466. *Syntheses of Fluoranthenes. Part I.* Michael Addition of Fluorene and of Methyl Fluorene-9-carboxylate to Crotononitrile. Syntheses of 2-Methyl- and of 2 : 4-Dimethyl-fluoranthene.*

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Methyl fluorene-9-carboxylate has been used in a Michael reaction with allyl cyanide (or crotononitrile which reacts as allyl cyanide) to prepare 2-(9′-carbomethoxy-9′-fluorenyl)propyl cyanide (I; R = R′ = Me). Hydrolysis of this cyanide has given rise to expected intermediates of the final product β-9-*fluorenylbutyric acid* (II), which has been cyclised to 4-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (III). This compound has given rise to (*a*) by reduction, followed by dehydrogenation, 2-methylfluoranthene, and (*b*) by a Grignard reaction, followed by dehydrogenation, to 2 : 4-dimethylfluoranthene.

The hydrogenation products of 2 : 4-dimethylfluoranthene have been investigated.

In the Michael reaction of fluorene with vinyl cyanide, in the presence of a base, two molecules of the cyanide add to one of fluorene to give 9 : 9-di-(2′-cyanoethyl)fluorene : monocyanoethylation has not been accomplished. On the other hand the less reactive crotononitrile reacts in unimolecular proportions with fluorene to give 2-9′-fluorenylpropyl cyanide (Bruson, *J. Amer. Chem. Soc.*, 1942, **64**, 2457). Bruson's reaction is limited, as far as fluorene is concerned, to these two reactions. Accordingly, in order to render the Michael reaction of wider application,

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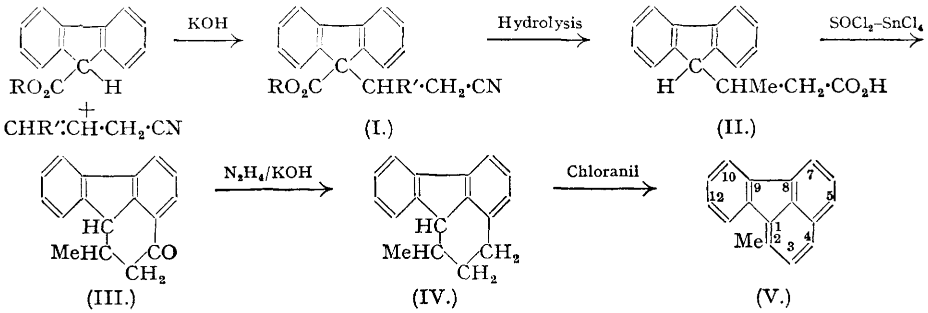
* This work is a continuation of " The Condensation of Fluorene with Acetone," Part VI, this vol., p. 632.

methyl (or ethyl) fluorene-9-carboxylate has been used. This procedure has two advantages: (*a*) the available 9-hydrogen atom is rendered more reactive, and (*b*) only one hydrogen atom is utilisable. This ester has been found to be of use, not only in condensations with αβ-unsaturated cyanides, but also with αβ-unsaturated ketones (the latter syntheses, as also corresponding ones with methyl indene-1-carboxylate will be reported later). Thus the synthesis of 2-methylfluoranthene has been accomplished by the series of reactions shown below; the intermediate (I) need not be isolated.



β-9-*Fluorenylbutyric acid* (II) was prepared in one operation by treating allyl cyanide with methyl fluorene-9-carboxylate in the presence of potassium hydroxide in 2-methoxyethanol. The intermediate 2-(9′-*carbomethoxy*-9′-*fluorenyl*)*propyl cyanide* (I; $R = R' = \mathrm{Me}$) was hydrolysed, without isolation, to the acid (II) (79% yield); actually, all the expected intermediates in the above process have been isolated, *viz.*, the ester-cyanide (I; $R = R' = \mathrm{Me}$), the acid-cyanide (I; $R = \mathrm{H}$, $R' = \mathrm{Me}$), the cyanide (II, CN for CO_2H), and the corresponding amide. Hydrolysis of the cyanide-ester (I; $R = R' = \mathrm{Me}$) by a mixture of water, and sulphuric and acetic acid (Reichstein, *Helv. Chim. Acta*, 1937, **20**, 1418) gave β-(9-*carboxy*-9-*fluorenyl*)-*butyric acid* (I; $R = \mathrm{H}$, $R' = \mathrm{Me}$, CO_2H for CN).

