POTASSIUM DERIVATIVES OF FLUORENE AS INTERMEDIATES IN THE PREPARATION OF C₉-SUBSTITUTED FLUORENES

I. THE PREPARATION OF 9-FLUORENYL POTASSIUM AND THE INFRARED SPECTRA OF FLUORENE AND SOME C_9 -SUBSTITUTED FLUORENES¹

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ABSTRACT

9-Fluorenylpotassium and 9,9-fluorenyldipotassium have been prepared from the reaction of potassium metal with fluorene in dioxane. These organometallic compounds upon reaction with alkyl and aralkyl halides gave 9-substituted fluorenes.

Six different absorption bands in the spectrum of fluorene could be associated with the methylene group: 2930, 1400, 1298, 952, and 692 cm⁻¹. Evidence for this assignment was obtained from deuteration of the organometallic compounds of fluorene and from 9-substituted fluorenes.

INTRODUCTION

During a study of the reactions of certain substances with fluorene it was found desirable to have at hand direct and relatively simple methods for the preparation of C_9 -mono- and C_9 -di-substituted fluorenes uncomplicated by contaminating side reactions due to addition of bases (1) usually required to effect reaction at the methylene group. In addition, quite indispensable would be a reliable and rapid method for distinguishing between mono- and di-substituted fluorenes and permit the investigator to follow more conveniently the separation of such mixtures. It was thought that monovalent metal "salts" of fluorene might lend themselves readily to the attainment of the first goal, while infrared spectroscopy should be most admirably suited to the second. Both the literature evaluation and the experiments described in this report show that this is indeed the case.

9-SUBSTITUTED FLUORENES FROM 9-FLUORENYLSODIUM AND 9,9-FLUORENYLDIPOTASSIUM

Synthesis of C_9 -substituted fluorenes has been reviewed by Rieveschl and Ray (2). Generally, alkaline conditions promote the transient formation of the 9-fluorenyl carbanion which then by nucleophilic attack upon compounds of suitable structure produces the desired structure (2, 3). Equimolar proportions of fluorene, base, and substrate are expected to form 9-monosubstituted fluorenes, but there are reports which show that di- rather than mono-substitution has in fact occurred (4).

The formation of 9-fluorenylsodium by direct reactions between fluorene and metallic sodium, although reported in the patent literature, has been found highly unsatisfactory both in this laboratory and by other workers (3). However, Greenhow *et al.* describe the preparation of 9-fluorenylsodium in good yield by the reaction of sodamide with fluorene in boiling decalin (3). Through this organometallic compound the C₉-monosubstituted fluorenes are accessible (3, 5–8). Indirect preparation of 9-fluorenylsodium via interchange with triphenylmethyl sodium (9) and, more conveniently, of 9-fluorenyllithium from alkyllithium compounds (10, 11) provide other routes, though somewhat more complicated, to the preparation of 9-substituted fluorenes. The Grignard reagent, 9-fluorenyl-

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magnesium bromide, is reported to lead to monosubstitution at C_9 , but reactions leading to dimeric products occur in some of the cases studied (10).

We have repeated the preparation of 9-fluorenylsodium according to Greenhow (3) and although the reported high yields and fine quality of the organometallic compound could not be duplicated, the salt was obtained in reasonable yield and in a state suitable for the synthesis of the 9-monosubstituted fluorenes as described by Greenhow and co-workers (3, 5). The 9-methyl-, 9-allyl-, and 9-benzyl-fluorenes required for this work were made by this method.

The 9,9-disubstituted fluorenes were readily obtained from 9,9-fluorenyldipotassium. Little work appears in the literature concerning the potassium salt of fluorene. Weissgerber (12) reported the preparation of 9-fluorenylpotassium by fusion of solid potassium hydroxide with fluorene at 280° from which was isolated a substance whose analysis indicated the composition $C_{13}H_9K$. This substance he then treated with benzyl chloride to form the 9-benzylfluorene. However, as Thiele and Henle have shown (13), the compound actually obtained was 9,9-dibenzylfluorene. A repetition of Weissgerber's experiment led to the conclusion that this method for the preparation of fluorenylpotassium also was quite unsatisfactory for our purpose.

