

## 11. The Condensation of Fluorene with Acetone. Part V. Contrasting Reactions of 9-Fluorenylmagnesium Bromide and of 9-Fluorenyllithium with $\alpha\beta$ -Unsaturated Ketones.

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Whereas 9-fluorenylmagnesium bromide adds to the carbonyl group (1:2-addition) of certain  $\alpha\beta$ -unsaturated ketones, with no evidence of addition to the conjugated double-bond system (1:4-addition), yet 9-fluorenyllithium adds in exactly the opposite way. Ketones investigated were mesityl oxide, benzylideneacetophenone (chalcone), benzylideneacetone, ethylideneacetone, and 3-methylpent-2-en-4-one. The constitutions of the condensation products derived from 9-fluorenyllithium and (a) chalcone, *viz.*, phenyl 2-phenyl-2-9'-fluorenyl-ethyl ketone, and (b) benzylideneacetone, *viz.*, methyl 2-phenyl-2-9'-fluorenyl-ethyl ketone, have been established; in particular, by the synthesis from the former of 2:4-diphenyl-fluoranthene, and, from the latter, of 2-phenyl-4-methylfluoranthene.

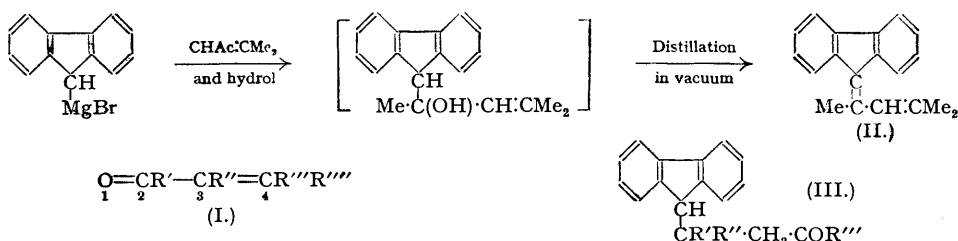
Methods for preparing the magnesium and lithium derivatives of fluorene have been improved.

ADDITION of organometallic compounds, RM, to the conjugated double-bond system in (I) may give rise (a) by 1:2-addition at the carbonyl group, followed by hydrolysis, to unsaturated carbinols,  $\text{HO}\cdot\text{CR}'\text{R}'\cdot\text{CR}''\cdot\text{CR}'''\text{R}''''$ ; (b) by 1:4-addition, with subsequent hydrolysis, to saturated ketones,  $\text{O}\cdot\text{CR}'\cdot\text{CHR}''\cdot\text{CR}'''\text{R}''''\text{R}$ . The possibility that this 1:4-addition may be actually 3:4-addition (Rupe and Liechtenhan, *Ber.*, 1906, **39**, 1119; cf. Kohler, *Amer. Chem. J.*, 1906, **36**, 181) is quite unlikely.

Grignard reagents add to  $\alpha\beta$ -unsaturated aldehydes (I,  $\text{R}' = \text{H}$ ) by 1:2-addition: 1:4-addition may rarely *also* occur (Stevens, *J. Amer. Chem. Soc.*, 1935, **57**, 1112).

With  $\alpha\beta$ -unsaturated ketones the position is much more complicated. Both types of addition, 1:2- and 1:4-, usually take place (Kohler, *loc. cit.*; *Amer. Chem. J.*, 1907, **37**, 369; **38**, 511; Kohler, Tishler, and Potter, *J. Amer. Chem. Soc.*, 1935, **57**, 2517. For summary see Kirby, *Iowa State Coll. J. Sci.*, 1937, **12**, 137). To particularise, investigations with mesityl oxide have shown that Grignard reagents add to its carbonyl group (1:2-addition) (Fellenberg, *Ber.*, 1904, **37**, 3578; 1906, **39**, 2064; Pastureur and Bernard, *Compt. rend.*, 1923, **177**, 327; Jitkow and Bogert, *J. Amer. Chem. Soc.*, 1941, **63**, 1981; Jacquemain, *Compt. rend.*, 1942, **214**, 880; Kohler, *Amer. Chem. J.*, 1907, **38**, 511; Stevens, *loc. cit.*).

We now find, in harmony with these results, that 9-fluorenylmagnesium bromide reacts with mesityl oxide, by 1:2-addition, to give, after hydrolysis and dehydration, the diene, 4-fluorenylidene-2-methylpent-2-ene (II), formerly isolated by the action of 9-fluorenylmagnesium bromide on diacetone alcohol, presumably after intermediate formation of mesityl oxide (Maitland and Tucker, *J.*, 1929, 2559).



