226. *The Condensation of Fluorene with Acetone. Part IV. Synthesis of 2 : 4-Dimethylfluoranthene.*

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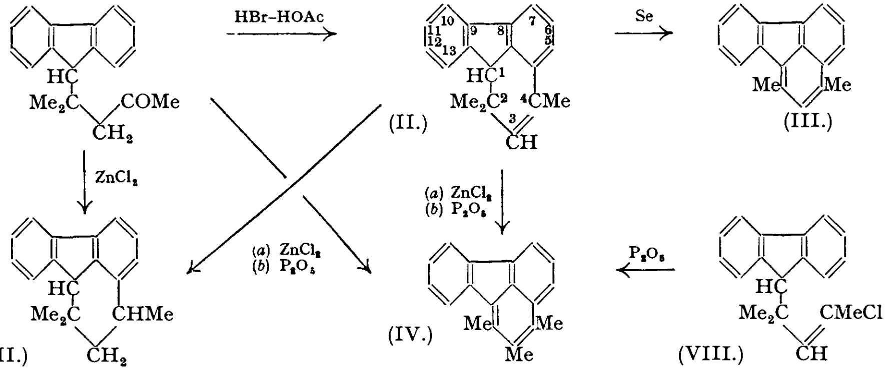
2 : 2 : 4-Trimethyl-1 : 2-dihydrofluoranthene (II) has been converted by dehydrogenation with selenium into 2 : 4-dimethyfluoranthene (III), and by heating with phosphoric oxide into 2 : 3 : 4-trimethylfluoranthene (IV). The migration of methyl from *gem*-dimethylated compounds is discussed. (III) has been synthesised from 1 : 3-dimethylnaphthalene, and an attempt made to synthesise (IV) starting from fluorenone-1-carboxylic acid.

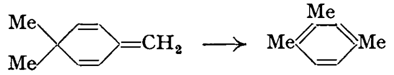
THE reaction of fluorene and acetone in presence of potassium hydroxide gives rise to methyl 2-(9-fluorenyl)-2-methyl-*n*-propyl ketone (I) [Maitland and Tucker, *J.*, 1929, 2559 (Part I); France, Maitland, and Tucker, *J.*, 1937, 1739 (Part II)] which can be readily transformed by the action of hydrogen bromide in glacial acetic acid into the fluoranthene derivative, 2 : 2 : 4-trimethyl-1 : 2-dihydrofluoranthene (II) [France, Tucker, and Forrest, *J.*, 1945, 7 (Part III)]. This substance undergoes interesting reactions : (*a*) selenium at 300° for 5 hours removes hydrogen and methyl with production of 2 : 4-*dimethylfluoranthene* (III); (*b*) phosphoric oxide at 250° for 90 minutes brings about migration of a methyl group of (II), with dehydrogenation, to give 2 : 3 : 4-*trimethylfluoranthene* (IV); (*c*) (IV) is also obtained, together with 2 : 2 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (VII), when (II) is heated with anhydrous zinc chloride at 250° for 4 hours.



Methyl groups are readily eliminated during dehydrogenation processes when they are attached to quaternary carbon, as, *e.g.*, when in angle positions or in *gem*-dimethyl groups (Linstead and Thomas, *J.*, 1940, 1127; *Ann. Reports*, 1936, **33**, 294; Kloetzel, *J. Amer. Chem. Soc.*, 1940, **62**, 3405). Hence the formation of (III) from (II) by the action of selenium is to be expected, since the *gem*-dimethylated ring of (II), having potentially two double bonds already present and a readily ionisable hydrogen atom (attached to the fluorene skeleton), should aromatise readily.

On the other hand, whilst *migration* of methyl groups during dehydrogenation is rare (Linstead and Thomas, *loc. cit.*) migration (without dehydrogenation) by the action of acidic reagents is well known, as in the ready conversion of (V) into (VI) (Auwers and Ziegler, *Annalen*, 1921, **425**, 217; for electronic interpretation, see Whitmore, " Organic Chemistry ", 1937, p. 808).

(V.)



(VI.)