β-9-Fluorenylbutyric acid (II), by the usual method of treatment with thionyl chloride or phosphorus pentachloride in benzene, and then with stannic chloride, gave 2-*methyl*-4-*keto*-1 : 2 : 3 : 4-*tetrahydrofluoranthene* (III), which by the Huang–Minlon modification (*J. Amer. Chem. Soc.*, 1946, **68**, 2487) of the Wolff–Kishner method of reduction gave 2-*methyl*-1 : 2 : 3 : 4-*tetrahydrofluoranthene* (IV). (IV) was dehydrogenated by a boiling solution of chloranil in xylene to 2-methylfluoranthene (V), m. p. 72—75°.*

Consideration of the formula (III) led obviously to a new synthesis of 2 : 4-dimethylfluoranthene (Forrest and Tucker, *J.*, 1948, 1137): methylmagnesium iodide and (III) gave, without isolation of the carbinol, 2 : 4-*dimethyl*-1 : 2(?)-*dihydrofluoranthene*, which by means of chloranil in boiling xylene gave 2 : 4-dimethylfluoranthene.

Catalytic hydrogenation of the above dihydro-compound gave 2 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrofluoranthene*, m. p. 79—81°, different in many properties from the isomer, m. p. 115—117°, previously described (Tucker and Whalley, *J.*, 1949, 634); they are presumably stereoisomers.

The crotononitrile used was prepared (Bruson and Riener, *J. Amer. Chem. Soc.*, 1943, **65**, 22) from allyl cyanide (*Org. Syn.*, **8**, 4; Vogel, *J.*, 1948, 661), but it was eventually found that they gave identical results under the alkaline conditions employed (cf. Buckley, Elliott, Hunt, and Lowe, *J.*, 1947, 1505).

Experimental.

Methyl Fluorene-9-*carboxylate*.—Fluorene-9-carboxylic acid (52·5 g.), suspended in anhydrous methanol (125 ml.) (Baker and Holdsworth, *J.*, 1947, 724), was treated with dry hydrogen chloride until a clear solution was obtained (15—20 minutes), set aside overnight, and then placed in ice. The pale brown crystals deposited were washed with and crystallised from methanol, giving methyl fluorene-9-carboxylate, m. p. 63—66° (lit., 63°) (47 g.). The residual liquor on treatment with water gave an oil which after being shaken with three changes of cold methanol gave a solid which crystallised from methanol (4·6 g.). The total yield was 51·6 g. (92%).

In one experiment the residual methanolic solution on treatment with water gave a material which crystallised slowly from light petroleum (b. p. 40—60°) after being scratched. Recrystallisation from aqueous methanol gave greenish prisms, m. p. 37—39° (Found: C, 80·0; H, 5·5%).

Ethyl fluorene 9-carboxylate was prepared similarly to the methyl ester. It crystallised readily from methanol or ethanol (scratch) (yield, 83%, m. p. 42—45°) (cf. Delacre, *Bull. Soc. chim.*, 1902, **27**, 881; Wislicenus and Mocker, *Ber.*, 1913, **46**, 2775).

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* (V) has been prepared independently and by a different method by Dr. H. Wang, Ph.D. thesis, Edinburgh, 1948; Campbell and Wang, this vol., p. 1513.

β-9-*Fluorenylbutyric acid* (II) was prepared from methyl fluorene-9-carboxylate and allyl cyanide by two routes, (*A*) with isolation of intermediates, and (*B*) a more direct approach.