It was found in this laboratory that potassium metal reacts readily with fluorene in boiling dioxane, protected by an atmosphere of nitrogen, to produce at will either the mono- or di-potassium salt as a reddish-brown precipitate. Hydrogen gas is evolved. This precipitate can be freed of unreacted fluorene by filtration and washing with dry hexane. The monopotassium derivative, obtained by the reaction of equimolar proportions of potassium and fluorene, can be isolated under nitrogen as a solid* quite suitable for further reaction. Usually it is more convenient to leave the solid suspended either in the original dioxane, or in the hexane wash liquid where it can be kept for some time with little decomposition. Exposure to air causes rapid decomposition to a dark mass which is essentially potassium hydroxide, 9-fluorenone, 9-fluorenol, and fluorene, the relative amounts of these depending upon the accessibility to oxygen or water of the air. Attempts to analyze the isolated monopotassium salt gave low values for potassium presumably due to absorption of water and/or oxygen from the air during weighing manipulations. Three analyses gave an average value of 15.3% of potassium. The theoretical value is 19.15%. It was felt that the highly elaborate procedure obviously necessary for a satisfactory potassium analysis was superfluous to our work at this time hence further attempts in this direction were abandoned.

The dipotassium compound, precipitated from the reaction of one equivalent of fluorene with two of potassium, could not be isolated readily as above, and therefore was used in dioxane suspension immediately following its preparation. That we were actually dealing with the dipotassium compound was supported by (a) the fact that *two* equivalents of potassium metal were totally consumed by *one* equivalent of fluorene whereas potassium metal itself showed no visible reaction when heated alone with dioxane over a period of 8 hours, (b) the infrared spectrum of dideuterated fluorene (described later) obtained from the dipotassium compound, and (c) the nuclear magnetic resonance analyses for deuterium[†] which showed the absence of any peak corresponding to the methylene group of fluorene. On the other hand, the monopotassium compound, when deuterated, showed strong evidence from the infrared spectra that essentially 9-mono-deuterofluorene had been obtained, contaminated with a small amount of unreacted

*The presence of particles of unreacted potassium accelerates the decomposition of the organometallic compound hence it is advisable to carry the reaction to completion with respect to the metal. †The deuterium analyses were made by Dr. W. Schneider of the National Research Council of Canada in

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fluorene and some 9,9-dideuterofluorene. This is supported by the nuclear magnetic resonance spectra which indicate approximately 75% monodeuteration. Rather than postulate that the "9-fluorenylpotassium" contained fluorene and 9,9-fluorenyldipotassium (a condition highly unlikely due to the great reactivity of the dipotassium compound) the results can be better explained by assuming that in the presence of KOD and excess D₂O, during the preparation and isolation procedure, a hydrogen-deuterium exchange has occurred, thus producing some C₉-dideuterated fluorene.

The addition of slightly more than two equivalents of alkyl or aralkyl halide to the suspension of the dipotassium compound in dioxane produced 9,9-disubstituted fluorenes in yields of about 65%. No further attempts were made at this time to improve yields since the reactions of the metallated fluorenes will be elaborated in a subsequent publication. In this way 9,9-dimethyl-, 9,9-dibenzyl-, and 9,9-diallyl-fluorene were prepared.

Reaction of the mono- and di-potassium compounds, in dioxane, with excess deuterium oxide gave 9-monodeutero- and 9,9-dideutero-fluorene respectively.

THE INFRARED SPECTRA OF FLUORENE AND SOME OF ITS C9-MONO- AND C9-DI-SUBSTITUTED DERIVATIVES

The information concerning the infrared studies of fluorene and its 9-substituted derivatives is meager. Fox and Martin (14) in a study of the absorption in the 3000 cm⁻¹ region, due to the methylene group in a number of organic compounds, attributes two frequencies, 2901 cm⁻¹ and 2795 cm⁻¹, to the $= CH_2$ of fluorene. In the present work the spectra of fluorene determined in carbon tetrachloride did not reveal absorption at these two frequencies which could be associated with the methylene group in fluorene. Richards and Thomson (15), investigating the spectral changes occurring in liquid-solid state transitions give two frequencies, 1303 cm⁻¹ and 1482 cm⁻¹, apparently characteristic of fluorene. Both of these frequencies are found in this work, that in the 1300 cm⁻¹ region is definitely associated with the CH_2 group while the 1482 cm⁻¹ band appears to be due to some other part of the fluorene structure.

