

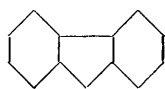
366. The Condensation of Fluorene with Acetone. Part II.

By HAROLD FRANCE, PETER MAITLAND, and S. HORWOOD TUCKER.

Fluorene reacts with acetone in the presence of potassium hydroxide. The acetone apparently condenses to form mesityl oxide, which, by a Michael reaction, combines with the fluorene, giving the compound (I). The action of certain reagents on (I) has given unexpected compounds, whose constitutions are being elucidated.

FLUORENE has been condensed with many aromatic aldehydes (Thiele, *Ber.*, 1900, **33**, 851; Thiele and Henle, *Annalen*, 1906, **347**, 290) by means of alcoholic sodium ethoxide or alcoholic alkali hydroxide, water being removed and the unsaturated compound formed. These authors (p. 291) state that fluorene does not react with aliphatic aldehydes or with aliphatic or aromatic ketones under these conditions. The same applies to 2:7-dibromofluorene (Siegitz, *Ber.*, 1920, **53**, 1232). It was found, however (Maitland and Tucker, *J.*, 1929, 2559), that when powdered potassium hydroxide was added to a solution of fluorene in acetone a vigorous reaction set in, and a white crystalline compound, $C_{19}H_{20}O$, m. p. 77—78°, was isolated (50% yield) together with a mixture of acetone condensation products—mesityl oxide, isoacetophorone, and higher-boiling materials having been characterised.

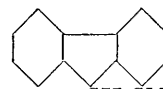
The compound, m. p. 77—78°, is methyl β -9-fluorenyl- β -methyl-*n*-propyl ketone (I), and is probably formed as a result of a Michael condensation of fluorenylpotassium and mesityl oxide (produced from acetone). This view has been confirmed by the synthesis of (I) by



CH·CMe₂·CH₂·COMe
(I.)



HO·C·CMe₂·CH₂·COMe
(II.)



CH·CMe₂·CH₂Et
(III.)

the condensation of (1) fluorene with mesityl oxide under comparable conditions (when pyridine was added, the yield was raised from 12 to 20%; it is still far below the 50% yield obtained with acetone), and (2) fluorenylsodium with mesityl oxide.

Methyl β -9-fluorenyl- β -methyl-*n*-propyl ketone (I) underwent the following reactions: (a) Dry distillation gave acetone, mesityl oxide, and fluorene—the simplest form of reversed Michael reaction (cf. Vorländer, *Ber.*, 1900, **33**, 3185; *Annalen*, 1906, **345**, 155; Ingold and Powell, *J.*, 1921, **119**, 1976; Linstead, *J.*, 1929, 2504). Similarly, by heating with concentrated alcoholic potassium hydroxide solution, fluorene was obtained.

(b) Heating with sodium in xylene (or potassium in benzene) gave rise to fluorene and isopropylidene-fluorene, m. p. 110—113° (Maitland and Tucker, *loc. cit.*, p. 2563).

(c) The presence of the keto-group was proved by the formation of an oxime, a semicarbazone, and a 2:4-dinitrophenylhydrazone, but a phenylhydrazone could not be obtained. The colour reactions of ketones (Täufel and Thaler, *Z. physiol. Chem.*, 1932, **212**, 256) containing the group CH₂·CO·CH₂ was positive for acetone but negative for (I). The presence of CH₂·CO was indicated by the ready condensation with piperonal and with 6-bromopiperonal in alkaline alcoholic solution. Whether the compounds contain the group R·CH·C·CO·CH₃ or CH₂·CO·CH·CHR was not investigated, but the latter is more likely for steric reasons. The substance (I) in solution appears to contain no enolic modification, since it failed to react with acid chlorides or phenyl isocyanate and gave no gas when treated with methylmagnesium iodide. Attempts to convert the terminal

CO·CH₃ group into CO₂H failed (cf. Ramage and Simonsen, J., 1935, 1583, for failure with a comparable side chain), but sodium hypobromite gave a smell of bromoform and sodium hypoiodite gave iodoform (test according to Fuson, *Chem. Rev.*, 1934, 15, 275; Fuson and Tullock, *J. Amer. Chem. Soc.*, 1934, 56, 1638; 1935, 57, 919).

