453. *New Syntheses of Heterocyclic Compounds. Part X. 4-Azafluorenones.*

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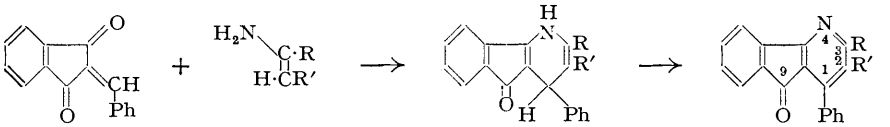
By condensing benzylideneindane-1 : 3-diones with ethyl β-aminocrotonate in glacial acetic acid, numerous *ethyl* 1-*aryl*-3-*methyldihydro*-4-*azafluorenone*-3-*carboxylates* have been prepared; they were oxidised to the corresponding 4-*azafluorenones*. When methyl 2-aminopropenyl ketone, phenyl-2-aminopropenyl ketone, and β-aminocinnamonitrile were employed in place of ethyl β-aminocrotonate in the above synthesis, 2-*acetyl*-1-*phenyl*-3-*methyl*-, 2-*benzoyl*-1-*phenyl*-3-*methyl*-, and 2-*cyano*-1 : 3-*diphenyl*-4-*azafluorenone* were obtained after oxidation.

Attempts to extend the synthesis to the preparation of 1-alkyl-4-azafluorenones were not successful. *Anilomethylindane*-1 : 3-*dione* (VI), prepared by reaction between indane-1 : 3-dione and diphenylformamidine, failed to give a 4-azafluorenone. *Ethyl* 1-2′-*furyl*-3-*methyl*-4-*azafluorenone*-2-*carboxylate* could not be degraded to a compound of the required type.

The *oxime* of ethyl 1-phenyl-3-methyl-4-azafluorenone-2-carboxylate (IV) gave *ethyl* 9-*diacetylamino*-1-*phenyl*-3-*methyl*-4-*azafluorenone*-2-*carboxylate* on reduction, but this compound could be hydrolysed only to the 9-*acetamido*-derivative. Attempts to hydrolyse (IV) to the corresponding acid also failed, concentrated sulphuric acid leading to the formation of 1′-*keto*-3-*methyl*-4-*azaindeno*(3′ : 2′-1 : 2)*fluorenone* (V).

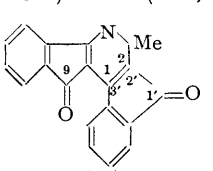
The preparation of some 4-azafluorenones was undertaken following the observation that certain 1 : 3-dimethyl-2-azafluorenones showed interesting biological properties (preceding paper). 4-Azafluorenones have hitherto been prepared by alkaline oxidation of 7 : 8-benzcinchoninic acids (Doebner and Kuntze, *Annalen*, 1883, **249**, 123), by condensation of indane-1 : 3-dione with *o*-aminobenzaldehyde (Noelting and Blum, *Ber.*, 1901, **34**, 2467) or with ethyl ethoxymethyleneacetoacetate (Errara and Casardi, *Gazzetta*, 1905, **35**, i, 9), or by ring closure of 2-phenylquinoline-3-carboxylic acid (Borsche and Sinn, *Annalen*, 1937, **532**, 146; *ibid*, 1939, **538**, 283). These methods proved unsuitable for extension and we therefore sought an alternative route to this little-studied ring system. Success was finally achieved by a new variation of the Hantzsch collidine synthesis.

Benzaldehyde reacts with indane-1 : 3-dione to give 2-benzylideneindane-1 : 3-dione (I) (Wislicenus and Kotzle, *Annalen*, 1889, **252**, 73). This compound is clearly the cyclic analogue of benzylideneacetylacetone and, like the latter compound (Knoevenagel and Ruschhaupt, *Ber.*, 1898, **31**, 1025), reacts with ethyl 2-aminocrotonate (II) at 100° to give bright-red *ethyl* 1-*phenyl*-3-*methyl*-1 : 4-*dihydro*-4-*azafluorenone*-2-*carboxylate* (III) in less than 30% yield,

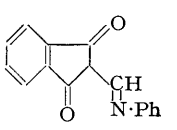


(I.) (II.) (III.) (IV.)