(A) *Stepwise Synthesis of β-9-Fluorenylbutyric Acid*.—2-(9′-*Carbomethoxy-9′-fluorenyl*)*propyl cyanide* (I; R = R′ = Me). Dioxan (5 ml.), potassium hydroxide (0·11 g., 0·2 mol.; powdered and added at once to avoid absorption of water), allyl cyanide (1·01 g., 1·5 mols.), and methyl fluorene-9-carboxylate (2·24 g.; 1 mol.) were mixed in that order, and the clear solution was set aside at room temperature for 4 days. It was then diluted with water and excess of 5% potassium hydroxide solution, and extracted with ether twice, the ether extracts being washed with water and evaporated without drying; finally the oily residue was warmed while a blast of air was passed over it to remove excess of allyl cyanide and solvent, and then dissolved in ethanol. 2-(9′-*Carbomethoxy-9′-fluorenyl*)*propyl cyanide* slowly crystallised (scratch) in octahedra, which felt very soft when crushed, m. p. 72—75° (2·15 g., 73%) (Found: C, 78·4; H, 5·8; N, 4·9. $C_{19}H_{17}O_2N$ requires C, 78·3; H, 5·9; N, 4·8%).

The alkaline extract, when treated with concentrated hydrochloric acid and set aside, gave a crystalline deposit of 2-(9′-*carboxy-9′-fluorenyl*)*propyl cyanide* (I; R = H, R′ = Me) (0·27 g., 10%), softening at 165° and melting at 179° (Found: C, 77·8; H, 5·5; N, 5·3. $C_{18}H_{15}O_2N$ requires C, 78·0; H, 5·45; N, 5·05%).

In the above preparation, warming the original mixture to 50°, or using an equivalent of potassium hydroxide, of benzyltrimethylammonium hydroxide (38% aqueous solution), sodium hydride, or sodamide caused formation of uncrystallisable oils. Aqueous potassium hydroxide (50%) which, as will be shown in a later communication, is most effective in the condensation of methyl fluorene-9-carboxylate with vinyl cyanide, gave a lower yield. Even the use of a smaller proportion (1·05 mols.) of allyl cyanide had a similar effect. When 2-methoxyethanol was used in place of dioxan the yield was as good, but when larger quantities were used frequently no crystalline product could be isolated, although hydrolysis of the oil obtained always gave a high yield of β-9-fluorenylbutyric acid (II) [see (B)]. Keeping the (dioxan) mixtures for longer than 4 days had no definite advantage: shortening the period of reaction to 1 day gave lower but considerable yields.

2-(9′-*Carbethoxy-9′-fluorenyl*)*propyl cyanide* was similarly prepared from ethyl fluorene-9-carboxylate (2·38 g.). It crystallised from methanol in large prisms, m. p. 74—76° (2·12 g., 70%) (Found: C, 78·8; H, 6·3; N, 4·9. $C_{20}H_{19}O_2N$ requires C, 78·7; H, 6·3; N, 4·6%). Like the corresponding methyl ester these crystals felt soft when powdered. The corresponding acid-cyanide (0·14 g., 5%) was also obtained.

2-9′-*Fluorenylpropyl cyanide* (II; CN for CO_2H). The ester-cyanide (I; R = R′ = Me) was readily hydrolysed to the corresponding acid-cyanide (I; R = H, R′ = Me) by dissolving it in warm ethanol, adding 10N-potassium hydroxide, and setting the mixture aside (*ca.* 5 minutes) until a drop gave no precipitate with water. Acidification with concentrated hydrochloric acid gave the acid-cyanide, 2-(9′-carboxy-9′-fluorenyl)propyl cyanide (I; R = H, R′ = Me) (*ca.* 100%). When this acid-cyanide or the ester-cyanide was heated with 10N-potassium hydroxide it rapidly effervesced and in a few minutes gave 2-9′-fluorenylpropyl cyanide (II; CN for CO_2H), m. p. 92—93° (high yield). Attempts to effect this decarboxylation by heating the acid at 200° gave unintelligible results. (II; CN for CO_2H) was also readily prepared by interaction of fluorene and crotononitrile in presence of benzyltrimethylammonium hydroxide in dioxan, but in lower yield than that claimed (Bruson, *loc. cit.*).

Attempts to bring about the above hydrolyses of the ester- (or acid-)cyanide to 2-9′-fluorenylpropyl cyanide by 10% potassium hydroxide solution gave only the acid-cyanide: 20% potassium hydroxide solution, with boiling for 3 hours, gave a mixture of products including β-9-*fluorenylbutyric acid* (II) crystallising from benzene–petroleum (60—80°) (1 : 1) and then from methyl cyanide in large rectangular prisms, m. p. 143—147° (Found: C, 80·9; H, 6·3. $C_{17}H_{16}O_2$ requires C, 80·95; H, 6·35%). Heating the ester-cyanide (I; R = R′ = Me) with 50% aqueous potassium hydroxide in ethanol for 1 hour gave the above acid (II) and (insoluble in aqueous alkali) β-9-*fluorenylbutyramide* which crystallised from benzene in nacreous leaflets, m. p. 158—160° after softening at 150° (Found: C, 81·1; H, 6·7; N, 5·9. $C_{17}H_{17}ON$ requires C, 81·3; H, 6·8; N, 5·6%).

