146. *Synthesis of Fluoranthenes. Part IX.* 3-Methylfluoranthene.*

By S. Horwood Tucker.

The Michael reaction between fluorene-9-carboxylates and vinyl cyanide and its derivatives has been improved by the use of sodium methoxide as reagent in methanolic solution. It has been found that αβ-unsaturated esters may be used with advantage instead of the vinyl cyanides. 3-Methylfluoranthene (V) has been synthesised from methyl fluorene-9-carboxylate by using both *iso*propenyl cyanide and methyl α-methylacrylate, and subsequently following the synthetic method developed in this series of papers.

This communication describes the synthesis of the last of the five isomeric monomethylfluoranthenes. The first to be prepared, 4-methylfluoranthene, was obtained by von Braun and Manz (*Ber.*, 1937, **70**, 1610; see further A. Campbell and Tucker, *J.*, 1949, 2623; Stubbs and Tucker, *J.*, 1950, 3288). 10- and 11-Methylfluoranthene were synthesised by Tucker and Whalley (*J.*, 1949, 3213; cf. Kloetzel and Mertel, *J. Amer. Chem. Soc.*, 1950, **72**, 4786) by the general method of Forrest and Tucker (*J.*, 1948, 1137). 2-Methylfluoranthene was synthesised by N. Campbell and Wang (*J.*, 1949, 1513), and also by the author (*J.*, 1949, 2182) using methyl fluorene-9-carboxylate and *n*-propenyl cyanide. Application of this general method has achieved the synthesis of 3-methylfluoranthene (V), as shown in the annexed scheme.

Formerly, in our general procedure for the Michael reaction we have used potassium hydroxide (0·2M) in dioxan or 2-methoxyethanol (*e.g.*, Tucker, *loc. cit.*), the latter solvent being preferable when hydrolysis of the intermediate cyano-compound to the carboxylic

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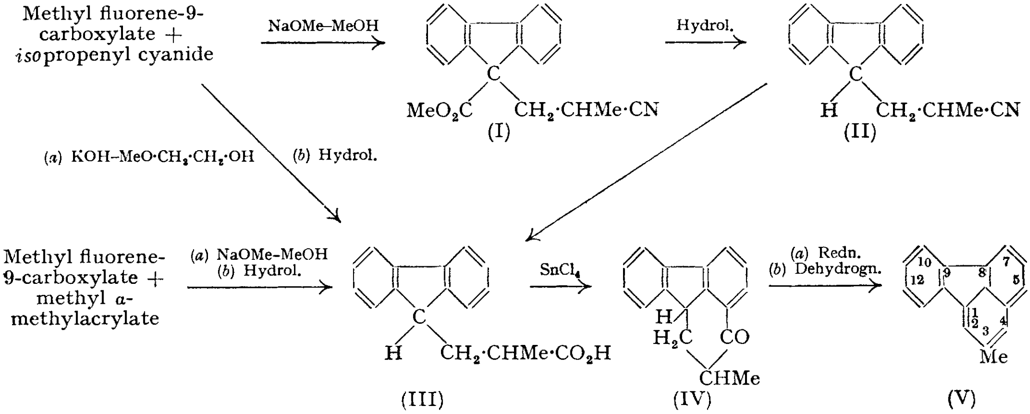
acid, without isolation of intermediates, is desired. But in this series Michael reactions in dioxan are slow and often incomplete. The use of sodium methoxide (0·2M) in methanol effects a decided improvement in the rate of reaction : the products either crystallise from the reaction mixture or can be readily isolated therefrom in high yields. This improved method has been used with vinyl, *n*-propenyl, and *iso*propenyl cyanides.