Formation of the aromatic compound (IV) from (II) by the action of acidic reagents is accordingly understandable. It throws light on the observation (France, Maitland, and Tucker, *loc. cit.*, p. 1744) that the ketone (I), by the action of zinc chloride or of phosphoric oxide at 250°, is transformed into a substance, m. p. 133—134°. This is now seen to be (IV), supported by the analytical figures previously found.

Whether in the conversion of the ketone (I) into the fluoranthene (IV) the aromatisation process takes place during *cyclo*-dehydration or *via* (II), intermediately formed, cannot be decided. The fact that (II) can be converted into (IV), under the same experimental conditions as those used in the conversion of (I) into (IV), shows that the latter reaction sequence, (I) →

(II) ⟶ (IV), is possible. At any rate methyl migration from a quaternary carbon atom during dehydration with acidic reagents at relatively high temperature is known (see, *e.g.*, Meerwein, *Annalen*, 1914, **405**, 129; Cohen, Cook, and Hewett, *J.*, 1935, 445; Kloetzel, *loc. cit.*), and conversion of (II) into (IV) follows possibly the same pattern; but in the transformation here considered it must not be forgotten that dehydrogenation also occurs. This must at least be facilitated by the mobility of the 1-hydrogen atom, and its tendency to separate as a proton.

The formation of a small quantity of 2 : 2 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (VII) (France, Tucker, and Forrest, *loc. cit.*) by the action of zinc chloride on (I) or (II) is clearly due to reduction of (II) [intermediately formed from (I)] by hydrogen derived from another molecule of (II) in its transformation into (IV). That it was not isolated in the corresponding reaction using phosphoric oxide may be due to oxidative action of this reagent.

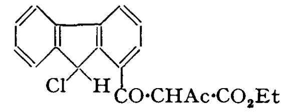
Fusion of 2-chloro-4-(9-fluorenyl)-4-methylpent-2-ene (VIII) (France, Tucker, and Forrest, *loc. cit.*) with phosphoric oxide also gave (IV).

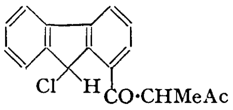
(IV) behaves unusually in that it forms a *picrate* containing two molecules of the hydrocarbon to one of picric acid; but it gives a normal *complex* (1 : 1 mols.) with trinitrobenzene. (III) gives 1 : 1-molecular *complexes* in both cases. The dihydro- and tetrahydro-fluoranthenes do not give addition complexes.

There is evidence for fixity of the double bonds in the methylated rings of (III) and (IV), since on microhydrogenation, using palladium black (Heilbron, Sexton, and Spring, *J.*, 1929, 929) in acetic acid, the amount of hydrogen absorbed indicates the presence in each compound of two double bonds. The olefinic nature of these exo-fluorene-skeleton double bonds is also indicated by the fact that (III) and (IV) are both oxidised by sodium dichromate in acetic acid solution to a mixture of 1-acetylfluorenone and fluorenone-1-carboxylic acid—incidentally also supporting the fluoranthene structure of these compounds.

Attempts were made to synthesise (IV) as follows: fluorenone-1-carboxylic acid $\xrightarrow{\text{redn.}}$ 9-*fluorenol*-1-*carboxylic acid* $\xrightarrow{PCl_5}$ 9-*chlorofluorene*-1-*carboxyl chloride* $\xrightarrow{CH_3\cdot CO\cdot CMeNa\cdot CO_2Et}$ *ethyl* 9-*chlorofluorene*-1-*carbonylmethylacetoacetate* to be followed by reaction with zinc or magnesium, etc. Model experiments using ethyl sodioacetoacetate showed that ethyl 9-chlorofluorene-1-carbonylacetoacetate (IX) was obtainable (as also the corresponding *bromo*-compound); but when ethyl methylacetoacetate was employed, the hydrolysis product (X) was obtained instead of the desired methyl derivative of (IX). Since compounds of types (IX) and (X) are obviously capable of enolisation, further advance (utilising, *e.g.*, the Reformatsky reaction) was unlikely, and the method was abandoned.

(IX.)





(X.)