(II; R = Me; R′ = CO_2Et.) (III; R = Me; R′ = CO_2Et.) (IV; R = Me; R′ = CO_2Et.)
(II*a*; R = Me; R′ = COMe.) (III*a*; R = Me; R′ = COMe.) (IV*a*; R = Me; R′ = COMe.)
(II*b*; R = Me; R′ = COPh.) (III*b*; R = Me; R′ = COPh.) (IV*b*; R = Me; R′ = COPh.)
(II*c*; R = Ph; R′ = CN.) (III*c*; R = Ph; R′ = CN.)



(V.)



(VI.)

together with much tar. Reaction in solvents such as ethanol led to the exclusive formation of resins, a result also obtained after addition of basic catalysts such as piperidine. However, in

boiling glacial acetic acid solution ready and rapid condensation took place, giving (III) in nearly quantitative yield; the pure crystalline product generally separated within a few minutes. Other aliphatic acids such as formic and propionic acids can be employed with equal success, but the reaction does not occur in toluene, light petroleum, pyridine, or nitrobenzene. Oxidation of (III) with chromic acid in acetic acid afforded *ethyl* 1-*phenyl*-3-*methyl*-4-*azafluorenone*-2-*carboxylate* (IV) in 90% yield.

In common with other azafluorenones of comparable complexity, (IV) was only slightly basic and could not be converted into a metho-salt (cf. Armit and Robinson, *J.*, 1922, 836). Its hydrolysis, too, proved difficult as the use of alkaline reagents led to secondary changes, whilst warm concentrated sulphuric acid caused hydrolysis and ring closure to 1′-*keto*-3-*methyl*-4-*aza*-*indeno*(3′ : 2′-1 : 2)*fluorenone* (V). (IV) readily formed an *oxime* which, on reduction with zinc dust in acetic anhydride solution, passed smoothly into *ethyl* 9-*diacetylamino*-1-*phenyl*-3-*methyl*-4-*azafluorene*-2-*carboxylate*. Attempts to convert this compound into the 9-amino-derivative by boiling alcoholic hydrochloric acid or by syrupy phosphoric acid at 160° led, however, to the loss of only one acetyl group and the formation of the 9-*acetamido*-derivative, which was remarkably resistant to hydrolysis, a behaviour associated with the sterically sheltered position of the acetamido-group (cf. preceding paper). (IV) failed to undergo the Schmidt reaction which has recently been successfully applied to some 2-azafluorenones (Petrow, *J.*, 1946, 200, 888).

The above synthesis of 1-aryl-4-azafluorenones (IV) has been extended in various ways. Thus various substituted *benzylideneindane*-1 : 3-*diones* have been prepared by direct fusion of the components at 130—140° and condensed with ethyl 2-aminocrotonate (II) in glacial acetic acid. The resulting bright-red *methyl*-, *methoxy*-, and *nitro*-substituted 1-phenyldihydro-4-azafluorenonecarboxylates, obtained in yields of 60—90%, have been converted into the corresponding 4-*azafluorenones* by chromic acid oxidation, and the nitrophenyl derivatives have been reduced to the *amino*-compounds by reduced iron in aqueous ethanol containing a little calcium chloride. *Ethyl* 1-(4′-*hydroxy*-3′-*methoxyphenyl*)-3-*methyl*-1 : 4-*dihydro*-4-*azafluorenone*-2-*carboxylate* had perforce to be acetylated before oxidation. *p*-Dimethylaminobenzylidene-indane-1 : 3-dione (Noelting and Blum, *loc. cit.*) condensed normally with ethyl 2-aminocrotonate, but the resulting *ethyl* 1-p-*dimethylaminophenyl*-3-*methyl*-1 : 4-*dihydro*-4-*azafluorenone*-2-*carboxylate* gave only coloured tars on oxidation with chromic acid. Sulphur dehydrogenation, employed by Hinkel and Cremer (*J.*, 1920, 139) with the analogous ethyl 4-*p*-dimethylamino-phenyldihydrolutidine-3 : 5-dicarboxylate, also proved unsuccessful. However, warming with dilute nitric acid in alcoholic solution led to simultaneous oxidation and nitration, giving *ethyl* 4-(2′-*nitro*-4′-*dimethylaminophenyl*)-3-*methyl*-4-*azafluorenone*-2-*carboxylate*. The structure assigned to this compound is based on its non-identity with the 3′-*nitro*-isomer prepared from 3′-nitro-4′-dimethylaminobenzylideneindane-1 : 3-dione (Noelting and Blum, *loc. cit.*).