(d) Bromination gave *mono-*, *di-*, and *tri-bromo-*substitution products. Oxidation of these (sodium dichromate and glacial acetic acid) gave fluorenone, proving that substitution was entirely in the side chain. Since the tribromo-derivative might conceivably contain the group CO·CBr₃, it was heated with aqueous potassium hydroxide to effect the change to CO₂H, but without avail.

(e) Oxidation with potassium permanganate in acetone solution gave a crystalline compound, C₁₉H₂₀O₂, m. p. 120—122°, which is possibly methyl β-9-hydroxy-9-fluorenyl-β-methyl-*n*-propyl ketone (II); it was not further investigated. Oxidation of (I) with sodium dichromate in glacial acetic acid solution gave fluorenone.

(f) Reduction by the Clemmensen or the Kischner-Wolff method gave β-9-fluorenyl-β-methylpentane (III), m. p. 84—85°, whose constitution was confirmed by two syntheses: (i) reaction between αα-dimethylbutylmagnesium chloride and fluorenone, with subsequent hydrolysis and reduction with hydriodic acid; (ii) reaction between αα-dimethylbutyl chloride and sodiofluoreneoxalic ester (or potassiofluorene-carboxylic ester), followed by hydrolysis.

(g) Hydriodic acid gave, instead of the expected compound C₁₉H₂₂ (III), a substance, C₁₉H₂₀, m. p. 103—104°, which was also obtained in small yield by the Clemmensen reduction of (I). It is a saturated compound, since it did not react with hydrogen in the presence of a palladium catalyst. Dry hydrogen bromide in glacial acetic acid reacted with (I) to give crystals which spontaneously, in air, lost hydrogen bromide, giving a substance, C₁₉H₁₈, m. p. 77—79°. This, on reduction, gave the substance C₁₉H₂₀.

(h) Heating with zinc chloride gave not only the saturated substance, C₁₉H₂₀, m. p. 103—104°, but also a yellow substance, C₁₆H₁₄(?), m. p. 131—133°. Phosphoric oxide acted similarly, but gave only the substance, m. p. 131—133°. This appears to be saturated, since it does not decolorise potassium permanganate solution.

Attempts to reduce the *oxime* of (I) failed. The Beckmann transformation of the oxime gave a product, C₁₉H₂₁ON, m. p. 167—169°, which, however, failed to give an isolable acid on hydrolysis.

2 : 7-Dibromofluorene could not be condensed with acetone, although Sieglitz (*loc. cit.*) has shown that with aromatic aldehydes 2 : 7-dibromofluorene reacts more readily than fluorene. Fluorene and methyl ethyl ketone also failed to give a condensation product.

The condensation of indene and acetone is being investigated.

EXPERIMENTAL.

*Methyl β-9-Fluorenyl-β-methyl-*n*-propyl Ketone* (I).—(a) *Condensation of fluorene and acetone.* Fluorene (20 g.) was dissolved in warm acetone (120 c.c.) in a large beaker, the solution allowed to cool somewhat—but without separation of fluorene—and fused (stick), finely powdered potassium hydroxide (80 g.; or 160 g. of laboratory powder, which invariably contains moisture) stirred in rapidly. The solution became deep blue-green, the acetone boiled vigorously, and, almost immediately after the violence of the reaction had subsided, the mixture thickened. An equal volume of cold water was *at once* added. The green oil which separated was removed and washed several times with 50% sulphuric acid (to remove acetone, mesityl oxide, and other acetone condensation products), the thick orange oil thus obtained was extracted with ether, and the extract washed with aqueous sodium carbonate, then with water, dried (sodium sulphate), and evaporated. The oily solid obtained crystallised from acetic acid or alcohol in colourless needles, m. p. 77—78° (15.5 g.; 50% yield) (Found: C, 86.4; H, 7.65; *M*, cryoscopic in benzene, 259. C₁₉H₂₀O requires C, 86.4; H, 7.6%; *M*, 264).