In this paper are reported the infrared spectra of the following compounds: fluorene, 9-mono- and di-deutero-, mono- and di-methyl-, mono- and di-benzyl-, mono- and di-allylfluorene as well as 9-benzylidenefluorene. They were found in both carbon disulphide and carbon tetrachloride solution to provide the whole range of absorption from 4000 cm^{-1} to 600 cm^{-1} except for a small region about 1450 cm⁻¹ to 1600 cm⁻¹ where both solvents show some absorption themselves (16). The instrument available was a Perkin-Elmer double-beam infrared spectrophotometer, equipped with a sodium chloride prism. Six frequencies of medium intensity were found definitely due to the methylene group of fluorene. These are at 2930, 1400, 1298, 1190, 952, and 692 cm⁻¹ (Fig. 1). Whether these are all fundamental frequencies or not is not known. There are, no doubt, other frequencies due to the methylene group arising from overtones and combinations, but these were felt to be unnecessary for our work and hence not examined. Two such frequencies of low intensity might be 867 and 853 cm^{-1} (Fig. 1). All six frequencies can be clearly discerned and are of approximately the same intensity in both solvents employed. Since additional frequencies associated with substituting groups appear in the 1400 to 600 cm^{-1} region this area was examined carefully and thus only the spectra for this region, found in carbon disulphide, are reported and shown in Figs. 1 to 13. Each of the six frequencies mentioned is markedly affected by substitution or deuteration at C₉. In all cases, monosubstitution by an alkyl or aralkyl group greatly reduces or eliminates the absorption at these frequencies while disubstitution removes it completely. The removal of some is masked by neighboring frequencies or new frequencies due to the substituting groups but can still

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be readily observed. Mono- and di-deuteration reduces or removes these frequencies similarly but new bands appear for the C—D functions at a lower frequency as expected (Figs. 2 and 3). The relative positions of these new C—D frequencies were estimated beforehand from Fig. 1 by using the suggested factor of 0.73 (16) and thus the new frequencies could be related at least tentatively, if not exactly, to the former C—H frequencies. The experimentally found ratio of the new C—D frequency to the original C—H frequency is approximately 0.7, in agreement with the shift expected by a simple application of Hooke's Law (16). The frequencies for the original C—H group, the new C—D group, the remaining C—H group on monodeuteration, and the ratio of the first two, both calculated and found, are shown in Table I.

TABLE I				
requencies associated with the methylene grou	ıp in	fluorene	and	in
monodeuterofluorene (cm ⁻¹)			

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Observed for CH ₂	Calculated ^a for HC—D	Observed for HC—D	$\frac{\text{Observed}}{\nu C - H}$	Observed for remaining DC—H
$\begin{array}{c} 692\\ 952\\ 1190\\ 1298\\ 1400\\ 2930 \end{array}$	50569486994710222050	$ \begin{array}{r} $	$\begin{array}{c} 0.70 \\ 0.70 \\ 0.72 \\ 0.70 \\ 0.73 \end{array}$	677 939 —_d d d

^aThe product of the observed frequency in column 1, and the factor 0.73 obtained from reference 16.

^bBeyond the range of the instrument.

"This is a very weak absorption and is not certain.

 d Overlapping and multiplicity of neighboring absorption makes any assignment highly questionable.