Attempts are being made to synthesise 2 : 4-dimethylfluoranthene (III) from β-9-fluorenylbutyronitrile but since this follows the synthetic line herein described, starting with fluorene, it was decided to confirm the fluoranthene structure unambiguously by commencing with a naphthalene foundation. Accordingly, (III) has now been synthesised by the following outlined process: 1 : 3-dimethylnaphthalene $\xrightarrow{NaI-NaNO_2-HOAc}$ 1-iodo-2 : 4-dimethylnaphthalene $\xrightarrow{o\text{-bromonitrobenzene-Cu}}$ 1-(2-*nitrophenyl*)-2 : 4-*dimethylnaphthalene* $\xrightarrow{\text{redn.}}$ *amine* $\xrightarrow{\text{Pschorr reactn.}}$ (III) (cf. Ullmann, *Annalen*, 1904, **332**, 38; Lesslie and Turner, *J.*, 1930, 1758; 1931, 1188; Rule and Smith, *J.*, 1937, 1096). Under the conditions employed there was no evidence of the formation of 2-methyl-3 : 4-benzofluorene, which might have arisen by analogy with the work of Mascarelli and Longo who have obtained dimethylfluorenes from 2-nitro-2 : *x* : *y*-trimethyldiphenyls (*Gazzetta*, 1941, **71**, 289, 293, 297; cf. also *Atti R. Accad. Sci. Torino*, 1940—41, **76**, 66, 70).

Probably the greater reactivity of hydrogen in the α-position of the naphthalene nucleus than that in the methyl group accounts for the course taken in our fluoranthene synthesis.

As a model experiment fluoranthene was synthesised by this method. The method of preparing fluorenone-1-carboxylic acid by oxidation of fluoranthene (Fieser and Seligman, *J. Amer. Chem. Soc.*, 1935, **57**, 2174) has been improved.

(III) and (IV) have no growth-inhibitory effect (Badger, Elson, Haddow, Hewett, and Robinson, *Proc. Roy. Soc.*, 1942, *B*, **130**, 268, 270) and no carcinogenic activity (Badger, Cook, Hewett, Kennaway, Kennaway, and Martin, *ibid.*, 1942, *B*, **131**, 170).

EXPERIMENTAL.

Preparation of 2 : 4-*Dimethylfluoranthene* (III).—(a) *From* 2 : 2 : 4-*trimethyl*-1 : 2-*dihydrofluoranthene* (II). (II) (2 g.) mixed with selenium powder (0·7 g.) was heated at 300° for 5 hours. The product was extracted with boiling acetic acid; on cooling, faintly green plates separated and were recrystallised from ethanol, giving 2 : 4-*dimethylfluoranthene* (III), m. p. 113—115° (1·6 g.; yield, 80%). It slowly turns yellow superficially even when preserved in closed tubes (Found : C, 94·1; H, 6·3. $C_{18}H_{14}$ requires C, 93·9; H, 6·1%). Microhydrogenation of (III), using palladium in acetic acid, indicated 2·17 double bonds. (III) forms an orange *picrate* from ethanol, softening at 200°, melting at 206° (Found : C, 62·9; H, 3·9; N, 9·05. $C_{18}H_{14},C_6H_3O_7N_3$ requires C, 62·7; H, 3·7; N, 9·15%). (III) gives a *s*-trinitrobenzene *complex*, yellow needles from methanol, softening at 210°, melting at 223° (Found : C, 65·0; H, 3·8; N, 9·5. $C_{18}H_{14},C_6H_3O_6N_3$ requires C, 65·0; H, 3·8; N, 9·5%).

(b) *From* 2 : 2 : 4-*trimethyl*-1 : 2 : 3 : 4-*tetrahydrofluoranthene* (VII). (VII) (2 g.) was treated with selenium (1·3 g.) as under (a) above and similarly gave (III) (1·15 g.; yield, 60%). Similar results were obtained when sulphur was used; also a substance, which contained sulphur, was isolated as scarlet needles, m. p. > 250° (Found : C, 67·1; H, 3·3%).