When, in early experiments, the sulphuric acid used as above was dilute, the condensation products were not removed and (I) could not be isolated from the oil. If, however, the oil was steam-distilled, (I) (which distils very slowly) was left behind in a form which could be easily crystallised. The acetone condensation products distilled: of these, mesityl oxide, phorone, and isophorone (giving two oximes, m. p.'s 74—75° and 99—100°; Bredt, *Annalen*, 1898, 299, 170; Kerp and Müller, *ibid.*, p. 219) were identified.

(b) *Condensation of fluorene and mesityl oxide.* Fluorene (10 g.) was dissolved in warm mesityl oxide (30 c.c.) (prepared by distilling diacetone alcohol with a crystal of iodine), pyridine (2 or 3 drops) added, then potassium hydroxide (fused, powdered; 30 g.) with vigorous stirring. The mixture darkened at once and the reaction became violent, but judicious cooling prevented charring (which is inevitable if the reaction gets out of control). When the mixture became semi-solid, it was worked up as above. The product (15—20% yield) melted at 77—78° alone or mixed with that obtained by process (a). When pyridine was omitted, the reaction was more violent and the yield reduced to 12%. When piperidine (a few drops) replaced pyridine, only a trace of (I) was obtained.

The possibility that in the condensation of mesityl oxide with fluorene the former is decomposing into acetone, which then condenses with the latter, as shown under (a), is rendered unlikely by the observation that mesityl oxide (10 c.c.), treated with potassium hydroxide under the above conditions of experiment (but omitting fluorene), gave only a trace of acetone (3—5 drops). The possibility that continuous removal (by fluorene) of acetone as soon as it is formed might enable the reaction to go to completion cannot apply in method (c).

No condensation of fluorene and mesityl oxide (in absence of potassium hydroxide) could be effected by molar quantities of piperidine, sodium ethoxide or sodamide (for lack of reactivity of mesityl oxide in analogous cases, see Rapson, J., 1936, 1626).

(c) *Condensation of fluorenylsodium and mesityl oxide.* Fluorenylsodium was prepared thus: Fluorenone \rightarrow fluorenol \rightarrow 9-bromofluorene \rightarrow 9-methoxyfluorene \rightarrow fluorenylsodium.

Fluorenol. Magnesium turnings (35 g.; excess) were added, with cooling, to a solution of fluorenone (70 g.) in methyl alcohol (1 l.) at 45°. The mixture was heated for 2 hours, an excess of acetic acid added to dissolve unchanged magnesium and magnesium methoxide, methyl alcohol removed by distillation, and the residue treated with excess of water. The white precipitate obtained crystallised from benzene or alcohol in colourless needles, m. p. 154—156° (containing benzene of crystallisation, removed at 100°).

9-Methoxyfluorene. Kliegl (*Ber.*, 1929, 62, 1327) gives a method of preparation from 9-chlorofluorene. 9-Bromofluorene (5 g.) and silver nitrate (3.4 g., finely powdered) were refluxed in methyl alcohol (100 c.c.) for $\frac{1}{2}$ hour. The filtered solution was poured into water; the oil which separated solidified in ice and crystallised from ligroin in white needles, m. p. 42—43° (3.4 g.; 85% yield).

Fluorenylsodium. This was prepared by the Schlenk technique (Houben-Weyl, 1924, Vol. IV, pp. 957—965), 9-methoxyfluorene being acted upon with atomised sodium in dry ether (distilled from phosphoric oxide) and an atmosphere of pure dry nitrogen (cf. benzhydrylsodium; Bergmann, J., 1936, 412). After 48 hours' shaking, the solution became dark red-brown. It was filtered, from one Schlenk tube to another, through an intermediate straight "calcium chloride tube" packed with ignited asbestos, this being found preferable to a sinter disc tube.