β-9-Fluorenylbutyric acid was readily obtained by hydrolysis of either the ester-cyanide (2·91 g.), acid-cyanide (2·77 g.), or 2-9′-fluorenylpropyl cyanide (2·37 g.) by boiling its solution in 2-methoxyethanol (10 ml.) with 10N-potassium hydroxide (15 ml.) for 2—3 hours. Pouring the mixture into water gave a turbid yellow solution (even after 5 hours' boiling). Filtration through charcoal and addition of excess of concentrated hydrochloric acid gave β-9-fluorenylbutyric acid (II) (2·17 g., 86% from the ester-cyanide).

β-(9-*Carboxy-9-fluorenyl*)*butyric acid* (I; R = H, R′ = Me, CO_2H for CN). 2-(9′-Carbomethoxy-9′-fluorenyl)propyl cyanide (I; R = R′ = Me) (0·29 g.), glacial acetic acid (5 ml.), concentrated sulphuric acid (2 ml.), and water (2 ml.) were boiled for 3 hours, and the solution was diluted with excess of alkali, filtered from insoluble material (0·02 g.; recrystallised from methanol, m. p. 245°; 9 : 9′-difluorenyl), and treated with concentrated hydrochloric acid, to give, after recrystallisation from methyl cyanide, β-(9-*carboxy-9-fluorenyl*)*butyric acid* (I; R = H, R′ = Me, CO_2H for CN) as prisms, m. p. 121—123° (turbid melt until 160°) (0·18 g., 64%) (Found: C, 73·2; H, 5·6. $G_{18}O_{16}O_4$ requires C, 73·0; H, 5·4%). When, however, this acid was boiled in, and then crystallised from, toluene it gave nodules softening at 155°, melting slowly to 170° (samples had m. p. 166—170°) (Found: C, 73·7; H, 5·3. The anhydride, $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·1%). Wislicenus and Mocker (*loc. cit.*, p. 2790) obtained an anhydride from (I; R = R′ = H CO_2H for CN).

β-9-*Fluorenylbutyric Acid* (II) was similarly obtained from 2-9′-fluorenylpropyl cyanide (II; CN for CO_2H) (2·33 g.) by boiling it with glacial acetic acid (25 ml.), concentrated sulphuric acid (5 ml.), and water (5 ml.) for 4—5 hours. Dilution with water and setting the mixture aside gave the acid (II) (2·06 g., 82%), m. p. 143—147°. It was also obtained by heating β-(9-carboxy-9-fluorenyl)butyric acid over a free flame until effervescence ceased (good yield).

(B) *Direct Synthesis of β-9-Fluorenylbutyric Acid* (II).—The preparation of (II), without isolation of any intermediate, from methyl fluorene-9-carboxylate and allyl cyanide was effected in 2-methoxyethanol rather than in dioxan. 2-Methoxyethanol (redistilled, b. p. 124°; 12·5 ml.) and potassium hydroxide pellets (0·28 g., 0·2 mol.) were heated to dissolve the latter, the solution was cooled, allyl cyanide (2·51 g., 1·5 mols.) and then methyl fluorene-9-carboxylate (5·60 g., 1 mol.) were added and set aside with occasional shaking for 7 days. 2-Methoxyethanol (25 ml.) and 10N-potassium hydroxide (35 ml.) were then added and the mixture was boiled. The precipitated oil rapidly dissolved to give a clear green liquid (owing, probably, to hydrolysis of ester-cyanide to acid-cyanide), then after 1 minute suddenly became turbid [decarboxylation to the cyanide (II)], again rapidly clarified (amide formation), and slowly darkened. After boiling for 3 hours the solution was poured into water to give a turbid, yellow, fluorescent liquid, which after filtration through charcoal was treated with concentrated hydrochloric acid until only slightly alkaline, and then rendered acid with glacial acetic acid. The precipitated soft, grey mass was crystallised from methyl cyanide in rectangular plates (5·0 g., 79%) of β-9-fluorenylbutyric acid (II), m. p. 143—147°. A similar experiment in which the mixture was set aside for 4 days and the period of boiling was 4 hours gave almost the same yield (75%) of (II), but the product was yellow. When the mixture was kept for 5 or 24 *hours*, the yields of (II) were 24 and 33%, respectively.