The 692 cm^{-1} Band

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This band, probably due to methylene rocking vibrations (16), is quite distinct. Monodeuteration (via the monopotassium compound) reduces it markedly (Fig. 2). The residual absorption noticeable at this frequency is most likely due to unreacted fluorene, a contaminant undoubtedly present since the deuterium oxide available at the time of these experiments contained 95% of D₂O. A three- to five-fold excess of deuterium oxide was used to ensure as complete a reaction as possible with the precipitated potassium compound. Purification by separation of deuterated from undeuterated fluorene obviously is extremely difficult. Dideuteration via the dipotassium compound completely eliminates the 692 cm⁻¹ band (Fig. 3). The spectrum of the monodeuterated fluorene shows a new

band at 677 cm⁻¹ which is thought to be associated with the remaining DC-H, shifted

from the original frequency of 692 cm^{-1} by the presence of the deuterium atom. This point of view is supported by the fact that dideuteration reduces this 677 cm⁻¹ band to a very small value, this residual absorption arising, no doubt, from contaminating mono-

deuterated fluorene. The frequency corresponding to the new HCD--group, calculated to

be in the region of 505 cm^{-1} , is beyond the range studied.

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Figs. 1-4.

Monomethylation reduces the band at 692 cm^{-1} to one of weak absorption at the same frequency (Fig. 4). This was found to be due to contamination by unreacted fluorene since repeated purification by chromatography on activated alumina eliminated the

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absorption at 692 cm⁻¹ (Fig. 5). The melting point of the "contaminated" monomethyl-fluorene is $43-44^{\circ}$ C whereas that of the "pure" monomethylfluorene is $45-46^{\circ}$ C. Thus, a routine melting point determination of this compound should be carefully done to



FIGS. 5-8.

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differentiate between 100% purity and slight contamination, sufficient to be visible clearly in the infrared spectrum.

The melting point found for 9-methylfluorene is the same as that reported by Greenhow (3). However, other workers give a melting point of 58° (17). This may be another example of two polymorphic forms, a situation already demonstrated in the case of 9,9-dimethylfluorene (18).

The disappearance of the 692 cm⁻¹ band on monobenzylation and dibenzylation (Figs. 8 and 9) is masked by the strong absorption at 697 cm⁻¹ due to out-of-plane C—H vibrations of monosubstituted benzene (16). Mono- and di-allylation (Figs. 11 and 12) show more clearly the disappearance of the 692 cm⁻¹ band.

The expected complete elimination of the 692 cm⁻¹ absorption in the 9-benzylidene-fluorene (Fig. 13) is obscured by the strong absorption at 697 cm⁻¹ due to monosubstituted benzene.

The 952 cm^{-1} Band

This band whose origin is unknown to us is also quite distinct (Fig. 1). It is nearly eliminated by monodeuteration, the residual absorption most likely being due to contaminating fluorene (Fig. 2). Dideuteration causes complete disappearance of absorption

at this frequency. The corresponding HC-D band, calculated to occur in the region of

 694 cm^{-1} appears at 667 cm^{-1} and its intensity increases markedly upon dideuteration.

The considerably greater intensity of the HC—D band at 667 cm⁻¹ as compared to that

of the DC - H band at 677 cm⁻¹ indicates that in deuteration of the monopotassium

compound with excess D_2O , some dideuteration had occurred probably by hydrogen-deuterium exchange.

The band due to the remaining DC—H, if analogous to that of 677 cm⁻¹ found for the 692 cm⁻¹ band, should occur in the region of 935 cm⁻¹. One actually does appear at 939 cm⁻¹ and may contain the DC—H absorption. However, the magnitude of its intensity as well as the fact that dideuteration makes no significant change in its size favors the view that the 939 cm⁻¹ band is due in part to the methylene absorption originally at 1298 cm⁻¹, shifted due to formation of the —C—D bond, and in part to absorption from

the remaining -C-H bond affected by the deuterium atom.

The monomethyl-, monobenzyl- and monoallyl-fluorene (Figs. 4, 5, 8, 11) all show very strong reduction of intensity or complete elimination of absorption at 952 cm^{-1} , any residual absorption again being due to contamination by unreacted fluorene.

As expected, 9-benzylidenefluorene shows no absorption in the 950-956 cm⁻¹ region

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FIGS. 9-12.

(Fig. 13). A similar result occurs for the other 9,9-disubstituted fluorenes (Figs. 7, 9, 12). The position of the absorption for the remaining C_9 —H bond in the monosubstituted fluorenes is determined by deuteration. Comparison of Figs. 5 and 6 show that two bands,





FIGS. 13–15.

