# ALIPHATIC CHEMISTRY OF FLUORENE

# PART I. DERIVATIVES OF 9-BENZOYLFLUORENE<sup>1</sup>

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#### ABSTRACT

Several C-alkylation products of 9-benzoylfluorene have been prepared. 9-Methyl-9-benzoylfluorene has been transformed into 9-methyl-10-phenylphenanthrene, 9-phenylphenanthrene-10-carboxylic acid, and 1,2:3,4-dibenzfluorenone.

Phenyl-9-allyl-9-fluorenylmethanol has been cyclized and rearranged in one step to 14methyl-13,14-dihydrodibenz[a,c]phenanthrene.

Phenyl-9-methyl-9-fluorenylmethyl chloride readily decomposes to 9-methyl-10-phenylphenanthrene when heated alone or in formic acid, but reacts with silver or mercuric acetates to give unrearranged acetate.

This series of papers will be concerned with reactions of fluorene anions (I), particularly where R is an electron-demanding group, and with systems potentially capable of forming cations (II), the products being utilized in the synthesis of complex polycyclic systems.

We have shown that methyl fluorene-9-carboxylate anion (I,  $R = CO_2CH_3$ ) reacts rapidly with a very wide range of alkyl halides (1, 2). Of particular interest was the formation in good yield of the 9-*t*-butyl derivative (1). Experiments with 9-benzoylfluorene anion (I,  $R = CO \cdot C_6H_5$ ) are now reported.



The keto form of 9-benzoylfluorene crystallizes from acetone as colorless needles which are insoluble in aqueous sodium hydroxide. The enol has been reported only as an oil which rapidly passes into the keto form. Solutions of either tautomer in alcoholic sodium alkoxide are deep orange, with the color attributed to the anion (I,  $R = CO \cdot C_6 H_5$ ) (3, 4), also referred to as the enolate ion.

Initial attempts to alkylate the anion  $(I, R = CO \cdot C_6H_5)$  with methyl or isopropyl iodides gave very low yields of the desired products, even when only 1 equivalent of methoxide ion was used to generate (I). The low yields were attributed to facile cleavage by strong base of the non-enolizable ketonic products, the cleavage being facilitated and its direction controlled by the formation of the mesomeric anion (I, R = alkyl), Fig. 1. These conclusions found support in the isolation of methyl benzoate and 9-methylfluorene among the products of attempted methylation.

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Weaker bases were next examined. Pyridine, piperidine, and triethylamine generated the anion (I) from 9-benzoylfluorene as shown by the color of methanolic solutions, but apparently formed quaternary salts too rapidly to permit C-alkylation. Suitable conditions were eventually found in the mixed solvent acetone-methanol containing a little water, with potassium carbonate as base. The 9-alkyl-9-benzoylfluorenes (III, R = alkyl) prepared in this way were methyl, ethyl, isopropyl, allyl, benzyl, and cyclohexyl, all in satisfactory yields. The reaction with *t*-butyl chloride followed a different course and will be discussed in a later paper.

The structures of the products were shown by their lack of color (the enol ethers would be yellow like other 9-fluorenylidene compounds, e.g. see (5)) and by the presence of carbonyl stretching absorption bands in their infrared spectra. In particular, the 9-methyl derivative formed an oxime in pyridine solution, was cleaved by strong base to 9-methylfluorene, and was reduced to an alcohol by lithium aluminum hydride.

Compounds of structure (IV) are potential phenanthrene intermediates through the cation (II). The transformations of 9-methyl-9-benzoylfluorene are summarized for clarity in Fig. 2. Reduction to the alcohol (IV, R = methyl; X = OH) followed by dehydration-rearrangement brought about by phosphorus pentoxide in boiling xylene gave 9-methyl-10-phenylphenanthrene, which was oxidized\* by aqueous sodium dichromate at 250° to a mixture of 9-phenylphenanthrene-10-carboxylic acid (5–10%) and 1,2:3,4-dibenzfluorenone (70–80%). The acid cyclizes particularly readily, even in cold thionyl chloride. Although 1,2:3,4-dibenzfluorenone becomes readily available by this route, insufficient of the acid was obtained to allow synthesis of the phenol (V, R = OH), a potential carcinogen.