The yield of this crystalline, phototropic substance was only 30%, based on unrecovered fluorene, but neither the 1:4-addition product,  $\text{C}_{13}\text{H}_9\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COMe}$ , methyl 2-9'-fluorenyl-2-methyl-*n*-propyl ketone (III,  $\text{R}' = \text{R}'' = \text{R}''' = \text{Me}$ ) (France, Maitland, and Tucker, *J.*, 1937, 1739), nor its 2:4-dinitrophenylhydrazide could be isolated.

It must be borne in mind that this reaction is carried out under conditions which are generally classed as "forced" (125°/2.5 hours). However, it has been stated (Kirby, *loc. cit.*) that changes of temperature and solvent, whilst they may be influential in bringing about a reaction, do not affect the ratio of 1:2- to 1:4-addition product (cf. Gilman and Kirby, *J. Amer. Chem. Soc.*, 1941, **63**, 2047). Lüttringhaus and Scholtis (*Annalen*, 1945, **557**, 70) endeavoured without success to convert the 1:2-addition product derived from phenyl-lithium and chalcone into the 1:4-addition product.

Similar condensations to that carried out with mesityl oxide were attempted between

9-fluorenylmagnesium bromide and ethylideneacetone, benzylideneacetone, and chalcone, but no crystalline products could be isolated. This is not surprising since the anticipated products are substituted butadienes: many such polymerise with ease [cf. Backer and Strating (*Rec. Trav. chim.*, 1941, **60**, 402), who failed to isolate either 1-diphenylenebutadiene, or its maleic anhydride adduct, but obtained uncrystallisable polymers]. Oxidation of the thick oils obtained as above gave in each case fluorenone in good yield, and from the benzylideneacetone and the chalcone adduct, benzoic acid.

Tests by means of 2:4-dinitrophenylhydrazine and hydroxylamine for the presence of ketones (derivable from 1:4-addition) gave negative results. This is all the more surprising when one remembers that ethylideneacetone gives not only 1:2- but 1:4-addition products with certain alkylmagnesium bromides (Stevens, *loc. cit.*; cf. Kohler, *Amer. Chem. J.*, 1907, **38**, 511; Gry, *Bull. Soc. chim.*, 1908, **3**, 377). Similarly, benzylideneacetone and chalcone give high yields of 1:4-addition products with certain Grignard reagents (Kohler, *Amer. Chem. J.*, 1907, *loc. cit.*).

Addition of cuprous bromide or iodide to the xylene suspension of 9-fluorenylmagnesium bromide followed by addition of mesityl oxide merely decreased the yield of the 1:2-addition product (cf. Kharasch and Fields, *J. Amer. Chem. Soc.*, 1941, **63**, 2308; Birch and Robinson, *J.*, 1943, 501; Hook and Robinson, *J.*, 1944, 15).

It is well known that lithium organo-compounds not only react similarly to Grignard reagents with carbonyl compounds, generally giving improved yields of carbinols, but often react when Grignard reagents fail to do so (Wittig, *Ber.*, 1931, **64**, 2405; 1935, **68**, 924; Allen and Gilman, *J. Amer. Chem. Soc.*, 1936, **58**, 937). Similarly, lithium organo-compounds react with  $\alpha\beta$ -unsaturated ketones to give almost invariably high yields of carbinols (1:2-addition) even when the corresponding Grignard reagents give high yields of saturated ketones (1:4-addition). Gilman and Kirby (*J. Amer. Chem. Soc.*, 1941, **63**, 2046), using lithium reagents, invariably obtained high yields of carbinols (1:2-addition) but also isolated saturated ketones (1:4-addition) in small yield (cf. Lüttringhaus, *Ber.*, 1934, **67**, 1602; Lüttringhaus and Scholtis, *Annalen*, *loc. cit.*). Koelsch and Rosenwald (*J. Amer. Chem. Soc.*, 1937, **59**, 2166) obtained the unusual 1:4-addition of phenyl-lithium in reaction with 8-phenylperinaphthindane-7:9-dione, but the reaction was somewhat abnormal since it involved the "double bond" of an aromatic ring. It is surprising, therefore, to find that 9-fluorenyl-lithium not only does not react with the highly reactive carbonyl group of mesityl oxide, but in 45 minutes' reaction in boiling petroleum (b. p. 67–69°) gives a good yield (52%) of the saturated ketone (III,  $R' = R'' = R''' = \text{Me}$ ), by 1:4-addition.

That none of the phototropic 1:2-addition product (II) was present was shown by exposing solid fractions obtained in the reaction to sunlight, no colour change taking place.