The condensation of *cinnamylideneindane*-1 : 3-*dione* with ethyl 2-aminocrotonate presented certain anomalous features. The characteristic red colour developed normally when the components were heated together under reflux in acetic acid. The only product isolated, albeit in 30% yield, was golden-yellow and, in addition, resistant to chromic acid oxidation unless drastic experimental conditions leading to profound degradation were employed. It has therefore been formulated as an *ethyl* 1-2′-*phenylethyl*-3-*methyl*-4-*azafluorenone*-2-*carboxylate* and presumably results from the initially-formed 1-styryldihydro-derivative by hydrogen transfer.

Ethyl 2-aminocrotonate may frequently be replaced by the "ammonia derivatives" of 1 : 3-diketones in pyridine syntheses of the Hantzsch–Knoevenagel type (Knoevenagel and Ruschhaupt, *loc. cit.*). We therefore examined the reaction of benzylideneindane-1 : 3-dione (I) with methyl 2-aminopropenyl ketone (II*a*) and found, as expected, that smooth condensation took place in glacial acetic acid, giving 2-*acetyl*-1-*phenyl*-3-*methyl*-1 : 4-*dihydro*-4-*azafluorenone* (III*a*), oxidised by chromic acid to the corresponding *pyridine* derivative (IV*a*). *Ethyl* 2-*acetyl*-1-m-*nitrophenyl*- and *ethyl* 2-*acetyl*-1-p-*nitrophenyl*-3-*methyl*-4-*azafluorenone* were likewise prepared and reduced to the corresponding *amino*-compounds.

Condensation of phenyl 2-aminopropenyl ketone (II*b*) with benzylideneindane-1 : 3-dione (I) in glacial acetic acid for 1 hour under reflux resulted in only a 20% yield of the bright-red 2-*benzoyl*-1-*phenyl*-3-*methyl*-1 : 4-*dihydro*-4-*azafluorenone* (III*b*); when the time of heating was prolonged to 2 hours, a bright-yellow product was obtained which was clearly the corresponding 2-*benzoyl*-1-*phenyl*-3-*methyl*-4-*azafluorenone* (IV*b*), as it was also formed by direct oxidation of the foregoing red product (III*b*). The spontaneous loss of hydrogen of some dihydropyridines of similar types has previously been recorded by Michael (*Ber.*, 1885, **18**, 2020).

A further extension of the 4-azafluorenone synthesis was achieved by replacing ethyl

2-aminocrotonate by 2-aminocinnamonitrile (II*c*) (cf. Meyer, *J. pr. Chem.*, 1908, **78**, 507), whereupon 2-*cyano*-1 : 3-*diphenyldihydro*-4-*azafluorenone* (III*c*) was readily obtained in good yield.

The above 1-aryl-4-azafluorenones were, in general, too insoluble for adequate biological testing. The possibility of preparing the corresponding 1-alkyl derivatives was therefore examined. The use of aliphatic aldehydes in the above synthesis would clearly furnish the desired 1-alkyl derivatives. Aliphatic aldehydes, however, fail to react with indane-1 : 3-dione in the required manner. Thus Radulescu and Georgescu (*Bull. Soc. chim.*, 1925, **37**, 1069) report that a complex reaction takes place between aliphatic aldehydes and the diketone, leading principally to the formation of the corresponding methylenebisindane-1 : 3-dione. We have nevertheless examined the use of aliphatic aldehydes of somewhat higher molecular weight in the hope that their greater complexity would have some influence on the course of the reaction. All attempts to condense indane-1 : 3-dione with *n*-heptaldehyde, crotonaldehyde, or chloral under a variety of experimental conditions failed to give products of the required type.