Synthesis of 2 : 4-*Dimethylfluoranthene* (III).—1-*Iodo*-2 : 4-*dimethylnaphthalene*. 1 : 3-Dimethylnaphthalene (Barnett and Sanders, *J.*, 1933, 434) (5·2 g. purified by means of its picrate), sodium iodide (5 g.), and sodium nitrate (3·5 g.) were boiled in glacial acetic acid (100 ml.) until the iodine colour had disappeared (~ 1 hr.). The solution was poured into water, extracted with chloroform or carbon tetrachloride, and the washed extract distilled under reduced pressure. The fraction boiling at 139—144°/1 mm., a pale yellow oil, was retained as 1-iodo-2 : 4-dimethylnaphthalene (6·5 g.; yield 70%). The substance rapidly darkened owing to separation of iodine; accordingly, analyses were discordant.

1-(2-*Nitrophenyl*)-2 : 4-*dimethylnaphthalene*. 1-Iodo-2 : 4-dimethylnaphthalene (5 g.) and *o*-bromonitrobenzene (4 g.) were heated at 220—230°; copper bronze (6 g.) was added at intervals, and heating continued with occasional shaking for 2 hours. The mixture was finally heated at 270° for 10 minutes, then steam distilled to remove unchanged *o*-bromonitrobenzene, and the residue extracted with methanol (charcoal). On concentration of the solution, pale brown hexagonal prisms separated, and more grew during several days; the 1-(2-*nitrophenyl*)-2 : 4-*dimethylnaphthalene* crystallised from glacial acetic acid in lemon-yellow hexagonal plates, m. p. 119—120° (1·38 g.; yield, 28%) (Found : C, 77·85; H, 5·3; N, 5·2. $C_{18}H_{15}O_2N$ requires C, 78·0; H, 5·4; N, 5·0%).

1-(2-*Aminophenyl*)-2 : 4-*dimethylnaphthalene*. The nitro-compound prepared above (0·24 g.) was reduced by palladium black (0·1 g.) in glacial acetic acid (15 ml.) in 1 hour. The filtered solution, on being made alkaline with potassium hydroxide solution, gave a pale brown precipitate which was extracted with ether. Evaporation, extraction of the residue with dilute hydrochloric acid, extraction of this solution with ether, and treatment of the acid solution with alkali gave, after crystallisation from methanol diluted with a trace of water (scratching), slightly brown, thick, square-sided plates, of 1-(2-*aminophenyl*)-2 : 4-*dimethylnaphthalene*, softening at 107°, melting at 110°. The crystals contained methanol of crystallisation, and were dried in a vacuum at 70° before being analysed (0·12 g.; yield, 55%) (Found : C, 87·1; H, 6·8; N, 5·9. $C_{18}H_{17}N$ requires C, 87·4; H, 6·9; N, 5·7%).

The nitro-compound was also reduced by platinum (from PtO_2) in acetic acid; reduction was slower (4 hours) with palladium on strontium carbonate and ethanol. It was also reduced by stannous chloride in acetic acid saturated with hydrogen chloride, but the product was difficult to purify and the yield much lower than that obtained by catalytic reduction.

The *acetyl* derivative of the amine was obtained by boiling (1 minute) with acetic anhydride, and gave prisms from methanol, softening at 138°, melting at 142° (Found : C, 83·4; H, 6·6. $C_{20}H_{19}ON$ requires C, 83·1; H, 6·6%).

2 : 4-*Dimethylfluoranthene* (III). The above amine was diazotised with sodium nitrite and dilute sulphuric acid, and copper bronze added. The red solution was warmed until nitrogen evolution ceased; the solution became pale yellow (10 minutes), and brown solid aggregated about the copper powder. The solid was extracted by methanol to give a violet fluorescent solution from which there separated first oil and then crystalline nodules, or the solid was sublimed in a vacuum at 130—140°/11 mm., to give (III), which was identified by m. p., m. p. of a mixture with (III) prepared by method (a) above, and by its *s*-trinitrobenzene complex. The yield was very poor.