The chloride (IV,  $R = CH_3$ ; X = Cl), prepared from the alcohol by the action of warm thionyl chloride, proved to be particularly interesting. It melted with slow decomposition in the range 90–100°, varying with the sample. The decomposition was rapid at 150° and gave 9-methyl-10-phenylphenanthrene in essentially quantitative yield. Related toluenesulphonates also melt with decomposition to phenanthrene derivatives

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(1), but attempts to prepare the toluene- or methane-sulphonate of (IV,  $R = CH_3$ ; X = OH) were not successful. The formate and acetate have been prepared. The chloride was recovered essentially unchanged after heating with methanol, acetic acid, pyridine, or quinoline and did not react with sodium iodide in acetone. Decomposition to 9-methyl-10-phenylphenanthrene in hot formic acid was complete in 2 hours. It reacted rapidly with silver or mercuric acetates in dry acetic acid to give the *unrearranged acetate* (IV,  $R = CH_3$ ;  $X = O \cdot CO \cdot CH_3$ ), the structure of which has been confirmed by esterification of the alcohol with acetic anhydride and by reduction of the acetate with lithium aluminum hydride back to the alcohol. Under similar conditions neopentyl chloride reacts with silver acetate to give the *rearranged t*-amyl acetate (7). The difference in behavior is tentatively attributed to stabilization of the cation (II) by the phenyl group. Experiments designed to test this postulate are under way.

When heated with phosphorus pentoxide and xylene, the allyl derivative (IV,  $R = CH_2CH=CH_2$ ; X = OH) underwent dehydration-rearrangement and cyclization in one step to 14-methyl-13,14-dihydrodibenz[a,c]phenanthrene (VI,  $R = CH_3$ ), isolated as the picrate in almost 90% yield. Like Bradsher and Rapoport (8) and despite rigorous purification procedures the hydrocarbon was not obtained crystalline. Dehydrogenation gave 14-methyldibenz[a,c]phenanthrene (V,  $R = CH_3$ ) of m.p. 115–116°. Through the

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kindness of Professor Bradsher it has been established beyond doubt that this is a metastable form, the stable form showing m.p.  $150-151^{\circ}$  (see Experimental for details). The ultraviolet spectrum showed good agreement with that of dibenz[a,c]phenanthrene having the bathochromic shift of approximately  $3 \text{ m}\mu$  associated with the introduction of a methyl group.

The spiro-alcohol (VII) undergoes dehydration-rearrangement under the action of phosphorus pentoxide to give 13,14-dihydrodibenz[a,c]phenanthrene (VI, R = H) (2). Consequently the reaction of (IV,  $R = CH_2CH = CH_2$ ; X = OH) may follow either of the sequences rearrangement-cyclization or cyclization-rearrangement. Cyclization must proceed through the cation  $R \cdot CH_2CH_3$  and it is surprising that the mesomeric ion  $R \cdot CH_2CH_3$  is not formed, leading to a derivative of 1,2:3,4-dibenzfluorene.



Oxidation of (V,  $R = CH_3$ ) with aqueous sodium dichromate at 250° gave the pale yellow very sparingly soluble acid, characterized as its methyl ester.

The transformations of (IV,  $R = CH_2CH=CH_2$ ; X = OH) are summarized in Fig. 3. The corresponding chloride (IV,  $R = CH_2CH=CH_2$ ; X = Cl) failed to yield decomposition products useful for the synthesis of (V, R = OH).



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BAVIN: FLUORENE. I

### EXPERIMENTAL

### 9-Methyl-9-benzoylfluorene

To a boiling solution of 9-benzoylfluorene (20 g) (9) in acetone (200 ml) were added successively hot methanol (200 ml), a solution of potassium carbonate (15 g, anhydrous) in hot water (30 ml), and methyl iodide (25 g). The mixture was boiled gently under an efficient reflux condenser for 1 hour during which time the initial deep orange color faded to pale yellow. The mixture was diluted with water (800 ml) and a rapid stream of air passed through overnight. Next day the crystalline *ketone* was collected, washed, and crystallized from acetone-methanol, from which it separated as large colorless tablets (17 g, 81%), m.p. 99–101°, raised to 101-102° by two further crystallizations. Found: C, 89.48; H, 5.72%. Calculated for C<sub>21</sub>H<sub>16</sub>O: C, 88.70; H, 5.67%. Carbonyl stretching frequency: 1665 cm<sup>-1</sup>.