792 cm⁻¹ and 722 cm⁻¹, are eliminated on deuteration, hence it is clear that these are due to C₉—H in 9-monomethylfluorene. Whether one of these corresponds to the absorption of the methylene group at 952 cm⁻¹ is not known. Similarly, the bands at 787 cm⁻¹ (weak) and 719 cm⁻¹ (strong) in the spectrum of 9-monobenzylfluorene (Figs. 8 and 10) and those at 789 cm⁻¹ (weak) and 727 cm⁻¹ (strong) in the 9-monoallylfluorene (Fig. 11) are likewise to be associated with the remaining C₉—H bond, since deuteration or disubstitution eliminates the absorption.

In addition it might be pointed out that the bands at 1100, 1167, and 1185 cm⁻¹ are eliminated upon deuteration of the 9-monomethylfluorene (Figs. 5 and 6) hence can be considered as associated with the remaining C_9 —H bond.

The 1190 cm^{-1} Band

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The cause of absorption at this frequency is not known. It was at first believed to be composed of absorption due to the methylene group *and* to some other structural feature

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since monodeuteration reduces it to about one-half its former intensity while dideuteration produces little further change (Figs. 1–3). However, monosubstitution reduces the band markedly while disubstitution practically removes it, hence the absorption seen at 1190 cm⁻¹ in the dideuterated molecule may be due to shifts, or combinations of overtones, stemming from deuteration at C₉.

The frequency of the -C-D bond is thought to appear at 827 cm⁻¹ in agreement with

the calculated value.

The position of absorption of the remaining $-\overset{c}{-}H$ bond as affected by the presence

of the deuterium atom could not be defined in view of the complexity of the neighboring bands.

The 1298 cm⁻¹ Band

This absorption is probably due to methylene wagging vibration (16) and, in agreement with previous observations, is of lower intensity than that from rocking vibration. The band is reduced on monodeuteration or monosubstitution at C_9 while dideuteration or disubstitution largely eliminates it. Neighboring absorption bands mask these effects somewhat with the result that this frequency is less useful than are the others mentioned above.

The -C - D bond frequency appears at 939 cm⁻¹ in the monodeuterated molecule.

Since its intensity is practically unchanged upon dideuteration, the view is supported that it is a composite band in the monodeuterated structure, with a contribution from the

remaining $-\dot{C}$ -H band shifted slightly from 952 cm⁻¹. Dideuteration removes this

contribution but adds that from the second C—D bond in dideuterated fluorene (1298 cm^{-1} shifted to 939 cm^{-1}).

The 1400 cm^{-1} Band

This absorption is quite likely derived from scissoring vibration of the methylene group (16) since any type of mono- or di-substitution at C₉ eliminates this band. The absorption attributed to the new -C-D bond obtained on monodeuteration might be that appearing at 974 cm⁻¹ and increasing on dideuteration. This agrees quite well with the calculated value (Table I). The band at 1038 cm⁻¹ appearing on monodeuteration and increasing in magnitude upon dideuteration agrees roughly with the calculated shift, but examination of the spectra of mono- and di-substituted compounds (Figs. 1–13) shows that any mono- or di-substitution at C₉ gives rise to a band, increasing upon disubstitution, at about the same frequency. Hence the absorption at 1038 cm⁻¹ certainly cannot be due

to the
$$-C - D$$
 bond.

The 2930 cm^{-1} Band

This absorption, arising from C—H stretching frequency, must be due to the methylene

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group since it disappears upon deuteration (Figs. 14 and 15).* No firm assignment could be made for the -C-D band, although weak absorption appears at 2150 cm⁻¹ in the deuterated molecule (Table I) in agreement with the calculated shift.