The preparation of 2-acetyl- and 2-formyl-indane-1 : 3-dione has previously been reported in the literature and it is apparent that these compounds would form valuable intermediates for the synthesis of the required 4-azafluorenones. In our hands the condensation of diethyl phthalate with acetone in the presence of sodium ethoxide, as described by Schwirin (*Ber.*, 1894, **27**, 105), led to a variety of products in low yield, none of which appeared identical with the acetylindane-1 : 3-dione described in the literature. Attempts to synthesis 2-propionyl- and 2-benzoyl-indanediones were likewise unsuccessful. The preparation of 2-formylindane-1 : 3-dione, reported by Errara (*Gazzetta*, 1902, **32**, 330; 1903, **33**, i, 417) could not be repeated, nor could this compound be obtained by the action of amyl formate and sodium upon indane-1 : 3-dione in ether. These failures must be attributed to the highly reactive character of these intermediates and their consequent tendency to undergo auto-condensation in the alkaline environment necessary for their preparation. The disadvantages inseparable from these methods were nevertheless overcome, and 2-*anilomethylindane*-1 : 3-*dione* (*i.e.*, *formylindane*-1 : 3-*dione anil*) (VI) was prepared in excellent yield by direct condensation of indane-1 : 3-dione with diphenylformamidine at 145°. This elegant reaction, discovered by Piggott and Rodd (B.P. 344,409), has been widely employed, for the introduction of the formyl group, in cyanine dye chemistry. Anilomethylindane-1 : 3-dione (VI), however, failed to react with ethyl 2-aminocrotonate on fusion at 140°, in boiling alcohol in the presence of piperidine, or in boiling acetic anhydride, a failure which cannot be attributed to the employment of the anil, *per se*, as Borsche, Barthenheier, and Wagner-Roemnick (*Annalen*, 1942, **550**, 160) have shown that anils may be advantageously employed in place of the aldehydes in certain quinoline and naphthyridine syntheses. As these attempts to prepare a 1-alkyl-4-azafluorenone proved abortive, an indirect approach was attempted, by way of *ethyl* 1-2′-*furyl*-3-*methyl*-4-*azafluorenone*-2-*carboxylate*. This compound was readily prepared from *furfurylideneindane*-1 : 3-*dione*, followed by oxidation of the resulting *dihydro*-base with nitric acid in alcoholic solution. Unfortunately all attempts at the degradation of the furan ring of this compound, either by prolonged heating with concentrated hydrochloric acid in glacial acetic acid, or by oxidation with chromic acid in sulphuric acid, failed to give compounds of the required type.

Experimental.

M. p.s are corrected. Microanalyses are by Drs. Weiler and Strauss, Oxford.

Substituted Benzylideneindane-1 : 3-*diones, etc.*—Indane-1 : 3-dione (0·1 mol.) and the appropriate aldehyde (0·1 mol.) were fused together at 130—140° in an oil-bath. Water vapour was vigorously evolved and the melt generally solidified after 10—20 minutes. Heating was then continued for a further 15 minutes, whereafter the product was isolated by crystallisation from acetic acid (charcoal). The benzylidene compounds listed in Table I were thus prepared as were the two following compounds.

2-*Cinnamylideneindane*-1 : 3-*dione*, golden needles (70%) (from alcohol), m. p. 161—162° (Found : C, 82·7; H, 4·7. $C_{15}H_{12}O_2$ requires C, 83·1; H, 4·6%).

2-2′-*Furfurylideneindane*-1 : 3-*dione*, small needles (43%) (from acetic acid), m. p. 209—210° (Found : C, 75·7; H, 3·7. $C_{14}H_8O_3$ requires C, 75·0; H, 3·6%).

Ethyl 1-*Phenyl*-3-*methyl*-1 : 4-*dihydro*-4-*azafluorenone*-2-*carboxylate* (III).—(*a*) Benzylideneindane-1 : 3-dione (3·9 g.) and ethyl β-aminocrotonate (2·1 g.) were fused together at 100° for 8 hours. The solid product was extracted with alcohol, and the insoluble residue recrystallised from acetic acid. *Ethyl* 1-*phenyl*-3-*methyl*-1 : 4-*dihydro*-4-*azafluorenone*-2-*carboxylate* (1·8 g., 31%) separated in dark-red plates, m. p. 252—254° (Found : C, 76·1; H, 5·5; N, 4·1. $C_{22}H_{19}O_3N$ requires C, 76·5; H, 5·5; N, 4·1%).

(*b*) A solution of benzylideneindane-1 : 3-dione (5·3 g.) in acetic acid (25 ml.) was treated at the b. p. with ethyl β-aminocrotonate (6·5 g.). A deep-red colour immediately developed, followed after a minute's boiling by the separation of (III) in dark-red plates (6·8 g., 87%), m. p. 251—252°.

The dihydro-compounds listed in Tables II and III were similarly prepared.