The ketone was first obtained by alkylating 9-benzoylfluorene (2.7 g) in cold methanol containing sodium methoxide (from sodium, 0.23 g, 1 equivalent) with methyl iodide (3 g). The product crystallized from chloroform-hexane as colorless prisms (0.4 g), m.p. and mixed m.p. 99-101°. Methyl benzoate and 9-methylfluorene (see below) were obtained by distilling the mother liquors.

The oxime, prepared in pyridine, crystallized from chloroform-hexane as colorless needles, more rarely as prisms, m.p. 206–207°. Found: C, 84.66; H, 5.66%. Calculated for C<sub>21</sub>H<sub>17</sub>NO: C, 84.25; H, 5.73%.

After the ketone (2 g) was warmed for a few minutes with potassium hydroxide (2 g) in 95% alcohol (10 ml), isolation and distillation of the neutral product gave 9-methyl-fluorene as a rapidly crystallizing oil, which formed bipyramidal prisms from methanol, m.p. 45–47°. (Lit. m.p. 45–47° (10).)

### Phenyl-9-methyl-9-fluorenylmethanol

Reduction of the ketone with ethereal lithium aluminum hydride gave an almost quantitative yield of the *alcohol*, which crystallized from hexane as colorless needles, m.p. 100–101°. Found: C, 87.60; H, 5.90%. Calculated for  $C_{21}H_{18}O$ : C, 88.08; H, 6.33%. Hydroxyl stretching frequency: 3350 cm<sup>-1</sup>.

### Phenyl-9-methyl-9-fluorenylmethyl Chloride

The alcohol was warmed for a few minutes with four times its weight of thionyl chloride. After excess reagent was destroyed with water, a solution of the product in hexane was passed through a column of activated alumina. The *chloride* crystallized from the eluant as massive colorless prisms (70–85%), melting point with decomposition in the range 91–99°, varying with the sample. Found, for two preparations: C, 83.03, 82.60; H, 5.70, 5.36%. Calculated for  $C_{21}H_{17}Cl: C, 82.74; H, 5.62\%$ .

The chloride was recovered essentially unchanged after the solution was boiled with moist methanol, acetic acid, pyridine, or quinoline, or with a solution of sodium iodide in acetone. More fruitful experiments are recorded below.

# 9-Methyl-10-phenylphenanthrene

(i) The alcohol (10 g) and phosphorus pentoxide (10 g) were boiled under reflux for 3 hours with xylene (100 ml). The *hydrocarbon*, isolated in the usual way, crystallized from acetone-methanol as colorless blades (8.7 g), m.p. 98–99°, depressed to 84–90° by addition of the alcohol. Found: C, 93.73; H, 6.01%. Calculated for  $C_{21}H_{16}$ : C, 93.99; H, 6.01%.

The 1,3,5-trinitrobenzene complex crystallized from methanol as bright yellow silky

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needles, m.p. 126–128°. Found: C, 67.62; H, 4.15%. Calculated for  $C_{27}H_{19}N_3O_6$ : C, 67.35; H, 3.98%.

(ii) The chloride (1 g) was carefully pyrolyzed over a microburner until evolution of hydrogen chloride ceased. Crystallization of the residue from acetone-methanol gave blades (0.7 g), m.p. and mixed m.p.  $97-99^{\circ}$ .

(*iii*) The chloride (0.2 g) was boiled under reflux for 2 hours with 98% formic acid (100 ml). The product crystallized from hexane as blades (0.15 g), m.p. and mixed m.p.  $96-98^\circ$ .