Mesityl oxide (0.75 g.) was added to a solution of fluorenylsodium (from 1.5 g. of 9-methoxyfluorene) in ether contained in a Schlenk tube (nitrogen atmosphere), which was then sealed. After 48 hours, the solution was treated with water and the ethereal solution was separated, washed with dilute acid and with water, and dried. Evaporation gave an orange oil, which on crystallisation from alcohol gave fluorene (0.8 g.), then colourless needles of (I), m. p. 77—78° (0.5 g.; 55% yield, calc. on unrecovered fluorene). Its identity was confirmed by the mixed m. p. method.

9-Benzoylfluorene (m. p. 136—138°; Werner, *Ber.*, 1906, 39, 1287) was similarly obtained by the action of fluorenylsodium on benzyl benzoate.

Attempts were made to condense 9-fluorenyldimethylcarbinyl chloride (Courtot, *Ann. Chim.*, 1915, 4, 162). The yield is improved by keeping the alcoholic solution of the carbinol cold during the passage of hydrochloric acid and also the corresponding bromide (Maitland and Tucker, *loc. cit.*, p. 2563) with sodioacetoacetic ester, but without avail.

Dry Distillation of (I).—Gentle heating of (I) (50 g.) during 4 hours gave a distillate, which was fractionated into acetone (4 c.c.) and mesityl oxide (6 c.c.), the latter being identified by its semicarbazone (m. p. 156°). The solid residue was fluorene.

Fluorene (m. p. 115°; 2—2.5 g.) was likewise obtained by boiling (I) (10 g.) with potassium hydroxide (20 g.) in alcohol (20 c.c.) for 5 minutes and acidifying and steam-distilling the product. (I) remained unchanged after boiling with sulphuric acid solutions (10—50%).

Action of Sodium on (I).—The substance (1 g.) was heated with atomised sodium in xylene (4 c.c.) for 4 hours. A good yield of fluorene was obtained.

Action of Potassium on (I).—The substance (2 g.) was heated with atomised potassium (0.4 g.)

in benzene (50 c.c.) for 8 hours. The mixture turned red. After filtration and removal of benzene by distillation, the residue was crystallised from excess of alcohol and gave, first, long orange-yellow needles of 9-isopropylidene-fluorene (m. p. 113—117°) and then, on evaporation, fluorene.

9-isoPropylidene-fluorene, on keeping, turns to an oil, which after successive crystallisation from alcohol and ligroin, gives yellow plates of fluorenone, m. p. 80—82°.

Piperonylidene Derivative of (I).—The substance (4 g.) and piperonal (2.5 g.) were dissolved in alcohol (25 c.c.), 20% sodium hydroxide solution (0.3 c.c.) added, and the mixture boiled ($\frac{1}{2}$ —1 hour) and concentrated. The crystals obtained on cooling were recrystallised from alcohol or alcohol-glacial acetic acid until very faintly green cubes were obtained, m. p. 167—168° (Found : C, 81.7; H, 6.1. $C_{27}H_{24}O_3$ requires C, 81.8; H, 6.1%).

The 6-bromopiperonylidene derivative was similarly prepared (Found : Br, 16.9. $C_{27}H_{23}O_3Br$ requires Br, 16.8%).

Oxidation of (I).—(a) *With potassium permanganate in acetone.* The substance (20 g.) was dissolved in acetone (200 c.c., purified by boiling with potassium permanganate, drying, and distillation), and potassium permanganate (40 g.) added during 10 hours. After filtration, and addition to the filtrate of an acetone extract of the residue, evaporation gave an oil. Crystallisation of this from alcohol gave, first, unchanged material, then crops of mixed prisms and needles. Warming with alcohol removed the needles. The prisms on recrystallisation gave the compound (II) (1 g.), m. p. 120—122°. It was neutral to litmus (Found : C, 81.1; H, 7.2. $C_{19}H_{20}O_2$ requires C, 81.4; H, 7.1%).

(b) *With sodium dichromate in glacial acetic acid.* The substance (I) (5 g.) was boiled with sodium dichromate (40 g.) in glacial acetic acid (200 c.c.) for 5 hours, and the product poured into water. A chloroform extract, on steam distillation, gave fluorenone.