Synthesis of Fluoranthene.—α-Iodonaphthalene (7 g.), *o*-bromonitrobenzene (6 g.), and copper bronze (5 g.) were heated at 240—250° for 3 hours. The product, worked up as for the corresponding 2 : 4-dimethyl derivative above, gave pale yellow prisms from methanol, m. p. 88—90°, of 1-(2-*nitrophenyl*)*naphthalene* (Found : C, 77·0; H, 4·5; N, 5·8. $C_{16}H_{11}O_2N$ requires C, 77·1; H, 4·4; N, 5·6%). Reduction of this nitro-compound (1·20 g.) by palladium–strontium carbonate (0·5 g.) in acetone (10 ml.) for 6—7 hours followed by crystallisation of the product from light petroleum (b. p. 40—60°) gave, slowly, cream crystals of 1-(2-*aminophenyl*)*naphthalene*, softening at 61°, melting at 65° (0·74 g.; yield, 70%) (Found : C, 87·8; H, 6·0; N, 6·5. $C_{16}H_{13}N$ requires C, 87·7; H, 5·9; N, 6·4%). Reduction with stannous chloride in glacial acetic acid saturated with hydrogen chloride gave the amine in poorer yield (30%). Diazotisation of this amine as for the corresponding 2 : 4-dimethyl derivative but in acetic acid solution gave leaflets of fluoranthene (yield, ~ 48%) from methanol, but more concentrated solutions gave prisms which, alone or mixed with genuine fluoranthene, had m. p. 110°. The picrate, orange prisms from ethanol, had m. p. 182—183° alone or mixed with fluoranthene picrate.

2 : 3 : 4-*Trimethylfluoranthene* (IV)—(II) (0·62 g.) and phosphoric oxide (1·24 g.) were heated at 250° for 1½ hours. After treatment with water, extraction with glacial acetic acid gave a brown insoluble residue (0·24 g.) and a solution which deposited a dirty yellow solid, thereafter insoluble. The acetic acid filtrate mixed with excess of picric acid solution in acetic acid gave a scarlet precipitate which when treated with dilute ammonia solution and washed gave a canary-yellow solid. After crystallisation from glacial acetic acid it was necessary in order to obtain an analytically pure specimen to pass the benzene solution through a column of alumina and crystallise the recovered material from acetone and then from ethanol. The pale green crystals of 2 : 3 : 4-*trimethylfluoranthene* (IV) so obtained softened at

131° and melted at 133—134°, as did a mixture with the substance previously described but not identified (France, Maitland, and Tucker, *loc. cit.*, p. 1744) (Found : C, 93·4; H, 6·7. $C_{19}H_{16}$ requires C, 93·4; H, 6·6%). Micro-hydrogenation (palladium black–acetic acid) indicated the presence of 2·07 double bonds. With picric acid in ethanol (IV) gave needles of a scarlet *picrate*, m. p. 208° (Found : C, 73·6; H, 4·9; N, 5·9. $2C_{19}H_{16},C_6H_3O_6N_3$ requires C, 73·6; H, 4·9; N, 5·9%). (IV) with *s*-trinitrobenzene in ethanol gave fine yellow needles of the *complex*, m. p. 228—230° (Found : C, 65·7; H, 4·4; N, 9·2. $C_{19}H_{16},C_6H_3O_6N_3$ requires C, 65·6; H, 4·2; N, 9·2%).

Oxidation of (III).—(III) (0·57 g.), sodium dichromate (6 g.), and glacial acetic acid (25 ml.) were boiled for 9 hours and the mixture worked up as previously described (France, Tucker, and Forrest, *loc. cit.*, p. 10), giving 1-acetylfluorenone (0·02 g.) and fluorenone-1-carboxylic acid (0·16 g.; yield, 29%).

Oxidation of (IV).—(IV) (0·49 g.), sodium dichromate (6 g.), and glacial acetic acid (25 ml.) were boiled for 18 hours. Working as above, 1-acetylfluorenone (0·01 g.) and fluorenone-1-carboxylic acid (0·24 g.; yield, 54%) were isolated. In each of the above experiments the identity of the 1-acetylfluorenone was established by m. p. of a mixture with previously analysed material, and by conversion, by means of iodine and dilute potassium hydroxide solution in methanol, into iodoform and the salmon-pink fluorenone-1-carboxylic acid.