# Phenyl-9-methyl-9-fluorenylmethyl Acetate

(*i*) The chloride (1 g) was boiled for 5 minutes with silver or mercuric acetate (2 g) in anhydrous acetic acid (100 ml). The *acetate* slowly crystallized from hexane as colorless prisms, m.p. 80–81° after three crystallizations. Found: C, 84.06; H, 5.98%. Calculated for  $C_{23}H_{20}O_2$ : C, 84.12; H, 6.14%. No trace of the easily crystallized 9-methyl-10-phenylphenanthrene could be found.

(*ii*) The alcohol (0.2 g) was warmed for 12 hours with acetic anhydride (4 ml) containing 1 drop of concentrated sulphuric acid. The colorless prisms obtained by crystallization from hexane had m.p. and mixed m.p. 78–80°.

Reduction of the acetate with ethereal lithium aluminum hydride gave the original alcohol, identified by melting point and mixed melting point.

## Phenyl-9-methyl-9-fluorenylmethyl Formate

Attempts to esterify the alcohol with *p*-toluenesulphonyl or methanesulphonyl chloride in pyridine under a range of conditions were unsuccessful. Boiling the crude products with 98% formic acid usually gave only unchanged alcohol but occasionally the *formate* was obtained, which slowly crystallized from cyclohexane as massive colorless prisms, m.p. 126–128°. Found: C, 84.24; H, 5.83%. Calculated for  $C_{22}H_{18}O_2$ : C, 84.05; H, 5.77%.

# 9-Phenylphenanthrene-10-carboxylic Acid and 1,2:3,4-Dibenzfluorenone

In a typical experiment, 9-methyl-10-phenylphenanthrene (13.4 g) was heated at 250–260° for 8 hours with technical sodium dichromate (25 g) and water (250 ml) in a 500-ml, rotating autoclave. After the container was cooled and opened, the contents were heated to boiling with the addition of 1250 ml water. Chromium sesquioxide was removed by filtration, acidification of the filtrate with dilute sulphuric acid precipitating the *phenanthroic acid* (5–10%). It formed colorless prisms from benzene-hexane, m.p. 192–193° after two crystallizations. Found: C, 84.65; H, 4.85%. Calculated for C<sub>21</sub>H<sub>14</sub>O<sub>2</sub>: C, 84.54; H, 4.73%.

The acid dissolved in cold thionyl chloride to give an orange solution, dilution of which with water precipitated 1,2:3,4-dibenzfluorenone, orange needles from heptane, m.p. 185–187° (Lit. m.p. 185–186° (11).)

The chromium sesquioxide formed in the oxidation was contaminated with an orange gum, removed by percolation with methylene chloride. The extracted material formed orange rods from benzene-hexane (10.1 g), m.p. and mixed m.p. 184-186°.

The following ketones were prepared as described for the methyl analogue:

9-Ethyl-9-benzoylfluorene, white needles from hexane, m.p. 129–130°. Found: C, 88.34; H, 5.91%. Calculated for  $C_{22}H_{18}O$ : C, 88.56; H, 6.08%. Carbonyl stretching frequency: 1663 cm<sup>-1</sup>.

9-Isopropyl-9-benzoylfluorene, small colorless prisms from acetone-methanol, m.p. 226-227°. Found: C, 88.17; H, 6.40%. Calculated for  $C_{23}H_{20}O$ : C, 88.42; H, 6.45%. Carbonyl stretching frequency: 1630 cm<sup>-1</sup>.

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9-Benzyl-9-benzoylfluorene, white prisms from acetone-methanol, m.p. 134-135°. Found: C, 89.81; H, 5.78%. Calculated for  $C_{27}H_{26}O$ : C, 89.97; H, 5.59%. Carbonyl stretching frequency: 1665 cm<sup>-1</sup>.

9-Cyclohexyl-9-benzoylfluorene, colorless prisms from methanol, m.p. 121–122°. Found: C, 88.33; H, 6.78%. Calculated for  $C_{26}H_{24}O$ : C, 88.60; H, 6.86%. Carbonyl stretching frequency: 1675 cm<sup>-1</sup>.

9-Allyl-9-benzoylfluorene, long colorless needles from acetone-methanol, m.p. 91–92°. Found: C, 89.11; H, 6.00%. Calculated for  $C_{23}H_{18}O$ : C, 89.00; H, 5.84%. Carbonyl stretching frequency: 1670 cm<sup>-1</sup>.