Cyclisation of β-9-Fluorenylbutyric Acid (II) *to* 4-*Keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrofluoranthene* (III).—(II) (5·04 g., 0·02 g.- mol.) was boiled for 10 minutes with excess of thionyl chloride (distilled from linseed oil), the excess of thionyl chloride removed in a vacuum, and dry thiophen-free benzene (10 ml.) added and then a solution of stannic chloride (4·6—4·7 ml., 0·04 g.-mol.) in benzene (5 ml.). After 1 hour a dark brown crystalline solid had separated. The whole mixture was treated with concentrated hydrochloric acid and extracted with hot benzene (the product is nearly insoluble in ether). Since shaking a portion of the benzene extract with 5% potassium hydroxide solution, followed by acidification of the alkaline extract, gave no precipitate of the acid (II), this treatment was dispensed with for the main benzene extract, evaporation of which, followed by crystallisation from ethanol and then from ethyl acetate gave 4-*Keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrofluoranthene* (III) as cream-coloured leaflets, m. p. 159—160° (2·9 g., 62%) (Found : C, 87·0; H, 6·0. $C_{17}H_{14}O$ requires C, 87·2; H, 6·0%). The use of phosphorus pentachloride [1 or 2 mols. per mol. of (II)] gave lower yields (42%) and some (II) was recovered. The acid (II) was recovered unchanged after being warmed with concentrated sulphuric acid in glacial acetic acid. The 2 : 4-*dinitrophenylhydrazone* of (III), prepared in methanol acidified with concentrated sulphuric acid, crystallised in very small scarlet needles from anisole; it darkened at 250° but melted sharply at 276° (decomp.) (Found : C, 66·8; H, 4·45; N, 13·2. $C_{23}H_{18}O_4N_4$ requires C, 66·7; H, 4·35; N, 13·5%).

2-*Methyl*-1 : 2 : 3 : 4-*tetrahydrofluoranthene* (IV).—4-Keto-2-methyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (III) (1·17 g.), potassium hydroxide (0·3 g.), hydrazine (90%; 1·0 ml.) in 2 : 2′-dihydroxydiethyl ether (4 ml.) were boiled for 1 hour, the water was removed by distillation, the surrounding bath being maintained at 195—200° for 3 hours. An air blast was used to remove water during the first 15 minutes. The cooled mixture was treated with hydrochloric acid. The precipitate (0·51 g.; 46%) was crystallised from methanol. Recrystallisation from acetic acid, containing a trace of water, gave faintly green, long, rectangular prisms of 2-*methyl*-1 : 2 : 3 : 4-*tetrahydrofluoranthene* (IV), m. p. 89—91° (Found : C, 92·5; H, 7·1. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%). It gave a 2 : 4 : 7-trinitrofluorenone *complex* as orange needles (from acetic acid), m. p. 208—209° (Found : N, 7·8. $C_{17}H_{16},C_{13}H_5O_7N_3$ requires N, 7·8%).

2-*Methylfluoranthene* (V).—(IV) (0·22 g.), chloranil (0·49 g.), were boiled in xylene (2 ml.). The blood-red solution rapidly deposited pale brown tetrachloroquinol and after 1 hour was pale brown. After cooling, the filtered solution was diluted with ether, extracted with 5% sodium hydroxide solution, washed, and evaporated. The crude product (0·2 g.) crystallised from light petroleum (60—80°) and then from ethanol in pale yellow blades, m. p. 72—75° (Wang, *loc. cit.*, gives m. p. 72—73°) of 2-methylfluoranthene (Found : C, 94·5; H, 5·7. Calc. for $C_{17}H_{12}$: C, 94·4; H, 5·6%). It fluoresces pale green in ultra-violet light. A *complex* with *s*-trinitrobenzene gave canary-yellow needles, m. p. 223—226°, from benzene (Found : C, 64·3; H, 3·5; N, 9·9. $C_{17}H_{12},C_6H_3O_6N_3$ requires C, 64·3; H, 3·5; N, 9·8%).