TABLE I.

Substituted Benzylideneindane-1 : 3-diones.

Substituent.	M. p.	Yield.	Formula.	%,	C.	H.	N.	Description.
4′-*Methyl*-	154·5—155°	50%	$C_{17}H_{12}O_2$	Found	82·5	5·0	—	Buff-coloured needles (*a*)
				Reqd.	82·3	4·8	—	
2′-*Methoxy*-	167·5—168	69	$C_{17}H_{12}O_3$	Found	77·3	4·5	—	Bright-yellow needles
				Reqd.	77·3	4·5	—	
3′-*Methoxy*-	143	71	$C_{17}H_{12}O_3$	Found	76·8	4·4	—	Peach-coloured needles
				Reqd.	77·3	4·5	—	
4′-*Methoxy*-	158	70	$C_{17}H_{12}O_3$	Found	77·1	4·5	—	Orange needles
				Reqd.	77·3	4·5	—	
3′-Nitro-	250·5	59	$C_{16}H_9O_4N$	Found	68·6	3·1	5·1	Cream-coloured needles (*b*)
				Calc.	68·8	3·2	5·0	
4′-*Nitro*-	231 (decomp.)	67	$C_{16}H_9O_4N$	Found	69·1	3·2	5·0	Lemon-coloured needles
				Reqd.	68·8	3·2	5·0	
4′-Dimethylamino-	203·5	70	$C_{18}H_{15}O_2N$	Found	77·6	5·7	5·4	Bronze-red needles (*c*)
				Calc.	78·0	5·7	5·4	

(*a*) Recrystallised from light petroleum.
(*b*) Radulescu and Georgescu (*loc. cit.*) give m. p. 246°.
(*c*) Recrystallised from large volumes of alcohol. Noelting and Blum (*loc. cit.*) record m. p. 99°.

Ethyl 1-*Phenyl*-3-*methyl*-4-*azafluorenone*-2-*carboxylate*.—The foregoing dihydro-compound (4·2 g.), dissolved in warm acetic acid (120 ml.), was treated with chromic acid (1·2 g.) in water. After 5 minutes the solution was diluted with water until the product began to separate. *Ethyl* 1-*phenyl*-3-*methyl*-4-*azafluorenone*-2-*carboxylate* (3·8 g., 88%) (IV) crystallised from aqueous spirit in flat, lemon needles, m. p. 174·5—175·5° (Found: C, 77·4; H, 5·1; N, 4·2. $C_{22}H_{17}O_3N$ requires C, 77·0; H, 5·0; N, 4·1%). The *oxime* separated from large volumes of alcohol in silver platelets, m. p. 281° (decomp.) (Found: C, 73·9; H, 5·3; N, 7·5. $C_{22}H_{18}O_3N_2$ requires C, 73·7; H, 5·0; N, 7·8%).

Other compounds similarly prepared are listed in Tables II and III.

1′-*Keto*-3-*methyl*-4-*azaindeno*(3′ : 2′-1 : 2)*fluorenone* (V) (with Mr. A. COURTS).—Ethyl 1-phenyl-3-methyl-4-azafluorenone-2-carboxylate (2 g.) was dissolved in concentrated sulphuric acid (20 ml.), and the solution maintained at 60° for 5 minutes. The yellow solid which separated on pouring the mixture on ice was collected and recrystallised from acetic acid, giving the *diketone* (V) in yellow needles, m. p. 263° (Found: C, 80·8; H, 4·0; N, 4·4 $C_{20}H_{11}O_2N$ requires C, 80·8; H, 3·7; N, 4·7%).

Ethyl 9-*diacetylamino*-1-*phenyl*-3-*methyl*-4-*azafluorene*-2-*carboxylate*, colourless octahedra, m. p. 135°, from ligroin (Found: C, 72·9; H, 5·6; N, 7·0. $C_{26}H_{24}O_4N_2$ requires C, 72·9; H, 5·6; N, 6·5%), was obtained by reduction of the above-mentioned oxime with zinc dust and acetic anhydride as described in the preceding communication. Hydrolysis of this compound (2·7 g.) with alcohol (15 ml.) and concentrated hydrochloric acid (30 ml.) under reflux for 1 hour, followed by precipitation with dilute aqueous ammonia, gave *ethyl* 9-*acetamido*-1-*phenyl*-3-*methyl*-4-*azafluorene*-2-*carboxylate* as octahedra (from benzene–ligroin), m. p. 196° (Found: C, 74·7; H, 5·9; N, 7·8; Ac, 11·6. $C_{24}H_{22}O_3N_2$ requires C, 74·6; H, 5·7; N, 7·3; Ac, 11·1%), in almost theoretical yield. The compound was recovered unchanged after being heated at 190° with syrupy phosphoric acid.