USEFUL BANDS ASSOCIATED WITH PARTICULAR SUBSTITUENTS AT C,

In all the spectra there is clearly discernible a characteristic strong band at 738 cm⁻¹ originating from the two ortho disubstituted benzene nuclei in fluorene (16). Monomethyl-, monoallyl-, and monobenzyl-fluorene and 9-benzylidenefluorene all show weak absorption between 787 and 793 cm⁻¹ and strong absorption in the region of 719 to 728 cm⁻¹ (overlapping to some extent with the major 738 cm⁻¹ band). Only for monomethylfluorene is this latter absorption of weaker intensity, though still quite readily discernible, and the former stronger than in all the other cases examined. Disubstitution at C₉ removed this absorption completely. We have attributed these two bands to the remaining C₉—H bond. The 719–728 cm⁻¹ band has been used to differentiate between the mono- and di-substitution and, in particular, to follow the preparation, purification, and identification of 9-monoallylfluorene and 9,9-diallyfluorene whose mixtures with each other and with fluorene itself are separated with difficulty.

Clear distinction of the methylated fluorenes from the allyl or benzyl fluorenes may be made by observation of the strong, isolated band at 758 cm⁻¹ in the spectrum of monomethylfluorene, which doubles in intensity upon dimethylation. The monomethyl compound shows another medium-weak, though impressive, band at 793 cm⁻¹ which is eliminated upon dimethylation or on deuteration of the remaining C₉—H. Allylfluorenes absorb at 913 cm⁻¹, the intensity of the diallyl being approximately double that found for the monoderivative. This absorption is no doubt that associated with the C—H out-of-plane bending found in olefinic structures (16). The band appearing at 681 cm⁻¹ for mono- and di-allylfluorene may also be of analytical value.

The strong absorption at 700 cm⁻¹ in 9-monobenzylfluorene (approximately doubled in the dibenzylfluorene) is due to the monosubstituted benzene moiety. Also of some assistance in identifying 9-benzylated fluorenes is the weak band at 905 to 909 cm⁻¹. This appears to be present in 9-benzylidenefluorene. Whether the same absorption is to be found in the allyl fluorenes cannot be shown since the strong 913 cm⁻¹ band interferes.

Of some assistance is the strong absorption at 761 to 764 cm⁻¹ for *diallyl*- and *dibenzyl*-fluorene, whereas for the *monoallyl*- and *monobenzyl*-fluorenes a similar strong absorption occurs at 754 cm⁻¹. Furthermore, a band at 746 to 748 cm⁻¹ appears for the mono- and di-benzylfluorene but not for mono- and di-allylfluorene.

The view that the dipotassium compound had been made from two equivalents of potassium and one of fluorene is supported by deuteration experiments. The 9-fluorenyl-potassium (also the 9-fluorenylsodium, prepared by Greenhow's method (3)), treated with excess deuterium oxide gave a spectrum (Fig. 2) in which the shifted frequency, due to C_8 —H, is thought to be at 677 cm⁻¹. If this assignment is correct, dideuteration should eliminate this band. Such elimination is actually observed in the spectrum of the dideuterated compound obtained from the experiment wherein two equivalents of potassium to one of fluorene were used. No change in extent of deuteration was found when a greater proportion of potassium metal was employed.

*The spectra for Figs. 14 and 15 were obtained in CCl₄ solution.

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EXPERIMENTAL

The fluorene used in this work was Eastman Kodak 98% practical grade.

Infrared spectra were obtained with the aid of a Perkin–Elmer model 21 double-beam spectrophotometer equipped with a sodium chloride prism. Solutions in carbon tetrachloride and carbon disulphide, containing 20 mg solute per ml of solvent were measured in sodium chloride cells of 0.5-mm thickness.

All melting points are uncorrected.

9-Fluorenylpotassium

Fluorene (8.3 g, 0.05 mole) and potassium metal (1.95 g, 0.05 mole) were heated in refluxing purified dioxane (19) protected by an atmosphere of purified dry nitrogen. In 3 hours all the potassium was consumed. The reaction mixture was cooled to room temperature and the reddish-brown precipitate isolated by filtration under suction and washed with dry hexane to remove unreacted fluorene. Isolation of the monopotassium compound was best carried out in a dry box containing an atmosphere of nitrogen. Samples for analysis were prepared by freeing the fluorenyl potassium from adhering solvent with a stream of nitrogen drawn through the solid product by suction. Analysis was carried out by first treating a weighed portion of the solid with water then titrating the basic solution with standard acid. In three attempts at analyses the "purified" precipitate showed values of 14.9, 15.3, and 15.7% for potassium. The value required for $C_{13}H_9K$ is 19.15%.

