane and then hexane containing 2.5% diethyl ether to give 6.7 g of essentially pure fluorenol. The analytical sample after two recrystallizations from hexane consisted of white crystals of **11d**, mp 146.5-147.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.9-2.1 (11 H, m), 2.28 (1 H, s, OH), 6.8-7.8 (8 H, m); ^{13}C NMR (DCl_3) δ 30.16 and 30.32 (4 C, two overlapping t), 36.6 (d), 39.0 (t), 54.4 (s), 84.7 (s), 119.5 (d), 124.9 (d), 126.9 (d), 128.3 (d), 139.8 (s), 149.1 (s); MS *m/e* (relative intensity) 276 (35, M^+), 247 (9), 229 (2.0), 215 (1.4), 207 (4), 191 (2), 181 (100), 180 (20). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.77; H, 7.32.

9-Methoxy-9-(1-norbornyl)fluorene (12d). To 7.45 g (27.0 mmol) of **11d** in 100 mL of THF cooled to -75 °C was added 35 mmol of *n*-butyllithium (1.4 *N* in hexane). The solution was allowed to warm to 0 °C and then excess of iodomethane (18 mL or 0.29 mol) was added and the solution stirred at rt for four days with a magnetic stirrer. The usual work up gave product which after recrystallization amounted to 6.73 g (89% yield) of **12d** of mp 106-107 °C; ^{1}H NMR ($CDCl_3$) δ 0.66-1.38 (11 H, m), 2.80 (3 H, s), 7.0-7.8 (8 H, m).

9-(chloromethyl)-9-(1-norbornyl)fluorene (14d). A solution of 6.58 g (22.7 mmol) of **12d** in 60 mL of diethyl ether was allowed to react with 3.7 g of finely divided eutectic Na-K alloy (2.9 g of K, 74 mmol) vigorously stirred in 250 mL of diethyl ether according to the general procedure (see **14a**). After amalgamation of the excess of alloy with 4 mL of mercury, the orange-brown solution (at -20 °C) was transferred by canula to 60 mL of chlorobromomethane (0.92 mole) in 100 mL of diethyl ether at -40 °C. The reaction flask was rinsed with 20 mL more of $ClBrCH_2$ in 200 mL of ether and the rinse combined with the major reaction mixture whose color disappeared at about 5 °C upon warm-up with magnetic stirring. The usual work-up the next day gave 6.4 g of crude product whose ^{1}H NMR analysis revealed that the product contained 40 mole % of the desired chloride (**14d**), 43% of 9-(1-norbornyl)fluorene, and (by GC analysis) a little **11d**. Fractional crystallization from hexane gave 2.8 g of nearly pure 9-(1-norbornyl)fluorene (mp 127-128 °C after recrystallization from methanol). Removal of solvent from the mother liquor and crystallization from methanol gave 1.25 g of the desired **14d** of mp 115-116 °C; ^{1}H NMR ($CDCl_3$) δ 0.65-2.35 (11 H, m), 4.33 (2 H, s), 7.0-8.0 (8 H, m); ^{13}C NMR ($CDCl_3$) 30.1 (2 C, t), 31.3 (2 C, t), 36.3 (1 C, d), 40.0 (1 C, t), 47.9 (1 C, t), 53.2 (1 C, s), 58.7 (1 C, d), 119.6 (2 C, d), 124.5 (2 C, d), 126.5 (2 C, d), 127.5 (2 C, d), 141.5 (2 C, s), 147.3 (2 C, s); MS *m/e* (relative intensity) 310 (M^+, ^{37}Cl, 13.6), 308 (M^+, ^{35}Cl, 40.9), 281 (4.5), 279 (15), 273 (8.2), 272 (21), 259 (64), 243 (28), 231 (7), 230 (6), 229 (10), 228 (10), 217 (25), 216 (15), 215 (27), 203 (13), 202 (18), 191 (36), 189 (5), 178 (100). Anal. Calcd for $C_{21}H_{21}Cl$: C, 81.67; H, 6.85; Cl, 11.48. Found: C, 81.50; H, 6.89; Cl, 11.56.

Reaction of 14d with Lithium at -73 °C and then 0 °C. This reaction was performed, unless otherwise specified, according to the first procedure described for **14b**. Compound **14d** (0.898 g, 2.91 mmol) was allowed to react with excess lithium sand (1.62 g of Li, 0.026 g of Na) in 270 mL of THF at -73 °C over a period of 0.7 h to give a green solution. The excess lithium was deactivated by addition of 6 mL of finely divided mercury and stirred for 15 min before carbonation of 120 mL of the solution (aliquot A). The remaining solution was warmed to -10 °C and stirred vigorously for 10 min to complete the amalgamation of the excess lithium. The now red solution was warmed to -4 to 0 °C and kept at this temperature range for 2 h before carbonation of the remainder of the reaction mixture (aliquot B). After the usual work-up including esterification of the acidic products with diazomethane, the products were analyzed semi-quantitatively by GC with use of 1,1,1-triphenylethane as internal standard (I.S.) and the arbitrary assumption (in absence of pure reference compounds) of calibration factors of all products being unity. The column for GC analysis was 10% SE-30 on Chromosorb packing and operated at 220 °C. Aliquot A gave products listed as approximate mol percentages yield (retention time relative to internal standard, identity): _ (1.00, 1,1,1-triphenylethane), 28 (1.7, **26**), 13 (2.9, **29**), 35 (3.4, **30**). Similarly aliquot B gave: <1 (0.46, **18**?), 44 (1.7, **28**), 10 (2.9, **29**), 11 (3.4, **30**). The GC MS of the neutral materials gave for **28** (essentially the sole volatile component) *m/e* (relative intensity) 274 (100, M^+), 259 (13), 245 (73), 231 (5), 230 (5), 229 (3), 217

(13), 216 (4), 215 (7), 205 (8), 203 (6), 202 (5), 191 (7), 189 (3), 179 (67), 178 (41). The GC MS of the methyl esters of the acidic materials, listed similarly, were for **29**: 318 (100, M^+), 289 (39), 259 (67), 258 (5), 231 (7), 230 (6), 229 (11), 224 (3), 217 (25), 215 (11), 203 (6), 202 (11), 195 (6), 191 (45), 180 (6), 179 (3), 165 (25); for **30**: 332 (100), 303 (47), 272 (24), 259 (26), 258 (10), 243 (12), 237 (6), 231 (3), 230 (12), 229 (34), 228 (4), 217 (11), 216 (7), 215 (9), 203 (6), 202 (8), 195 (25), 191 (18), 178 (39), 177 (4), 165 (9). The MS were identical for the products from aliquots A and B.

X-Ray Crystallographic Data. The compounds **14b**, **14c**, compound A or *cis*-3-*tert*-butyl-9a-methyl-3,9a-dihydro-9-fluorenone, and compound B or 2-(5-*tert*-butyl-4-hydroxy-2-methylphenyl)benzoic acid were subjected to x-ray crystallographic analysis. A description of data collection and tables of atomic coordinates, bond distances and angles have been deposited with the Editor of the Cambridge Crystallographic Data Centre.

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