Fluorene-1-*carboxylic Acid.*—Fluorenone-1-carboxylic acid (5 g.), lightly amalgamated granulated zinc (12 g.), and a mixture of glacial acetic acid and concentrated hydrochloric acid (1 : 1 by vol.; 150 ml.) were boiled vigorously for 1 hour. The colourless solution was poured into dilute acid and the precipitated solid crystallised from glacial acetic acid to give fluorene-1-carboxylic acid, m. p. 245° (4·5 g.; yield, 95%) (cf. Fieser and Seligman, *loc. cit.*). The *amide*, prepared in the usual way, crystallised from glacial acetic acid in laminae softening at 240°, melting at 249° (Found : C, 80·4; H, 5·4; N, 6·7. $C_{14}H_{11}ON$ requires C, 80·4; H, 5·3; N, 6·7%).

9-*Fluorenol*-1-*carboxylic Acid.*—(*a*) Fluorenone-1-carboxylic acid (16·8 g.) was reduced by magnesium (10 g.) in lime-dried, boiling methanol (300 ml.). The reaction, which was apt to be vigorous, gave a green then pale brown solution. It was poured into 25% hydrochloric acid. The precipitated alcohol-acid (16·4 g.; yield, 97%) was pure enough for subsequent use, but much was lost in complete purification by dissolving it in methanol, concentrating the solution, and adding 3 times the volume of hot glacial acetic acid to give 9-*fluorenol*-1-*carboxylic acid* (8·05 g.; yield, 48%). The acid crystallised from toluene, then softened at 184°, melting at 196° (Found : C, 74·5; H, 4·5. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·4%).

(*b*) Fluorenone-1-carboxylic acid was hydrogenated by means of hydrogen and Raney nickel (Pavlic and Adkins, *J. Amer. Chem. Soc.*, 1946, **68**, 1471) in a mixture of ethanol (previously left over Raney nickel) and 10% potassium hydroxide solution. Absorption was rapid. Again, nearly theoretical yields of the practically pure alcohol-acid were obtained, but again purification caused considerable loss.

Similarly, fluorenone (0·9 g.) by means of Raney nickel (~ 1 g.) in ethanol (purified by Raney nickel; 40 ml.) containing 10% potassium hydroxide solution (1 ml.) was reduced in 5 minutes to fluorenol (0·73 g.; yield, 80%) (cf. Delépine and Horeau, *Bull. Soc. chim.*, 1937, **4**, 43, who dispensed with alkali but worked at 96°). We find that reduction at room temperature is incomplete in 55 minutes in absence of alkali. Addition of platinic chloride had apparently no effect (cf. *idem, loc. cit.*; Smith and Lieber, *J. Amer. Chem. Soc.*, 1936, **58**, 1417; Reasenberg, Lieber, and Smith, *ibid.*, 1939, **61**, 384). Reduction of fluorenone by means of palladium on charcoal (5%) (Cheronis and Levin, *J. Chem. Educ.*, 1944, **21**, 606) was slow. Thus with the quantities given above, but with palladium–charcoal (0·2 g.) in place of Raney nickel, reduction took 4 hours, but the yield of (nearly pure) fluorenol was ~ 90% (cf. also Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 773; Miller and Bachman, *ibid.*, 1935, **57**, 770; France, Maitland, and Tucker, *loc. cit.*, p. 1741).

9-*Chlorofluorene*-1-*carboxyl Chloride.*—9-Fluorenol-1-carboxylic acid (3·2 g.) in chloroform (30 ml.) was treated portionwise with phosphorus pentachloride (10 g.); the mixture, after being boiled for ½ hour, was cooled in ice, the separated crystalline product extracted with hot chloroform (in which 9-chlorofluorene-1-carboxylic acid is insoluble), and the solution left to crystallise. More crystals were obtained by subsequently treating the filtered solution with light petroleum (b. p. 60—80°). 9-*Chlorofluorene*-1-*carboxyl chloride* was obtained in faintly greenish prisms, softening at 145°, and melting at 158° (2·43 g.; yield, 64%) (Found : C, 63·8; H, 3·0. $C_{14}H_8OCl_2$ requires C, 63·9; H, 3·0%). Treatment of this acid chloride with hot glacial acetic acid gave large prisms of 9-*chlorofluorene*-1-*carboxylic acid* (100%) which softened at 190°, and melted with effervescence at 242° (Found : C, 68·5; H, 3·6. $C_{14}H_9O_2Cl$ requires C, 68·7; H, 3·7%).