9-Deuterofluorene

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The 9-fluorenylpotassium was prepared from 1.66 g of fluorene and 0.39 g of potassium in 5 ml of pure dioxane refluxed for 3 hours until all the potassium had reacted. One milliliter of D_2O^* (95%) was slowly added and the mixture then stirred for 1 hour. Following the addition of ether, the dioxane and potassium hydroxide were readily removed by extracting the solution of deuterated fluorene with water. When the ethereal solution was dried and the solvent removed there was obtained, upon crystallization of the resulting solid from alcohol, 1.58 g of monodeuterated fluorene.

Analysis for deuterium by N.M.R. show approximately 75% monodeuteration.

9,9-Dideuterofluorene

A mixture of 0.01 mole (1.66 g) of fluorene and 0.02 mole (0.78 g) of potassium was heated for 3.5 hours in 5 ml of refluxing dioxane till all the potassium had been consumed. The addition of 1.5 ml of D_2O and isolation of the product as before gave 1.56 g of dideuterated fluorene.

N.M.R. analysis shows complete absence of absorption at the position attributable to

 CH_2 , indicating complete dideuteration.

9-Methylfluorene

This compound was prepared by the following modification of Greenhow's procedure (3). Fluorene (18 g) and finely powdered sodamide (3.9 g) were heated in a nitrogen atmosphere for 5 hours at 180° C in 50 ml of decahydronaphthalene (dried with sodium and distilled). When the reaction mixture had cooled to room temperature, the solvent was decanted and the remaining black amorphous solid which adhered to the lower portion of the flask was washed several times with hexane (dried with sodium). Methyl iodide (12 ml) in 50 ml of hexane was then added and the magnetically stirred mixture refluxed for 12 hours under nitrogen. After the cautious addition of water to dissolve the

*The D₂O was donated by the National Research Council of Canada.

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potassium iodide, the hexane layer was separated, dried, and the solvent removed. The yellow oil obtained, dissolved in pentane and cooled in a refrigerator, deposited unchanged fluorene. Further purification was accomplished by chromatography of the pentane mother liquor on a 50-cm column of dry, activated alumina (80–200 mesh). The first fraction, obtained by elution with hexane, gave 9-methylfluorene, m.p. 43–44° C. Further purification by repeated chromatography altered the infrared spectrum slightly and changed the melting point of the compound to $45-46^{\circ}$ C, lit. $45-47^{\circ}$ C (3). (Compare the melting point of 58° reported by Wieland (17).)

9,9-Dimethylfluorene

A solution of 16.6 g of fluorene in 80 ml of dioxane containing 7.8 g of potassium was boiled for 5 hours under an atmosphere of nitrogen. All the potassium was consumed in this time. The slow addition of 20 ml of methyl iodide, to the cooled mixture, produced a vigorous but controllable reaction. Stirring was continued for 1 hour whereupon both ether and water were added to the reaction flask. Several extractions of the ethereal solution with water removed the dioxane. The dried $(CaCl_2)$ solution was freed from ether and gave a yellow oil which could not be purified adequately by fractional distillation. However, chromatography with alumina of an hexane solution of this oil separated the unchanged fluorene and monomethyl compound from dimethylfluorene. The first fraction gave the 9,9-dimethylfluorene, m.p. 88–89° C, but when crystallized from methanol melted at 95–96° C, lit. 95–96° C (20). It is interesting that recrystallization from pentane of the 95–96° C c, which after a second crystallization from pentane gave $81-87^{\circ}$ C.