*Phenyl-9-allyl-9-fluorenylmethanol* crystallized as irregular prisms from benzene-hexane, m.p. 132–134°. Found: C, 88.46; H, 6.33%. Calculated for  $C_{23}H_{20}O$ : C, 88.43; H, 6.45%.

*Phenyl-9-allyl-9-fluorenylmethyl chloride* formed lustrous plates from methanol, m.p.  $81-82^{\circ}$ . Found: C, 83.49; H, 5.78%. Calculated for C<sub>23</sub>H<sub>19</sub>Cl: C, 83.50; H, 5.79%. Decomposition of the chloride by pyrolysis or by boiling with formic acid gave only gums, from which nothing useful was obtained by oxidation.

#### 14-Methyl-13,14-dihydrodibenz[a,c]phenanthrene

The allyl alcohol (20 g) and phosphorus pentoxide (30 g) were boiled under reflux for 1 hour with xylene (100 ml). The product was a pale yellow viscous oil which formed a 1,3,5-trinitrobenzene complex, crystallizing as vermilion rods from methanol, m.p. 194–195°. Found: C, 68.48; H, 4.23%. Calculated for C<sub>29</sub>H<sub>21</sub>N<sub>3</sub>O<sub>6</sub>: C, 68.63; H, 4.17%. This complex was not decomposed by passing a hexane solution through a column of activated alumina.

The *picrate* crystallized from ethanol as maroon needles, m.p.  $174-175^{\circ}$ . (Lit. m.p.  $170.5-171.0^{\circ}$ , corr. (8).) Decomposition of the picrate by passing a benzene solution through a column of alumina and evaporation of the eluant gave a colorless oil which has defied prolonged attempts to induce crystallization (cf. (8)).

# 14-Methyldibenz[a,c]phenanthrene, (9-Methyl-1,2:3,4-dibenzphenanthrene)

Prepared in almost quantitative yield by dehydrogenating the preceding hydrocarbon at 280-300° over 10% palladium-on-charcoal, 14-methyldibenz[a,c]phenanthrene slowly crystallized from benzene-methanol as large colorless prisms, m.p. 115-116°, not raised by further crystallizations. Subsequently, recrystallization with seeding by Bradsher's preparation gave small prisms, m.p. 150-151°. (Lit. m.p. 150.5-151.5°, corr. (8).)

The ultraviolet spectrum showed excellent agreement with that of dibenz[a,c]phenanthrene (12, 13); with peaks at:

Dibenzphenanthrene	276.5	286	308	321	334	352	371 mµ
Methyl derivative	278	288	311	323	337	$354^{*}$	$373 \text{ m}\mu$

The *picrate* crystallized from ethanol as bright red needles, m.p. 212–213°. (Lit. m.p. 207.5–208.5°, corr. (8).)

The 1,3,5-trinitrobenzene complex formed slender orange needles from methanol, m.p. 234-235.5°. Found: C, 68.91; H, 3.81%. Calculated for  $C_{29}H_{19}N_3O_6$ : C, 68.91; H, 3.79%.

An impure sample of Professor Bradsher's original preparation was converted to the picrate (m.p. and mixed m.p. 212-213°) from which the hydrocarbon was regenerated on alumina. Crystallization from benzene-methanol gave small prisms, m.p. 149-150°, not depressed by either the low or high melting forms described above.

\*Inflexion.

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#### Methyl Dibenz[a,c]phenanthrene-14-carboxylate

14-Methyldibenz[a,c]phenanthrene (5 g) was oxidized with sodium dichromate (20 g) as described for the methylphenylphenanthrene. The pale yellow acid (4.6 g) was very sparingly soluble but was esterified by boiling with methanol (1500 ml) for 4 hours while dry hydrogen chloride was bubbled in. A solution of the crude product in benzenehexane (5:1) was passed through a short column of alumina to remove traces of tar. Crystallization of the eluted material from acetone-methanol gave pale orange elongated prisms, m.p. 155-156°. Found: C, 85.75; H, 5.04%. Calculated for C<sub>24</sub>H<sub>16</sub>O<sub>2</sub>: C, 85.69; H, 4.80%.

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