Methyl 9-*chlorofluorene*-1-*carboxylate*, produced by boiling the above acid chloride with absolute methanol until a clear solution was obtained, separated, on cooling, in long needles, m. p. 89—92° (yield, 100%) (Found : 69·5; H, 4·1. $C_{15}H_{11}O_2Cl$ requires C, 69·7; H, 4·25%).

9-*Bromofluorene*-1-*carboxylic Acid.*—9-Fluorenol-1-carboxylic acid (8 g.) was dissolved in warm glacial acetic acid (45 ml.) and saturated with dry hydrogen bromide. The crystalline *bromo*-compound which separated crystallised from glacial acetic acid in faintly yellow stout prisms which decomposed slightly at 218° and were molten at 242° (8·7 g.; yield, 85%) (Found : C, 58·2; H, 3·3; Br, 27·5. $C_{14}H_9O_2Br$ requires C, 58·1; H, 3·1; Br, 27·7%).

9-*Bromofluorene*-1-*carboxyl Chloride.*—9-Bromofluorene-1-carboxylic acid (10 g.) in chloroform (60 ml.) was treated with phosphorus pentachloride (10 g.), the solution being then boiled until all the acid had dissolved and hydrogen chloride ceased to be evolved. The liquor, decanted from unchanged phosphorus pentachloride, was treated with light petroleum (b. p. 60—80°); the crystals of the *acid chloride* so obtained recrystallised from benzene in thick prismatic plates, m. p. 169—172° (8·3 g.; yield, 85%) (Found : C, 54·7; H, 2·7; Cl + Br, 37·7. $C_{14}H_8OClBr$ requires C, 54·6; H, 2·6; Cl + Br, 37·5%).

Methyl 9-*bromofluorene*-1-*carboxylate*, prepared as described for the corresponding chloro-compound, separated from methanol in long needles, m. p. 102—104° (1·9 g.; yield, 97%) (Found : C, 59·6; H, 3·8; Br, 26·5. $C_{15}H_{11}O_2Br$ requires C, 59·4; H, 3·6; Br, 26·4%).

9-*Bromofluorene*-1-*carboxyamide*, prepared in the usual way from the acid chloride and ammonia, crystallised from glacial acetic acid in felted needles, m. p. 238° (decomp.) (Found : C, 58·6; H, 3·7; N, 5·0; Br, 27·6. $C_{14}H_{10}ONBr$ requires C, 58·4; H, 3·5; N, 4·9; Br, 27·8%).

9-*Iodofluorene*-1-*carboxylic acid* was prepared by the action of sodium iodide on 9-bromofluorene-1-carboxylic acid in acetone solution. It crystallised from acetone in yellow needles, m. p. 175° (decomp.) (yield, 80%) (Found : I, 37·6. $C_{14}H_9O_2I$ requires I, 37·7%).

Ethyl 9-*Chlorofluorene*-1-*carbonylacetoacetate*.—9-Chlorofluorene-1-carboxyl chloride (0·66 g.) was added solid to a gelatinous suspension of ethyl sodioacetoacetate [from sodium (0·06 g.) and ethyl acetoacetate (0·33 g.)] in ether (10 ml.). After thorough shaking the mixture was boiled for 2 hours. Very dilute acetic acid was added to render the solution acid, the ethereal layer was thoroughly washed to remove acid, and after evaporation to dryness the residue was crystallised from glacial acetic acid. The *product* was extracted with light petroleum (b. p. 60—80°), filtered from an insoluble residue, and allowed to crystallise to give clusters of faintly cream-coloured prisms, softening at 130°, melting at 133—134° (0·3 g.; yield, 33%) (Found : C, 67·4; H, 4·8; Cl, 9·7. $C_{20}H_{17}O_4Cl$ requires C, 67·3; H, 4·8; Cl, 10·0%).