9-Fluorenyl-lithium adds likewise (1:4-addition) to chalcone to give phenyl 2-phenyl-2'-9'-fluorenylethyl ketone (III;  $R' = R''' = \text{Ph}$ ,  $R'' = \text{H}$ ), m. p. 125–127° (cf. Taylor and Connor, *J. Org. Chem.*, 1941, **6**, 696, who give m. p. 127–128°, corr.). It gave an *oxime*. 2:4-Dinitrophenylhydrazine gave an orange reaction product, which could not be purified. Oxidation of the ketone by means of sodium dichromate in glacial acetic acid gave fluorenone and benzoic acid. Its constitution has been called in question by Pinck and Hilbert (*J. Amer. Chem. Soc.*, 1946, **68**, 2015) who, following the method used by one of us (France, Maitland, and Tucker, *loc. cit.*, p. 1741) for the Michael condensation of fluorene with mesityl oxide, obtained a compound,  $\text{C}_{28}\text{H}_{20}\text{O}$ , m. p. 129°, which they assumed to be 3:5-diphenyl-2-2':2''-diphenylene-tetrahydrofuran, since it gave neither a "phenylhydrazone" nor a "carbazide", and "failed to show an OH-absorption in the infra-red". We have repeated their work and have obtained the same compound (III;  $R' = R''' = \text{Ph}$ ,  $R'' = \text{H}$ ) as that obtained by us from 9-fluorenyl-lithium and chalcone, as above described. Dr. G. B. B. M. Sutherland reports that the infra-red spectrum of this compound shows that it "possesses a carbonyl group adjoining a phenyl group".

9-Fluorenyl-lithium reacted similarly with benzylideneacetone to give methyl 2-phenyl-2'-9'-fluorenylethyl ketone (III;  $R' = \text{Ph}$ ,  $R'' = \text{H}$ ,  $R''' = \text{Me}$ ), m. p. 99–101° (cf. Taylor and Connor, *loc. cit.*), also obtained by the action of fluorene on benzylideneacetone in pyridine solution containing sodium hydroxide. Its constitution was confirmed by the preparation of a 2:4-dinitrophenylhydrazone and of an *oxime*; also by oxidation with sodium dichromate in acetic acid solution, which gave equimolecular proportions of fluorenone and benzoic acid.

It will be observed that 9-fluorenyl-lithium thus resembles 9-fluorenyl-sodium and -potassium in that all react with mesityl oxide by 1:4-addition (France, Maitland, and Tucker, *loc. cit.*). It is noteworthy that the nature of the solvent does not affect the result—experiments with lithium being conducted in petroleum, and those with sodium in ether, whilst 9-fluorenyl-

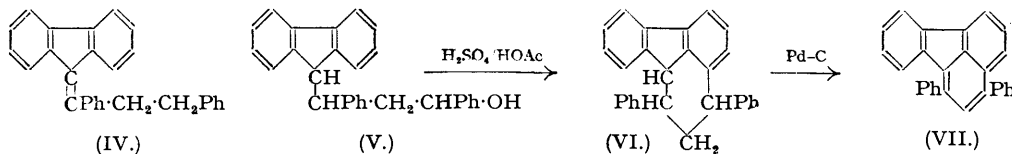
potassium was, presumably, intermediately formed in mesityl oxide-pyridine. Obviously, in view of the ease with which fluorene liberates a proton, one must conclude that the lithium, sodium, and potassium derivatives of fluorene exist in a highly ionised condition even in non-ionising solvents and that the 9-fluorenyl anion reacts preferentially by the Michael mode of addition.

These observations on the 1:4-addition of 9-fluorenylalkyls are of special interest since phenylpotassium adds exclusively to the 1:2-position of other  $\alpha\beta$ -unsaturated ketonic systems (Kirby, *loc. cit.*).

It is clear that steric effects can have no influence on the course of these reactions since (a), as shown above, the 9-fluorenyl radical can, according to whether the magnesium or the lithium compound is used, add to the carbon atom in the 2- or 4-position of an  $\alpha\beta$ -unsaturated ketone (see also Gilman and Jones, *J. Amer. Chem. Soc.*, 1940, **62**, 1243); (b) we find that 9-fluorenyl-lithium reacts with phenyl 2-phenylethyl ketone, in which only addition to a carbonyl group is possible, to give, eventually, 1:3-diphenyl-1-fluorenylidene propane (IV), which, by catalytic hydrogenation, has been converted into 1:3-diphenyl-1-9'-fluorenylpropane.