(c) Hypobromite and hypoiodite acted on (I) to give bromoform and iodoform respectively, but no other products could be isolated.

Reduction of (I).—(i) *Kischner-Wolff method.* Schönberg's modification (*Ber.*, 1921, 54, 2838) of the method was used. The semicarbazone of (I) (colourless rods, m. p. 218°, from alcohol. 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%) (5 g.) was heated with sodium ethoxide (1.5 g. of sodium in 20 c.c. of ethyl alcohol) in a sealed tube at 200° for 12 hours : a high pressure developed and an inflammable gas was formed. The partly crystalline product was treated with an excess of dilute hydrochloric acid, and the precipitated solid crystallised from alcohol. It was β -9-fluorenyl- β -methylpentane (III) (1.9 g.), m. p. 84—85° (Found : C, 91.0; H, 8.8; M, 221. $C_{19}H_{22}$ requires C, 91.2; H, 8.8%; M, 250).

(ii) *Clemmensen method.* The substance (I) (10 g.) and amalgamated zinc (150 g.) were heated for 12 hours with concentrated hydrochloric acid (addition of anisole was without advantage; cf. Robinson and Ramage, *J.*, 1933, 608), hydrogen chloride being passed in from time to time and more zinc added after the first 6 hours. After cooling, the whole was extracted with ether. The extract, washed with sodium carbonate solution, gave a yellow oil, which was dissolved in hot alcohol (charcoal); on slow cooling, a greenish-yellow oil separated, followed by tufts of white needles. These, together with a small amount of oil, were recrystallised from alcohol, giving white needles, m. p. 84—85°, of β -9-fluorenyl- β -methylpentane (III). Further crops of crystals, on recrystallisation from methyl alcohol or acetone, gave colourless needles of a substance, m. p. 103—104° (Found : C, 91.9; H, 8.1; M, 246. $C_{19}H_{20}$ requires C, 91.9; H, 8.1%; M, 248).

(iii) *By hydriodic acid.* A solution of the substance (I) (2 g.) in glacial acetic acid (70 c.c.) and hydriodic acid (*d* 1.7; 4 c.c.) was boiled under reflux for 2—3 hours. It was then poured into excess of sulphurous acid, the solution extracted with ether, and the extract made alkaline with concentrated sodium carbonate solution, washed with water, and dried (sodium sulphate). Evaporation left an oily solid, which crystallised from methyl alcohol in long white needles (0.4—0.5 g.), m. p. 103—104°, identical with the substance $C_{19}H_{20}$ described under (ii).

Attempts to reduce (I) by sodium in alcohol or by means of isopropylmagnesium bromide or cyclohexylmagnesium bromide (Gilman and Zoellner, *J. Amer. Chem. Soc.*, 1931, 53, 1945) were unsuccessful.

Syntheses of β -9-Fluorenyl- β -methylpentane (III).—(i) *From fluorenone and α -dimethylbutyl chloride.* Dimethylpropylcarbinol (Deschamps, *J. Amer. Chem. Soc.*, 1920, 42, 2670—the compound he describes as the phenylurethane of dimethylpropylcarbinol is, we find, diphenylurea; cf. Fessler and Shriner, *ibid.*, 1936, 58, 1384) was obtained in the usual way from acetone (145 c.c., purified by distillation of its sodium iodide compound) and the Grignard reagent prepared from *n*-propyl bromide (181 c.c.), magnesium (48 g.), and ether (500 c.c.). The yield of carbinol,

b. p. 121—125°, was 139 g. (62%). The carbinol (40 g.) was converted into α -dimethylbutyl chloride (Schreiner, *J. pr. Chem.*, 1910, **82**, 292) by addition of concentrated hydrochloric acid (130 c.c.); in a few seconds the clear liquid became turbid and separated into two layers. The mixture, after boiling for $\frac{1}{2}$ hour, was left for a day and the upper layer was removed, washed with water, shaken with concentrated sulphuric acid, kept until all acid had separated, and distilled. The chloride (40 g.), b. p. 111—113°, was thus obtained without fume. The washing with sulphuric acid removes carbinol, which otherwise causes fuming by reaction with the chloride.