Acrylates have not hitherto been condensed with fluorene-9-carboxylates (cf. Michael and Ross, *J. Amer. Chem. Soc.*, 1930, **52**, 4598 ; Connor and Andrews, *ibid.*, 1934, **56**, 2713 ; Connor and McClellan, *J. Org. Chem.*, 1938, **3**, 570 ; Floyd and Miller, *ibid.*, 1951, **16**, 882), but we find that in presence of sodium methoxide in methanol this condensation proceeds readily with methyl acrylate, crotonate, and α-methylacrylate. Although the vinyl cyanides are usually more reactive than the acrylates, the addition products of the latter with the fluorene-9-carboxylates often crystallise from the reaction mixture more readily than do those of the cyanides, and are much more easily and rapidly hydrolysed in high yield to pure carboxylic acids.

Attempts to add ethyl tiglate or tiglic nitrile to the fluorene-9-carboxylates in presence of sodium or potassium alkoxide in the corresponding alcohol failed (cf. Michael and Ross, *loc. cit.*), varying amounts of methyl 9-hydroxyfluorene-9-carboxylate being obtained. Ethyl β-methylcrotonate and ethyl α-cyano-β-methylcrotonate also failed to combine with methyl fluorene-9-carboxylate.

EXPERIMENTAL

Direct Synthesis of β-9-*Fluorenyl*iso*butyric Acid* (III) *from Methyl Fluorene*-9-*carboxylate and Methyl* α-*Methylacrylate.*—Methyl fluorene-9-carboxylate (5·60 g., 1 mol.), anhydrous methanol (12·5 ml.), a solution of sodium (0·115 g., 0·2 atom) in methanol (11·5 ml.), and methyl α-methylacrylate (2·75 g., 1·1 mols.) were mixed in that order and left at *ca.* 20° for 24 hours. Cooling and scratching the solution failed to give crystals (cf. successful analogous examples, later), so the mixture was warmed and submitted to an air-blast to expel methanol as rapidly as possible. The residual oil was boiled with a mixture of 10N-potassium hydroxide (10 ml.) and 2-methoxyethanol (25 ml.) for 15 minutes, the solution poured into water, and the clear solution treated with concentrated hydrochloric acid and a few drops of glacial acetic acid. The crude solid crystallised very slowly from dioxan, but rapidly from light petroleum (b. p. 60—80°), forming rods, m. p. 137—139° (5·40 g., 85%), of β-9-*fluorenyl*iso*butyric acid* (III) (Found : C, 81·0 ; H, 6·2. $C_{17}H_{16}O_2$ requires C, 80·9 ; H, 6·4%). When the above reaction mixture was worked up after only 6 hours, the yield was 67%. The *methyl* ester of (III), prepared by use of methanol and hydrogen chloride, crystallised from acetic acid–water, then from methanol–water in cream-coloured prisms, m. p. 48—51° (Found : C, 81·3 ; H, 6·7. $C_{18}H_{18}O_2$ requires C, 81·2 ; H, 6·8%).

Stepwise Synthesis of β-9-*Fluorenyl*iso*butyric Acid* (III) *from Methyl Fluorene*-9-*carboxylate and* iso*Propenyl Cyanide.*—Methyl fluorene-9-carboxylate (5·60 g., 1 mol.), anhydrous methanol (12·5 ml.), sodium (0·115 g., 0·2 atom) in anhydrous methanol (11·5 ml.), and *iso*propenyl cyanide (2·52 g., 1·5 mol.) were mixed and kept at 20° with occasional shaking. After 20 minutes the solution was clear, and after 5 hours a scratch started crystallisation. After being left overnight, the crystals were rinsed with methanol; the methanolic liquors gave more of the product. Recrystallisation from methanol gave soft crystals (typical of these cyano-esters) of *methyl* 9-2'-*cyano*-n-*propylfluorene*-9-*carboxylate* (I), m. p. 94—97° (6·54 g., 90%) (Found: C, 78·3; H, 6·0; N, 4·7. $C_{19}H_{17}O_2N$ requires C, 78·3; H, 5·9; N, 4·8%). Reduction of the relative proportion of *iso*propenyl cyanide (from 1·5 to 1·05 and to 1 mol.) caused a fall in yield (to 63 and 50%, respectively). When potassium hydroxide replaced sodium in the above reaction the yield of ester-cyanide (I) was 70%; but this must be considered a low estimate since recystallisation was slow and wasteful. Potassium *tert.*-butoxide in benzene gave a 50% yield of (I). When potassium hydroxide (0·2 mol.) in dioxan was used, and the mixture kept for 14 days, the crystallised product (methanol) gave (I) in *ca.* 50% yield; methyl fluorene-9-carboxylate (*ca.* 50%) was recovered from the methanol filtrate. In this, and in corresponding experiments, dioxan is less favourable for the Michael reaction than the alcoholic solvents.