In the preparation of 9-fluorenylmagnesium bromide (Courtot, *Ann. Chim.*, 1915, **4**, 84; Maitland and Tucker, *loc. cit.*, p. 2561), collection of the ethane evolved showed that (a) the period of heating in xylene could be reduced from 12 to 3 hours; (b) the use of two molecules of ethylmagnesium bromide to one of fluorene, in boiling xylene for 3 hours, raised the yield of ethane to 91%. A blank experiment, omitting fluorene, gave no gas. The use of excess of ethylmagnesium bromide introduced no complication since it is removed in the subsequent washing of the insoluble 9-fluorenylmagnesium bromide with xylene, before the reactant  $\alpha\beta$ -unsaturated ketone is added.

The preparation of 9-fluorenyl-lithium proved troublesome. The use of methyl-lithium in ether (Gilman, Zoellner, and Selby, *J. Amer. Chem. Soc.*, 1933, **55**, 1252), followed by heating with fluorene in xylene, gave no methane, and after addition of mesityl oxide an almost theoretical recovery of fluorene. This negative result was probably due to the great stability of methyl-lithium (Haubein, *Iowa State Coll. J. Sci.*, 1943, **18**, 48). We are unable to understand the comparable preparation of 9-fluorenyl-lithium by Miller and Bachman (*J. Amer. Chem. Soc.*, 1935, **57**, 766; cf. also Gilman, Moore, and Baine, *ibid.*, 1941, **63**, 2480, who state that methyl-lithium cannot be satisfactorily prepared in petroleum (b. p. 28—38°) because of its insolubility). *n*-Butyl-lithium, prepared in sulphur-free benzene (Ziegler and Colonius, *Annalen*, 1930, **479**, 135), gave similarly with fluorene low yields of butane and, after carbonation, a low yield (5%)



of acid. The preparation of *n*-butyl-lithium from lithium and *n*-butyl chloride was, however, accomplished by reaction in petroleum (b. p. 67—69°) in 4 hours (yield, 75%, by titration method, Gilman *et al.*, *J. Amer. Chem. Soc.*, 1923, **45**, 150; 1944, **66**, 1515) (cf. Gilman, Langham, and Moore, *ibid.*, 1940, **62**, 2334; Gilman, Moore, and Baine, *loc. cit.*; Gilman, Arntzen, and Webb, *J. Org. Chem.*, 1945, **10**, 377; Burtner and Cusic, *J. Amer. Chem. Soc.*, 1943, **65**, 264; Meals, *J. Org. Chem.*, 1944, **9**, 211; Wittig *et al.*, *Annalen*, 1947, **557**, 196, 204). Heating the product with fluorene for 45 minutes gave 9-fluorenyl-lithium, which by carbonation gave fluorene-9-carboxylic acid (66% on total, and 100% on unrecovered, fluorene). The action of acetyl chloride, acetic anhydride, and ethyl acetate on 9-fluorenyl-lithium in petroleum gave almost complete recovery of fluorene (cf. Miller and Bachman, *loc. cit.*; Von and Wagner, *J. Org. Chem.*, 1944, **9**, 155).

Since the ultimate aim of these researches is the synthesis of substituted fluoranthenes, it was decided to confirm the proposed formula for the fluorene-chalcone Michael condensation product (III; R' = R''' = Ph, R'' = H) by conversion into 2:4-diphenylfluoranthene. This was effected by reducing the above ketone (III), by means of (a) aluminium isopropoxide in isopropanol, or (b) hydrogen/Raney nickel in ethanol, to the carbinol, 1:3-diphenyl-3-9'-fluorenylpropanol (V), which by heating (100°/5 mins.) in a mixture of glacial acetic and sulphuric acids gave 2:4-diphenyl-1:2:3:4-tetrahydrofluoranthene (VI) (cf. France, Tucker, and Forrest, *J.*, 1945, 7). Catalytic dehydrogenation (Pd-C) of (VI) gave 2:4-diphenylfluoranthene (VII).

2-Phenyl-4-methylfluoranthene was similarly synthesised from methyl 2-phenyl-2-9'-fluorenyl-

ethyl ketone by catalytic hydrogenation of the ketone to 3-phenyl-3'-fluorenyl-1-methylpropanol, which cyclised to 2-phenyl-4-methyl-1:2:3:4-tetrahydrofluoranthene; dehydrogenation with selenium yielded 2-phenyl-4-methylfluoranthene.