A Grignard solution was prepared from the above chloride (10 c.c.), magnesium (1.5 g.), ether (15 c.c.), and a crystal of iodine. It was decanted from unchanged magnesium, and finely powdered fluorenone (6 g.) sifted in during 1 hour (ice). Next day, more ether (20 c.c.) was added, and the mixture boiled for 2 hours and worked up in the usual way. The oil obtained, on distillation in a vacuum, gave fluorenone and then an oil (1 g., b. p. 210—240°/25 mm.) which could not be crystallised. It was boiled with hydriodic acid (4 c.c.), red phosphorus (2 g.), and glacial acetic acid (40 c.c.) for 2 hours. After filtration and treatment with sulphurous acid, a sticky solid separated, which crystallised from alcohol and proved to be (III), m. p. 84—85°.

(ii) *From sodiofluoreneoxalic ester and α -dimethylbutyl chloride.* Sodium (1.2 g.) was dissolved in ethyl alcohol (25 c.c.) on the water-bath, and fluorene (8.4 g.) added, followed by ethyl oxalate (7.4 g.), which converted the white pasty mass into an orange solution of sodiofluoreneoxalic ester. This was heated on the boiling water-bath ($\frac{1}{2}$ hour), and α -dimethylbutyl chloride (10 g., excess) added; after 2—3 hours at 100° there was a considerable precipitate of sodium chloride, due to decomposition of the tertiary chloride, confirmed by the typical olefinic smell. The mixture was treated with water, and the oil which separated boiled with 20% sodium hydroxide solution for 1—2 hours. The mixture was extracted with ether, the inorganic matter removed and extracted with ether, and the combined extracts clarified (charcoal), dried (sodium sulphate), and allowed to evaporate in stages; the first crops of crystals were fluorene; later crops on recrystallisation from alcohol gave (III), m. p. 84—85° (0.3—0.4 g.; 5% yield). The identity of these synthetic products with that obtained by the Kischner-Wolff method was confirmed by the method of mixed m. p.'s.

(III) was synthesised similarly from potassiofluorene-carboxylic ester and α -dimethylbutyl chloride, but in very poor yield.

9-Fluorenyldimethylcarbinyl iodide, prepared by mixing 9-fluorenyldimethylcarbinol with a cold solution of hydriodic acid (*d* 1.7), separated in yellow needles after several hours and crystallised from ligroin (b. p. 70—80°) in colourless rods, m. p. 95—97° with evolution of iodine (Found: I, 38.1. $C_{16}H_{15}I$ requires I, 38.0%). It decomposed on standing, giving iodine.

Synthesis of tert.-Butylfluorene.—The method was essentially that described under (ii), sodiofluoreneoxalic ester and *tert.*-butyl iodide (15 g.) or *tert.*-butyl chloride (10 g.) being used. No decomposition of the tertiary compounds was observed and white needles (2%), m. p. 101—102°, were obtained from acetic acid or methyl alcohol. *tert.*-Butylfluorene could not be obtained when sodiofluorene-carboxylic ester was used.

Action of Hydrogen Bromide on (I).—Hydrogen bromide was passed into a solution of (I) (5 g.) in glacial acetic acid (50 c.c.) for 4 hours; crystals began to separate after about $\frac{1}{2}$ hour (when removed, these lost hydrogen bromide spontaneously, but their m. p. taken at once was 95—105°). Next day, the solid was collected and heated at 100° in a stream of air until hydrogen bromide was no longer evolved (1 hour). The brown solid left was dissolved in alcohol (charcoal), and finally obtained from methyl alcohol in white rods of a *substance* (2.9 g.), m. p. 77—79° (Found: C, 92.7; H, 7.3; *M*, 256. $C_{19}H_{18}$ requires C, 92.7; H, 7.3%; *M*, 246).