9-2'-*Cyano*-n-*propylfluorene*-9-*carboxylic Acid* (I; CO_2H for CO_2Me).—The ester-cyanide (I) (0·59 g.) was dissolved in ethanol, and 10N-potassium hydroxide added to the cold solution. After 5 minutes the solution became slightly milky; it was immediately extracted with ether, and excess of hydrochloric acid added to the aqueous portion. The nearly pure crystalline *acid* (0·49 g., 90%) recrystallised from benzene in burrs, losing benzene of crystallisation, and had m. p. 152—155° (softening at 150°) (Found: C, 78·2; H, 5·6; N, 4·9. $C_{18}H_{15}O_2N$ requires C, 78·0; H, 5·45; N, 5·05%).

Hydrolysis of Methyl 9-2'-*Cyano*-n-*propylfluorene*-9-*carboxylate* (I) *to* β-9-*Fluorenyl*-iso*butyric Acid* (III).—The ester-cyanide (I) (5·8 g.) and 10N-potassium hydroxide (20 ml.) in 2-methoxyethanol (30 ml.) were boiled for 2·5 hours, and poured into water. The clear solution, with concentrated hydrochloric acid, gave the acid (III), which after crystallisation from acetic acid–water and then from methyl cyanide had m. p. 137—139° (4·8 g., 95%). The use of 2-ethoxyethanol in place of 2-methoxyethanol gave a less pure product.

The acid (III) was also prepared directly from methyl fluorene-9-carboxylate (11·2 g., 1 mol.), *iso*propenyl cyanide (5·03 g., 1·5 mols.), and potassium hydroxide (0·56 g., 0·2 mol.) in 2-methoxyethanol (25 ml.); after 7 days, 10N-potassium hydroxide (75 ml.) and 2-methoxyethanol (50 ml.) were added, and the mixture was boiled vigorously for 4—5 hours and acidified as described for the corresponding preparation of β-9-fluorenylbutyric acid (Tucker, *loc. cit.*); the yield was 12·4 g. (98%).

1 : 2 : 3 : 4-*Tetrahydro*-4-*keto*-3-*methylfluoranthene* (IV).—A mixture of β-9-fluorenyl-*iso*butyric acid (III) (5·05 g.) and phosphorus pentachloride (5·05 g.) in benzene (25 g.; dried by phosphorus pentachloride) was boiled until evolution of hydrogen chloride ceased (*ca.* 15 minutes), cooled in ice, and added with shaking during 30 minutes to a solution of stannic chloride (5·5 ml.) in benzene (10 ml.) also kept ice-cold (Johnson and Glen, *J. Amer. Chem. Soc.*, 1949, **71**, 1094). After 2·5 hours in ice with occasional shaking, then at room temperature for 0·75 hour, the red liquid was treated several times with a mixture of concentrated hydrochloric acid and water (1 : 1 v/v) and with a small amount of ether. The pale yellow liquor obtained was washed with water, extracted with 5% sodium hydroxide solution (the extract gave a slight milky deposit with hydrochloric acid), washed with water just acid with hydrochloric acid, and evaporated to a pale yellow oil, which crystallised from light petroleum (b. p. 60—80°) and then from methyl cyanide to give 1 : 2 : 3 : 4-*tetrahydro*-4-*keto*-3-*methylfluoranthene* (IV; 3·78 g., 81%), m.p. 98—100° (Found: C, 87·4; H, 6·2. $C_{17}H_{14}O$ requires C, 87·15; H, 6·0%).