#### EXPERIMENTAL.

**9-Fluorenylmagnesium Bromide.**—Ethyl bromide (45.5 g.  $\equiv$  32 ml.; 2.5 mols.) and pure magnesium (10 g.; 2.5 atoms) in anhydrous ether (100 ml.) gave ethylmagnesium bromide ( $\sim$ 2 mols.) to which were added fluorene (27.7 g.; 1 mol.) and xylene (85 ml.). The ether was removed by gentle boiling of the mixture, with stirring. When practically all had been removed the apparatus was set for collection of residual ether, in a cooled receiver, and of ethane, scrubbed free from ether by bubbling through concentrated sulphuric acid, in a graduated cylinder. It was found advantageous to stir the gently refluxing mixture intermittently only. When no more ethane was evolved (3450 ml. N.T.P., in 3 hours; yield, 91%) the pale green powder of 9-fluorenylmagnesium bromide which had been deposited was washed by decantation with ether and with xylene to remove excess of ethylmagnesium bromide and unchanged fluorene, then covered with fresh xylene and so used in subsequent reactions. The use of *iso*amyl ether or of *p*-cymene in place of xylene possessed no advantage.

**Fluorene-9-carboxylic Acid.**—The xylene suspension of 9-fluorenylmagnesium bromide, prepared as above, was poured on solid carbon dioxide, then the suspension was heated at 100° whilst dry, air-free carbon dioxide was passed in (Tucker, *Analyst*, 1939, **64**, 410; 1942, **67**, 320). After filtration, the combined xylene and ether solutions (obtained in the preparation of the 9-fluorenylmagnesium bromide, and subsequently) were treated with dilute hydrochloric acid, and fluorene recovered (8.5 g.; 30% recovery). The carbonated solid was treated with dilute hydrochloric acid, and the insoluble carboxylic acid dissolved in sodium hydroxide solution and reprecipitated by acid. Crystallisation from toluene gave fluorene-9-carboxylic acid, softening very much below the m. p.  $\sim$ 225° (4.5 g.; 18% on unrecovered fluorene).

**9-Fluorenyldimethylcarbinyl acetate** prepared from the carbinol (Maitland and Tucker, *loc. cit.*, p. 2562) by means of acetyl chloride in benzene-pyridine solution at room temperature, crystallised from methanol in stellar clusters of prismatic rods, m. p. 115—116° (Found: C, 81.1; H, 6.6.  $C_{18}H_{18}O_2$  requires C, 81.2; H, 6.8%).

**Reaction of 9-Fluorenylmagnesium Bromide with (a) Mesityl Oxide, (b) Chalcone, (c) Benzylideneacetone, (d) Ethylideneacetone.**—These reactions were effected similarly; the method is illustrated by the case of mesityl oxide. (a) Mesityl oxide (24.5 g.; 0.25 g.-mol.) was added to 9-fluorenylmagnesium bromide (prepared from 41.5 g.  $\equiv$  0.25 g.-mol. of fluorene) in xylene (150 ml.). Vigorous stirring and heating at 125° were maintained for 2.5 hours, the Grignard reagent turning from green to brown. After treatment with dilute hydrochloric acid, extraction with ether, and evaporation of the xylene-ether extract, distillation gave, at 12 mm., fractions (i), 150—180°, fluorene (11.2 g., 27% recovery); (ii) 180—225°, a reddish oil which from petroleum (b. p. 40—60°) gave white needles which turned pink on exposure to light and, if exposure had not been too protracted, became again colourless when kept in the dark, m. p. 80—82° (1.1 g.); (iii) 225—233°, a thick oil which gave, as (ii), 4-fluorenylidene-2-methylpent-2-ene, m. p. 80—82° (14.7 g.; total yield 15.8 g., 26%, or 30% on unrecovered fluorene); (iv) higher fractions gave from ethanol merely 9:9'-difluorenyl, m. p. 243°. (b) Chalcone (26 g.; 0.125 g.-mol.) was added to 9-fluorenylmagnesium bromide (from fluorene, 20.8 g.; 0.125 g.-mol.) in xylene (70 ml.) and heated at 140° for 1.5 hours. After working up as above, distillation gave fluorene (7.0 g.) and at 200—210°/1 mm. an oil (6.3 g.), which did not react with 2:4-dinitrophenylhydrazine. (c) Benzylideneacetone similarly gave recovered fluorene (29%) and at 270—280°/14 mm. a red oil which gave no reaction with ketonic reagents, and on oxidation (1.3 g.) with sodium dichromate (7 g.) in boiling acetic acid (25 ml.) (3 hours) gave fluorenone (0.2 g.) and benzoic acid (0.14 g.), thus showing that the oil contained a reaction product of fluorene and benzylideneacetone. (d) Ethylideneacetone similarly gave recovered fluorene (28%) and at 215—235°/11 mm. a heavy red oil (5.1 g.).