9-Benzylfluorene

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The 9-fluorenylsodium was prepared from 18.3 g of fluorene and 3.9 g of sodamide heated in decahydronaphthalene for 4 hours at 180° C under a nitrogen atmosphere (3). The black solid, deposited in the flask, was washed with hexane as in the preparation of 9-methylfluorene and treated with a solution of 40 ml of benzyl chloride in 40 ml of hexane. This mixture was refluxed for 20 hours. To the hexane solution, now diluted with ether, was added water to remove the sodium chloride. Removal of the ether hexane solvent gave a yellow amorphous product which after solution in alcohol deposited 12.5 g of crystalline 9-benzylfluorene melting sharply at 134° C, lit. 135° C (3). Further purification by chromatography on activated alumina raised the melting point to 136° C. Crystallization from alcohol did not change the melting point.

9,9-Dibenzylfluorene

(a) From fluorene.—To the dioxane containing 9,9-fluorenyldipotassium (made from 16.6 g of fluorene and 7.8 g of potassium in 80 ml of dioxane) was added 21 ml of benzyl chloride (an excess). The product of this reaction, only slightly soluble in ether, was isolated quite simply by the addition of water and ether to the dioxane solution where-upon the solid which formed could then be removed by filtration. The 9,9-dibenzylfluorene weighed 11.2 g and melted at 146° C (from alcohol), lit. 147–148° C (13).

(b) From 9-benzylfluorene.—A mixture of 2.6 g of 9-benzylfluorene and 0.39 g of potassium metal (equimolar portions) in 12 ml of dioxane was heated till solution of the metal was complete. Forty minutes of refluxing with 1.2 ml of benzyl chloride gave a solid, isolated as above, with properties and melting point identical with those of 9,9-dibenzylfluorene.

9-Deutero-9-benzylfluorene

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Dioxane (15 ml) containing 2.56 g of *9-benzylfluorene* and 0.39 g of potassium was boiled for 40 minutes, cooled to room temperature, and treated with 0.8 ml (excess) of D_2O . The red precipitate disappeared and the product, isolated as usual by employing ether and water, and crystallized from alcohol, melted at 131° C, yield 0.5 g. Chromatography raised the melting point to 134° C, which crystallization from alcohol did not change.

9-Deutero-9-methylfluorene

This compound was prepared in the same manner as for 9-deutero-9-benzylfluorene and isolated as was 9-methylfluorene, m.p. 45.5° C.

9-Benzylidenefluorene

The procedure was a modified version of that employed by Thiele and Henle (13). The use of potassium ethylate, rather than sodium ethylate, gave the product in 3 days as compared with 14 days reported for Thiele and Henle's method.

To a solution of 2.5 g of potassium in 125 ml of dry ethyl alcohol was added 5 g of fluorene. Freshly distilled benzaldehyde (4.5 g) in 10 ml of alcohol was added and the reaction mixture kept at 45° C for 3 days. The 9-benzylidenefluorene (3.6 g) deposited from the solution was crystallized once from alcohol, m.p. $74^{\circ}-75^{\circ}$ C, lit. 76° C (13).

9-Allylfluorene

This compound was prepared by a modification of Greenhow's method (3).

Sodamide (3.9 g) and fluorene (18 g) were heated in refluxing decalin (40 ml) for 4 hours (nitrogen atmosphere). The decalin was then replaced by pentane (50 ml) and the 9-fluorenylsodium treated with 50 ml of allyl bromide (excess). After 8 hours reflux the product was isolated by removing the sodium chloride with water, then eliminating the solvent as well as the excess allyl bromide. Vacuum distillation gave 11.5 g of a light-yellow liquid boiling at 132–137° C/3 mm. Elution chromatography as described for the methylated fluorenes gave a sample suitable for infrared analysis.

9,9-Diallylfluorene

Fluorene (8.3 g) and potassium metal (3.9 g) were boiled for 4 hours in 100 ml of dioxane (N₂). When the reaction mixture was cooled to room temperature and treated with 8.65 ml of allyl bromide, added dropwise, an exothermic reaction occurred with simultaneous disappearance of the reddish-brown precipitate. After an additional period of stirring for 5 hours the product was isolated as usual by the additon of ether and water. The crude oil (12.1 g) obtained from the ether layer was fractionally distilled under vacuum to yield 7.9 g of light-yellow oil, b.p. 144° C/3 mm, which was submitted to chromatography for additional purification.

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SCHERF AND BROWN: POTASSIUM DERIVATIVES OF FLUORENE. I

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