If the above cyclisation mixture was left overnight or over a week-end, yields of 62 and 45%, respectively, of (IV) were obtained. A preparation in which thionyl chloride was used instead of phosphorus pentachloride, and the mixture kept at room temperature overnight, gave a 43% yield of (IV). Use of aluminium chloride (1·1 mols.) instead of stannic chloride gave a gelatinous product which may have hindered complete utilisation of the catalyst; the yield was 45%. Hydrogen fluoride effected cyclisation in lower yield (30%) but the product, after once crystallising from methyl cyanide, as rod prisms, was pure (m. p. 98—100°).

The 2 : 4-*dinitrophenylhydrazone* of (IV), bright scarlet small crystals (from dioxan), had m. p. 251—254° (decomp.) (Found: C, 66·4; H, 4·6; N, 13·2. $C_{23}H_{18}O_4N_4$ requires C, 66·7; H, 4·4; N, 13·5%).

1 : 2 : 3 : 4-*Tetrahydro*-3-*methylfluoranthene*.—The ketone (IV) (1·17 g.), 90% hydrazine solution (2 ml.), and ethylene glycol (11 ml.) were boiled under reflux for 15 minutes, then gently distilled until water and excess of hydrazine had been removed (*ca.* 30 minutes). Potassium hydroxide (0·6 g.) was added to the cooled solution, which was boiled under reflux for 2 hours

(King and Nord, *J. Org. Chem.*, 1949, **14**, 638), then concentrated somewhat, treated with dilute hydrochloric acid, and extracted with ether, the ethereal extract evaporated, and the yellow, green-fluorescing oil so obtained chromatographed in light petroleum (b. p. 60—80°) through alumina and eluted with benzene. Two bright yellow bands were left on the column, and the benzene eluate gave a yellow oil (0·90 g.) which crystallised from acetic acid–water very slowly (*ca.* 7 days) in pale yellow rectangular plates, m. p. 48—50°, of 1 : 2 : 3 : 4-*tetrahydro*-3-*methylfluoranthene* (Found: C, 92·45; H. 7·3. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%), which slowly became brown in air. It was also prepared by the Huang-Minlon process, diethylene glycol being used as solvent.

3-*Methylfluoranthene* (V).—The tetrahydromethylfluoranthene (0·84 g. as oil), chloranil (1·90 g.), and xylene (8 ml.) were boiled for 45 minutes. After cooling, crystals which separated were washed with benzene, and the filtrates combined and extracted twice with a mixture of sodium metabisulphite and 5% sodium hydroxide solutions, then with water. The benzene–xylene solution was evaporated, and the black residue extracted with boiling methanol; the solution gave salmon-tinted leaflets. The picrate (from methanol) was washed with sodium hydrogen carbonate solution, the pale brown residue dissolved in light petroluem (b. p. 60—80°), and the solution chromatographed (Al_2O_3; 10 cm.). Evaporation of the eluate gave after crystallisation from methanol ill-defined needles (0·56 g., 68%), m. p. 79—81°, of 3-*methylfluoranthene* (V) (Found: C, 94·6; H, 5·6. $C_{17}H_{12}$ requires C, 94·4; H, 5·6%). The *picrate*, orange needles (from ethanol), has m. p. 163—165° (Found: C, 62·1; H, 3·6. $C_{17}H_{12},C_6H_3O_7N_3$ requires C, 62·0; H, 3·4%), the 1 : 3 : 5-*trinitrobenzene* complex, canary-yellow needles (from ethanol), m. p. 187—189° (Found: C, 64·2; H, 3·6; N, 10·0. $C_{17}H_{12},C_6H_3O_6N_3$ requires C, 64·3; H, 3·5; N, 9·8%), and the 2 : 4 : 7-*trinitrofluorenone* complex, bright orange needles (from acetic acid), m. p. 186—187° (Found: C. 67·7; H, 3·0; N, 8·0. $C_{17}H_{12},C_{13}H_5O_7N_3$ requires C, 67·8; H, 3·2; N, 7·9%).