3-(9-*Chlorofluorene*-1-*carbonyl*)*butan*-2-*one*.—A suspension of 9-chlorofluorene-1-carboxyl chloride (0·26 g.) in ether (20 ml.) and ethyl sodiomethylacetoacetate [(from sodium (0·06 g.) and ethyl methylacetoacetate (0·36 g.)] was boiled for ½ hour. The whole was treated with very dilute acetic acid and the ether extract evaporated. The residual *compound* crystallised from light petroleum (b. p. 60—80°) in large colourless rhombohedra, m. p. 131—132°. The absence of colour and lowered m. p. of a mixture showed it to be different from the lower homologue above described (Found : C, 72·2; H, 5·3; Cl, 11·75. $C_{18}H_{15}O_2Cl$ requires C, 72·4; H, 5·0; Cl, 11·9%). A small amount of material insoluble in light petroleum was shown to be 9-chlorofluorene-1-carboxylic acid, m. p. 242°.

Ethyl 9-*Bromofluorene*-1-*carbonylacetoacetate*.—9-Bromofluorene-1-carboxyl chloride (6 g.) was added to ethyl sodioacetoacetate (6·1 g., *i.e.*, excess) suspended in ether (100 ml.) and the mixture boiled for 3 hours. The *product* obtained in the usual way crystallised from methanol in cream-coloured prisms, m. p. 128—130° (Found: C, 59·7; H, 4·2; Br, 20·1. $C_{20}H_{17}O_4Br$ requires C, 59·9; H, 4·2; Br, 19·9%).

Ethyl 9-iodofluorene-1-carbonylacetoacetate was prepared from the above bromo-compound by treatment with sodium iodide in acetone; it crystallised from methanol in yellow prisms, m. p. 115—120°. Owing to its instability, analytical results were valueless.

Oxidation of Fluoranthene to Fluorenone-1-*carboxylic Acid*.—A solution of chromic acid (7 g., *i.e.*, 30% excess) in water (5 ml.) and glacial acetic acid (5 ml.) was added during 10 minutes to a boiling solution of fluoranthene (2·02 g.) in glacial acetic acid (25 ml.), the residual oxidising mixture being rinsed in with more (5 ml.) glacial acetic acid. After being boiled for a further hour the hot mixture was poured into dilute sulphuric acid (1 : 4 v/v, 200 ml.). After cooling, the precipitated solid was collected, washed with dilute acid and water, dissolved in ammonia solution, the solution filtered from a very small amount of insoluble material, and the acid reprecipitated with sulphuric acid solution. It was nearly pure; m. p. 185° (yield, 73%). Purification by crystallisation from glacial acetic acid resulted in a 5—10% loss. The use of an oxidising mixture consisting of sodium dichromate (12 g., *i.e.*, 50% excess), water (7 ml.), glacial acetic acid (10 ml.), and concentrated sulphuric acid (2 ml.) gave slightly higher yields of the acid, but owing to separation of inorganic salts the solutions bumped badly, and accordingly this modification is not recommended.

Ethyl fluorenone-1-*carboxylate* was prepared from the acid, ethanol, and hydrogen chloride; it crystallised from methanol in greenish-yellow rods, m. p. 85—86° (Found : C, 76·3; H, 5·0. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%). It gave a *semicarbazone* which crystallised from ethyl acetate as a mixture of feathery and prismatic crystals which softened at 180° and melted at 202° (Found : C, 65·8; H, 4·9. $C_{17}H_{15}O_3N_3$ requires C, 66·0; H, 4·9%). A 2 : 4-*dinitrophenylhydrazone* crystallised from glacial acetic acid in salmon-red leaflets, softening at 248° and melting at 253° (Found : C, 61·1; H, 3·9; N, 13·0. $C_{22}H_{16}O_6N_4$ requires C, 61·1; H, 3·7; N, 13·0%).

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