Oxidation of the Substance $C_{19}H_{18}$, m. p. 77—79°.—A solution of the substance (1 g.) in acetone (20 c.c., purified by boiling with potassium permanganate) containing a trace of water and potassium permanganate (3 g.) was boiled for 3—4 hours, poured into water, made alkaline with sodium hydroxide, filtered, extracted with ether, acidified with sulphuric acid, and extracted with ether. Evaporation left a yellow oil, which crystallised from acetic acid, on dilution with water, in short colourless prisms of a *substance*, m. p. 163—164° (20% yield) (Found: C, 77.4; H, 6.2. $C_{19}H_{18}O_3$ requires C, 77.5; H, 6.1%). This substance was an acid. It gave the iodo-form reaction, and a precipitate with 2:4-dinitrophenylhydrazine.

Catalytic Hydrogenation of $C_{19}H_{18}$ to $C_{19}H_{20}$.—The substance $C_{19}H_{18}$ (4 g.) was dissolved in warm glacial acetic acid (100—150 c.c.) and treated with hydrogen in presence of a palladium catalyst prepared from palladous chloride (0.2 g.); occasional warming was necessary to maintain solution. The volume of hydrogen absorbed was somewhat in excess of that required

for the reduction of the double bond, but the yield of the hydrocarbon $C_{19}H_{20}$, m. p. 103—104°, was 95% of the theoretical.

Action of Zinc Chloride on (I).—The substance (I) (5 g.) was heated with anhydrous zinc chloride (10 g.) at 240—250° for 2 hours. The product was cooled, dilute hydrochloric acid added, and the mixture extracted with ether. Evaporation of the ether left an oil, which was taken up in acetic acid; from this solution, a yellow oily solid separated. From an alcoholic solution (charcoal), which was colourless and blue-fluorescent, there separated yellow prisms of a *substance*, m. p. 133—134° (after vacuum sublimation and crystallisation from acetone) (Found : C, 93·1; H, 6·7; *M*, 214. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%; *M*, 206). The alcoholic solution on concentration deposited the substance $C_{19}H_{20}$, m. p. (after recrystallisation from acetic acid) and mixed m. p. 102—104°.

Action of Phosphoric Oxide on (I).—Equal weights of the oxide and (I) were fused at 250° for 3 hours; the mixture, which finally became brown, was extracted with water. An ethereal extract of the residue had a green fluorescence and, after being washed with sodium carbonate solution, gave an oil which separated from glacial acetic acid (charcoal) in yellow crystals, m. p. 133—134° alone or mixed with the yellow product above.

Oxime of (I).—A solution of (I) (30 g.) in alcohol (300 c.c.) was boiled with hydroxylamine hydrochloride (28 g. in 80 c.c. of water) and potassium hydroxide (28 g. in 40 c.c. of water) for $\frac{3}{4}$ hour, poured into water, and left overnight. The *oxime* crystallised from alcohol in white needles (21 g.), m. p. 109—110° (Found : C, 81·9; H, 7·4; N, 5·0. $C_{19}H_{21}ON$ requires C, 81·7; H, 7·5; N, 5·0%). It dissolved in its own bulk of acetic anhydride with evolution of heat and after 2 days large thick plates of the *acetyl* derivative separated, m. p. 90—94° after recrystallisation from alcohol (Found : C, 78·8; H, 7·4; N, 4·4. $C_{21}H_{23}O_2N$ requires C, 78·5; H, 7·2; N, 4·4%).

Action of Phosphorus Pentachloride on the Oxime of (I).—The oxime (10 g.) in anhydrous ether (80 c.c.) was rapidly stirred at room temperature, and phosphorus pentachloride (10—12 g.) added during 10 minutes. After a further 45 minutes' stirring, most of the ether had evaporated. The residue, treated with iced water, gave a yellow paste, which was extracted with chloroform (60—70 c.c.). The pale yellow extract was washed with sodium carbonate solution and with water, dried, and evaporated. The yellow viscous residue was left in a vacuum, overnight; it separated from toluene or methyl alcohol in white crystals, m. p. 167—169° (Found : N, 5·25. $C_{19}H_{21}ON$ requires N, 5·0%). Hydrolysis of this *amide* gave uncrystallisable amines and no solid acid.