Michael Condensations by Use of Sodium Methoxide in Methanol and (A) *Vinyl Cyanides*, (B) *Alkyl Acrylates.*—(A) Methyl 9-2′-cyanoethylfluorene-9-carboxylate was prepared from methyl fluorene-9-carboxylate (1·12 g., 1 mol.), sodium (0·023 g., 0·2 atom), and vinyl cyanide (0·29 g., 1·1 mols.) in anhydrous methanol (2·5 ml.) as described for the methyl homologue (I) except that the cyano-ester did not crystallise from the reaction mixture after 24 hours. It was isolated in the usual way, and had m. p. 84—86° (1·04 g., 76%).

2-(9-Carbomethoxy-9-fluorenyl)propyl cyanide, prepared analogously from allyl cyanide (crotononitrile), had m. p. 72—75° (0·82 g., 57%). Loss in crystallisation accounts for the low yield. Hydrolysis and isolation of the carboxylic acids has repeatedly in this work given higher yields (see below).

(B) *Methyl* β-(9-*carbomethoxy*-9-*fluorenyl*)*propionate*. Methyl fluorene-9-carboxylate (1·12 g., 1 mol.), methanol (2·5 ml.), sodium (2·3 ml. of a solution of 0·23 g. of sodium in 23 ml. of methanol), and methyl acrylate (0·65 g., 1·5 mols.) (containing 0·1% of quinol) were left for 4 hours, then scratched. Crystals separated rapidly, and reaction was probably complete in 6 hours, but the mixture was invariably left overnight in a refrigerator to complete crystallisation. The main crop (1·25 g.) was pure. The filtrate, on being worked up as usual, gave a further crop (0·12 g.). This *diester* crystallised in thick rectangular plates (from methanol) (1·37 g., 88%), m. p. 68—69° (Found: C, 73·4; H. 5·7. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·8%). Hydrolysis of the diester (1·55 g.) by boiling it with 10N-potassium hydroxide (2 ml.) in 2-methoxyethanol (5 ml.) for 20 minutes, pouring the whole into water, and adding hydrochloric acid to the clear solution, gave β-9-fluorenylpropionic acid (1·07 g., 90%); on recrystallisation from methyl cyanide this had m. p. 145—147°, *i.e.*, higher than that of the acid prepared by hydrolysis of the cyanide (140—145°, A. Campbell and Tucker, *loc. cit.*; Wislicenus and Mocker, *Ber.*, 1913, **46**, 2789, gave 148—149°).

β-9-Fluorenylbutyric acid was prepared from methyl fluorene-9-carboxylate (1·12 g., 1 mol.), methyl crotonate (0·75 g., 1·5 mols.), and sodium (0·023 g., 0·2 atom) in methanol (5 ml.), which were left for 4 days at room temperature. Stellar clusters of crystals of dimethyl 9 : 9′-difluorenyl-9 : 9′-dicarboxylate, m. p. 237° (0·04 g., from acetic acid) (Found: C. 80·3; H, 5·2. Calc. for $C_{30}H_{22}O_4$: C, 80·7; H, 5·0%), were removed, and the filtrate was evaporated on the steam-bath in an air-blast. The residue was boiled with 10N-potassium hydroxide (2 ml.) and 2-methoxyethanol (5 ml.) for 15 minutes, and the solution poured into water, giving a milky suspension cleared when boiled with charcoal (0·5 hour). Hydrochloric acid gave β-9-fluorenylbutyric acid, m. p. 145° (0·74 g., 60%), which after crystallisation from methyl cyanide had m. p. 147—149°—again, higher than that of acid prepared from the cyanide (Tucker, *loc. cit.*, gives m. p. 143—147°). Ethyl esters gave somewhat lower yields. When in the above the original mixture was left for 3 weeks, the yield was slightly less and there was also isolated (at the water-precipitation stage) fluorenol (0·13 g.). Fluorene failed to react with ethyl crotonate in presence of sodium ethoxide in ethanol even when the mixture was boiled for 3 days.

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UNIVERSITY OF GLASGOW. [*Received, October* 31*st*, 1951.]