**9-Fluorenyl-lithium.**—*n*-Butyl chloride (10.2 g.; 0.11 g.-mol.) in petroleum (b. p. 67—69°, 30 ml.) extracted with concentrated sulphuric acid and distilled from sodium) was added to a boiling mixture of petroleum (30 ml.) and finely divided lithium (1.39 g., 0.2 g.-atom; grated into the flask in a current of dry nitrogen). After refluxing with stirring for 4 hours (in nitrogen), fluorene (12.4 g., 0.075 g.-mol.) and petroleum (45 ml.) were added, and refluxing maintained for 45 minutes. Orange 9-fluorenyl-lithium slowly deposited and butane was evolved (during 30 mins.). The latter was collected in order to determine the end of the reaction, but since it was saturated with petroleum vapour the volume collected is only an approximate measure of the yield (1420 ml. N.T.P.  $\equiv$  85% calculated on fluorene used). The use of 0.075 g.-mol. of fluorene to 0.2 g.-atom of lithium was determined by the fact that independent experiments showed that the yield of *n*-butyl-lithium was 75% (Gilman, Moore, and Baine, *loc. cit.*).

Experiments to be reported later indicate that the above preparation may be improved by using the technique for atomising lithium (Bartlett, Swan, and Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 3229).

**Fluorene-9-carboxylic Acid.**—9-Fluorenyl-lithium, prepared as above, and vigorously stirred, was treated with dry, air-free carbon dioxide until the mixture was colourless (*ca.* 1.5 hours). Water was added, the petroleum layer evaporated for recovery of unattacked fluorene (4.2 g., 34%), and the aqueous solution acidified with hydrochloric acid to give fluorene-9-carboxylic acid (10.5 g., 66%, or 100% on unrecovered fluorene). It was recrystallised from toluene. The use of solid carbon dioxide, wiped to free it from superficially acquired ice, possessed no advantage.

**Reaction of 9-Fluorenyl-lithium with (a) Mesityl Oxide, (b) Chalcone, (c) Benzylideneacetone, (d) 3-Methylpent-2-en-4-one.**—(a) 9-Fluorenyl-lithium prepared as above from fluorene (16.6 g., 0.1 g.-mol.), was treated with mesityl oxide (9.8 g.; 0.1 g.-mol.) in petroleum (b. p. 67—69°; 40 ml.). After refluxing in nitrogen for  $\frac{1}{2}$  hour and acidification, the product was worked up as described for the corresponding Grignard reaction. Fluorene (2.2 g.; 13% recovery) and, at 210—235°/14 mm., a viscous red oil were obtained. The oil solidified on standing, and after crystallisation from methanol or ethanol gave the characteristic white needles of methyl 2-9'-fluorenyl-2-methyl-*n*-propyl ketone, m. p., alone or mixed

with an authentic specimen, 77—78° (12 g.; yield 45% on used, and 52% on unrecovered, fluorene). Its 2 : 4-dinitrophenylhydrazone, m. p. 200—202°, was identical with a sample previously prepared. The 2 : 4-dinitrophenylsemicarbazone, prepared in methanol containing a trace of concentrated sulphuric acid, crystallised from glacial acetic acid in pale yellow, pointed crystals, m. p. 225—228° (efferv.) (Found : C, 63.9; H, 5.1; N, 14.1.  $C_{25}H_{25}O_5N_5$  requires C, 64.1; H, 5.1; N, 14.4%). The semicarbazone gave micro-crystals from ethanol, softening at 190°, melting at 214° (Found : C, 74.7; H, 7.1; N, 13.1.  $C_{20}H_{23}ON_3$  requires C, 74.8; H, 7.2; N, 13.1%).

(b) Chalcone (10.4 g.; 0.05 g.-mol.) in petroleum (b. p. 67—69°; 50 ml.) was added to 9-fluorenyl-lithium (from fluorene, 8.3 g., 0.05 g.-mol.), the mixture refluxed (1 hour), treated with dilute hydrochloric acid, extracted with benzene, the mixture of solvents removed, and the residual solid crystallised first from benzene-alcohol (1 : 1) and then from ethyl acetate to give phenyl 2-phenyl-2'-9'-fluorenylethyl ketone, m. p. 125—127° (Found : C, 89.7; H, 5.7; M, 354. Calc. for  $C_{28}H_{22}O$  : C, 89.8; H, 5.8%; M, 374) (cf. Taylor and Connor, *loc. cit.*, who give m. p. 127—128°, corr., and Pinck and Hilbert, *loc. cit.*, m. p. 129°).