Bromination of (I).—*Monobromo-derivative.* The substance (I) (10 g.) was dissolved in carbon disulphide (100 c.c.), and bromine (7 g., slight excess) in carbon disulphide (70 c.c.) added during 1 minute; after 5 minutes, the solvent was removed by a current of air. The residue crystallised from ligroin (160 c.c.) in large stout rods (6 g.), m. p. 83—85° (Found : Br, 23·5. $C_{19}H_{19}OBr$ requires Br, 23·3%); the mother-liquor on concentration deposited the dibromo-compound.

Dibromo-derivative. Bromine (3·9 g.) in carbon disulphide (20 c.c.) was added gradually to a boiling solution of (I) (4 g.) in carbon disulphide (40 c.c.). After $\frac{1}{2}$ hour's boiling, the solvent was evaporated in a current of air, and the oily residue dissolved in hot alcohol (56 c.c.). The semi-crystalline mass after recrystallisation melted at 102—104° (Found : Br, 34·2. $C_{19}H_{18}OBr_2 \cdot C_2H_5 \cdot OH$ requires Br, 34·2%. Found for material crystallised from ligroin : Br, 38·1. $C_{19}H_{18}OBr_2$ requires Br, 37·9%).

Tribromo-derivative. The substance (I) (4 g.) was dissolved in carbon disulphide (40 c.c.), and bromine (10·5 g.) in carbon disulphide (60 c.c.) added while the temperature was gradually raised. After an hour's boiling, the bromine-coloured solvent was evaporated, and the sticky residue crystallised from alcohol, plates and then needles separating. After two recrystallisations the *tribromo-derivative* was obtained in stout white needles, m. p. 173—175° (Found : Br, 48·0. $C_{19}H_{17}OBr_3$ requires Br, 47·9%).

Attempts to prepare a mono- and a dibromo-derivative by the condensation of the corresponding bromo-derivative of fluorene with acetone by means of potassium hydroxide were unsuccessful.

Nitration of (I).—The substance (2 g.) was dissolved in glacial acetic acid (8 c.c.), and a mixture of concentrated nitric and sulphuric acids (4 : 1, 12 c.c.) added during 5 minutes, with cooling. After 1 minute the solution was poured into water, and the yellow sticky mass washed by decantation with water. It crystallised from alcohol in light yellow needles, m. p. 110—114° (Found : C, 74·1; H, 6·4; N, 4·6. $C_{19}H_{19}O_3N$ requires C, 73·8; H, 6·1; N, 4·5%). On one occasion there was obtained a *substance* crystallising from alcohol in yellow plates, m. p. 98—100° (1·7 g.) (Found : N, 5·3. $C_{16}H_{15}O_3N$ requires N, 5·2%).

Reduction of the Nitro-compound of (I), m. p. 110—114°.—Reduction with zinc in glacial acetic acid gave a substance, crystallising in brownish prisms, m. p. about 220°, which was not an amine and was not identified. Reduction in alcoholic solution with tin and hydrochloric acid was ineffective.

The nitro-compound (12 g.) was dissolved in alcohol (600 c.c.), sodium sulphide (60 g.) in water (150 c.c.) added, and the solution boiled for 3 hours (water being added occasionally to prevent bumping) and poured into water. The yellow solid obtained was dried and dissolved in alcohol, an equal bulk of concentrated hydrochloric acid added together with a few pieces of tin, and the whole boiled for a few minutes. The clear solution was decanted into excess of concentrated potassium hydroxide solution. The precipitate obtained was redissolved in concentrated hydrochloric acid, and again poured into concentrated potassium hydroxide solution. The solid was washed, dried, and crystallised twice from alcohol (charcoal), forming cream-coloured needles (8 g.), m. p. 143—146° (Found: C, 81.7; H, 7.2; N, 5.2. $C_{19}H_{21}ON$ requires C, 81.7; H, 7.5; N, 5.0%).

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UNIVERSITY OF GLASGOW.

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