2 : 4-*Dimethylfluoranthene*.—4-Keto-2-methyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (III) (2·34 g., 0·01 g. mol.), suspended in anhydrous ether (5 ml.), was added to an ethereal solution of methylmagnesium iodide [from methyl iodide, 1·25 ml. (2·84 g., 0·02 g.-mol.), pure magnesium, 0·48 g. (0·02 g.-atom), and ether, 15 ml.]. (III) dissolved, and a white precipitate then slowly separated. The mixture was kept at the b. p. with stirring for ½ hour, treated with dilute hydrochloric acid, and worked up as usual. The product, 2 : 4-*dimethyl*-1 : 2(?)-*dihydrofluoranthene*, was crystallised from glacial acetic acid (to ensure removal of water) and then from ethanol in thick, diamond-shaped plates, m. p. 98—100° (1·62 g., 70%) (Found : C, 92·9; H, 6·9. $C_{18}H_{16}$ requires C, 93·1; H, 6·9%). Its 2 : 4 : 7-trinitrofluorenone *complex*, prepared in glacial acetic acid, gave orange-coloured rosettes, m. p. 143—146° (softening 140°), from glacial acetic acid (Found : C, 67·9; H, 4·0; N, 7·75. $C_{18}H_{16},C_{13}H_5O_7N_3$ requires C, 68·0; H, 3·9; N, 7·7%). Picric acid and *s*-trinitrobenzene gave scarlet and orange-coloured complexes, respectively, but they could not be isolated free of reactants.

2 : 4-Dimethyl-1 : 2(?)-dihydrofluoranthene (0·464 g.), chloranil (0·492 g.), and xylene (2 ml.) were boiled for ½ hour. Working up as usual gave a reddish-brown powder (0·35 g.) which after recrystallisation from methyl cyanide gave 2 : 4-dimethylfluoranthene as faintly greenish-yellow rectangular prisms (0·23 g., 50%), m. p. 116—117° (softening at 114°) (cf. Forrest and Tucker, *loc. cit.*). It fluoresced greenish-yellow in ultra-violet light (cf. Tucker and Whalley, *loc. cit.*, p. 633). Its identity with 2 : 4-dimethylfluoranthene was established by comparison of the picrates and identity of the *complex* with 2 : 4 : 7-trinitrofluorenone prepared from each. The complex was prepared in glacial acetic acid and crystallised from methyl cyanide in very small orange-red needles, m. p. 200° (Found : C, 67·9; H, 3·7; N, 7·7. $C_{18}H_{14},C_{13}H_5O_7N_3$ requires C, 68·25; H, 3·5; N, 7·7%).

2 : 4-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydrofluoranthene*.—2 : 4-Dimethyl-1 : 2(?)-dihydrofluoranthene (0·232 g.) was hydrogenated [Cheronis–Levin 5% Pd–C (0·2 g.)] in ethanol (15 ml.) in ½ hour (23 ml. of H_2 absorbed). The mixture was filtered, the charcoal extracted with boiling ethanol and ether, and the solution evaporated to give, after crystallisation from methanol, 2 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetramethylfluoranthene* as long faintly steel-blue prisms, m. p. 79—81° (0·18 g., 77%) (Found: C, 92·1; H, 7·6. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). It fluoresces pale blue in ultra-violet light. Its *complex* with

2 : 4 : 7-trinitrofluorenone was unstable in ethanol but gave orange-red prisms from glacial acetic acid : these, however, melted after repeated crystallisation capriciously at 80° or 190° and were obviously the complex with one component or the other predominating. The isomeric 2 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (Tucker and Whalley, *loc. cit.*.) fluoresces pale violet in ultra-violet light. Repetition of the preparation of this isomer in a mixture of equal parts of acetone and glacial acetic acid indicated that this mixture is slightly preferable to ethanol : the acetone acts as a solvent, no hydrogenation taking place in it alone.

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