Fluorene reacted with chalcone in presence of pyridine and sodium hydroxide solution (Pinck and Hilbert, *loc. cit.*, p. 2014) to give the same compound. It gave an orange precipitate with 2 : 4-dinitrophenylhydrazine in methanol acidified with concentrated sulphuric acid but a pure product could not be prepared. The ketone reacted, however, in the usual way to give an oxime, rectangular prisms from methanol, softening at 155°, melting at 162° (Found : C, 86.3; H, 5.9; N, 3.6.  $C_{28}H_{23}ON$  requires C, 86.4; H, 5.9; N, 3.6%). Furthermore, oxidation of the ketone (1.5 g.) by boiling (1.5 hours) with sodium dichromate (3 g.) in glacial acetic acid (25 ml.), followed by addition of more dichromate (3 g.) and continued boiling (1.5 hours), gave after the usual procedure fluorenone (0.3 g.; 42%) and benzoic acid (0.4 g.; 26%).

(c) Benzylideneacetone was employed as described for chalcone (see b). Fluorene (5.4 g.; 32% recovery) was obtained at 165—200°/20 mm., and a thick orange oil at 195—205°/0.5 mm., which crystallised slowly from ethanol in prisms of methyl 2-phenyl-2'-9'-fluorenylethyl ketone, m. p. 99—101° (5.2 g.; yield 17%, or 25% on unrecovered fluorene) (Found : C, 88.6; H, 6.4.  $C_{23}H_{20}O$  requires C, 88.45; H, 6.4%). The 2 : 4-dinitrophenylhydrazone crystallised in orange-red prisms from glacial acetic acid, m. p. 167—169° (Found : C, 70.8; H, 4.9; N, 11.3.  $C_{29}H_{24}O_4N_4$  requires C, 70.7; H, 4.9; N, 11.4%). The oxime crystallised from methanol in small needles, m. p. 155—159° (Found : C, 84.3; H, 6.3; N, 4.7.  $C_{23}H_{21}ON$  requires C, 84.4; H, 6.4; N, 4.3%). A mixture of fluorene (1.66 g.) and benzylideneacetone (1.46 g.) in pyridine (15 ml.) and concentrated sodium hydroxide (1 ml.) was allowed to stand with intermittent shaking for 5 days, then acidified with dilute hydrochloric acid, the deposited oil extracted with carbon tetrachloride, and after recovery crystallised from ethanol (during several days) in prisms, m. p. and mixed m. p. with methyl 2-phenyl-2'-9'-fluorenylethyl ketone, prepared as above, 99—101° (0.7 g.; 22%). Oxidation, as described above, gave fluorenone (22%) and benzoic acid (21%).

(d) 3-Methylpent-2-en-4-one (4.9 g.; 0.05 g.-mol.) in petroleum (b. p. 67—69°; 20 ml.) was added to 9-fluorenyl-lithium (prepared from fluorene 8.3 g.). After standing overnight, and working up as before, there were obtained fluorene (2.6 g.; 31% recovery) and a heavy oil, b. p. 210—215°/15 mm. (3.8 g.; 29% on total, and 42% on unrecovered, fluorene). It gave a 2 : 4-dinitrophenylhydrazone, crystallising in orange-red prisms from anisole, m. p. 184—187° (Found : C, 67.4; H, 5.3; N, 12.5.  $C_{25}H_{24}O_4N_4$  requires C, 67.6; H, 5.4; N, 12.6%). Oxidation as above gave fluorenone (30% yield).

9-Fluorenyl-lithium and Phenyl  $\beta$ -Phenylethyl Ketone.—The ketone (5.2 g.) in petroleum (20 ml.) was added fairly rapidly with vigorous stirring to 9-fluorenyl-lithium (prepared from fluorene, 4.2 g.), and the mixture refluxed (5 mins.). After acidification and extraction with carbon tetrachloride a crystalline solid was obtained. Extraction of this with ethanol removed fluorene (0.2 g.); the residue crystallised from benzene-ethanol (1 : 1 v/v) in needles of 1 : 3-diphenyl-1-fluorenylidene propane (IV), m. p. 147—149° (1.9 g.; 20%) (Found : C, 93.8; H, 6.05.  $C_{26}H_{22}$  requires C, 93.85; H, 6.15%). Catalytic hydrogenation (Pd-C-EtOH) of (IV) gave nodules (from ethanol), m. p. 96—98°, of 1 : 3-diphenyl-1-9'-fluorenylpropane (Found : C, 93.4; H, 6.5.  $C_{26}H_{24}$  requires C, 93.3; H, 6.7%).

Synthesis of 2 : 4-Diphenylfluoranthene (VII).—1 : 3-Diphenyl-3-9'-fluorenylpropanol (V). (a) Phenyl 2-phenyl-2'-9'-fluorenylethyl ketone (1 g.) in isopropanol (BaO-dried) (15 ml.) mixed with a solution of aluminium isopropoxide (aluminium, 1 g.; mercuric chloride, trace; isopropanol, 20 ml.) was slowly distilled until the distillate failed to give a positive test for acetone (2 : 4-dinitrophenylhydrazone). Practically all the propanol was removed, and the residue treated with dilute hydrochloric acid and extracted with benzene. After evaporation the residue crystallised (several weeks) from glacial acetic acid.

(b) The ketone (10 g.) in suspension in ethanol (treated with nickel) (80 ml.) was treated with hydrogen in presence of Raney nickel. The evaporated ethanol filtrate gave a glass-like solid which, as above, crystallised extremely slowly from acetic acid. The product obtained, of doubtful purity, was essentially 1 : 3-diphenyl-3-9'-fluorenylpropanol (V) (6.5 g.; 61%), greenish nodules, m. p. 98—105° (Found : C, 89.8; H, 6.2.  $C_{28}H_{24}O$  requires C, 89.4; H, 6.4%). It gave, from boiling pyridine, a 3 : 5-dinitrobenzoyl derivative which formed orange nodules, from a colourless solution in benzene to which petroleum (b. p. 60—80°) was added, softening at 199°, melting at 202° (Found : C, 63.8; H, 4.8; N, 4.9.  $C_{33}H_{26}O_6N_2$  requires C, 73.7; H, 4.6; N, 4.9%).

2 : 4-Diphenyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (VI). The carbinol (V) (4.1 g.) in glacial acetic acid (15 ml.) was treated with a solution of concentrated sulphuric acid (15 ml.) in glacial acetic acid (15 ml.), and the mixture heated (5 mins.) on the steam-bath. Water precipitated a solid which crystallised from glacial acetic acid in needles of 2 : 4-diphenyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (VI), m. p. 209—211° (2.4 g.; 61%) (Found : C, 93.8; H, 6.1.  $C_{28}H_{22}$  requires C, 93.85; H, 6.15%).

2 : 4-Diphenylfluoranthene (VII). Dehydrogenation of the above tetrahydro-compound (VI) (1.5 g.) was effected by heating with selenium [also with palladium-charcoal (Cheronis and Levin, *J. Chem. Educ.*, 1944, 21, 603) in a stream of carbon dioxide at 300° for 3 hours]. Ether extraction gave a bright blue-fluorescing solution which after evaporation gave 2 : 4-diphenylfluoranthene (VII), crystallising in pale green-fluorescing needles from glacial acetic acid, softening at 153°, m. p. 158—160° (0.9 g.; 60%) (Found : C, 94.8; H, 5.2.  $C_{28}H_{18}$  requires C, 94.9; H, 5.1%). Its picrate crystallised from ethanol in

orange needles, m. p. 162—164° (Found : C, 69.8; H, 3.6; N, 7.3.  $C_{23}H_{18}, C_6H_3O_7N_3$  requires C, 70.0; H, 3.6; N, 7.2%). *s*-Trinitrobenzene gave an unstable derivative.

*Synthesis of 2-Phenyl-4-methylfluoranthene.*—*3-Phenyl-3-9'-fluorenyl-1-methylpropanol.* Methyl 2-phenyl-2-9'-fluorenylethyl ketone (4.7 g.) in ethanol (40 ml.) was treated with hydrogen in the presence of Raney nickel and sodium hydroxide (essential) as above. The product, which was principally 3-phenyl-3-9'-fluorenyl-1-methylpropanol, crystallised in small white needles from ethanol, m. p. 88—91° (3.4 g.; 77%).

*2-Phenyl-4-methyl-1:2:3:4-tetrahydrofluoranthene.* The above carbinol (2.4 g.) was treated with concentrated sulphuric acid and glacial acetic acid to give *2-phenyl-4-methyl-1:2:3:4-tetrahydrofluoranthene*, which crystallised from benzene-ethanol in needles, m. p. 211—213° (1.5 g.; 66%) (Found : C, 93.3; H, 6.6.  $C_{23}H_{20}$  requires C, 93.2; H, 6.75%).

*2-Phenyl-4-methylfluoranthene.* The above tetrahydro-compound (0.5 g.) was dehydrogenated with selenium at 280° for 5 hours. Extraction with carbon tetrachloride, evaporation, and crystallisation from glacial acetic acid gave yellow-fluorescing needles, m. p. 150—153°, of *2-phenyl-4-methylfluoranthene* (0.3 g.; 61%) (Found : C, 94.5; H, 5.4.  $C_{23}H_{16}$  requires C, 94.5; H, 5.5%). Its *complex* with *s*-trinitrobenzene crystallised from ethanol in fine yellow needles, m. p. 174—177° (Found : C, 69.0; H, 3.7.  $C_{33}H_{16}, C_6H_3O_6N_3$  requires C, 68.9; H, 3.8%). Its picrate was unstable.

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