Ethyl 1-p-*Dimethylaminophenyl*-3-*methyl*-1 : 4-*dihydro*-4-*azafluorenone*-2-*carboxylate*.—This *compound* (40% yield) formed orange needles from aqueous alcohol (charcoal), m. p. 170° (Found: C, 74·5; H, 6·1; N, 7·3. $C_{24}H_{24}O_3N_2$ requires C, 74·2; H, 6·2; N, 7·2%). Treatment of a boiling alcoholic solution of it (1·5 g.) with nitric acid (2·5 ml.; *d* 1·4), followed by precipitation with dilute aqueous ammonia gave *ethyl* 1-(2′-*nitro*-4′-*dimethylaminophenyl*)-3-*methyl*-4-*azafluorenone*-2-*carboxylate*, which formed felted deep-yellow needles, m. p. 179°, from benzene–ligroin (Found: C, 67·2; H, 4·9; N, 9·8. $C_{24}H_{21}O_5N_3$ requires C, 66·8; H, 4·9; N, 9·7%). The compound gave a depression in m. p. in admixture with the isomeric 3′-nitro-compound (Table II).

Ethyl 1-2′-*Phenylethyl*-3-*methyl*-4-*azafluorenone*-2-*carboxylate*.—A solution of cinnamylideneindane-1 : 3-dione (5 g.) in acetic acid (20 ml.) was treated with ethyl 2-aminocrotonate (5 g.). The oil which separated on adding water to the red solution was purified initially from alcohol (charcoal) and finally from *n*-hexane, giving *ethyl* 1-2′-*phenylethyl*-3-*methyl*-4-*azafluorenone*-2-*carboxylate* (17%) in thin golden needles, m. p. 139—140° (Found: C, 77·8; H, 5·4; N, 3·8. $C_{24}H_{21}O_3N$ requires C, 77·6; H, 5·7; N, 3·8%). The compound was recovered unchanged after treatment with chromic acid in acetic acid. The yield was not improved by heating the reaction mixture under reflux, or by carrying out the condensation in boiling acetic anhydride.

2-*Benzoyl*-1-*phenyl*-3-*methyl*-1 : 4-*dihydro*-4-*azafluorenone*.—Benzylideneindane-1 : 3-dione (4·2 g.), phenyl 2-aminopropenyl ketone (5·5 g.; Knoevenagel, *Ber.*, 1903, **36**, 2187), and acetic acid (35 ml.) were heated under reflux. The characteristic red colour developed only after 10—15 minutes, and heating was therefore continued for 1 hour. Addition of water precipitated a dark-red oil which, when recrystallised from aqueous alcohol (charcoal), gave carmine platelets of 2-*benzoyl*-1-*phenyl*-3-*methyl*-1 : 4-*dihydro*-4-*azafluorenone* (22%), m. p. 166—167° (Found: N, 3·9. $C_{26}H_{19}O_2N$ requires N, 3·7%).

2-*Benzoyl*-1-*phenyl*-3-*methyl*-4-*azafluorenone*.—(*a*) Benzylideneindane-1 : 3-dione (3·4 g.), phenyl 2-aminopropenyl ketone (4·0 g.), and acetic acid (25 ml.) were heated under reflux for 2 hours. Isolation of the product as described above gave 2-*benzoyl*-1-*phenyl*-3-*methyl*-4-*azafluorenone* (18%), lemon-yellow needles, m. p. 175°, from benzene–ligroin (Found: C, 82·9; H, 4·5; N, 3·9. $C_{26}H_{17}O_2N$ requires C, 83·2; H, 4·5; N, 3·7%). The compound gave a depression of the m. p. in admixture with the preceding dihydro-compound.

(*b*) The corresponding dihydro-compound was oxidised with chromic acid in the usual manner. The

TABLE II.

Ethyl 3-Methyl-4-azafluorenone-2-carboxylates.

Substituent.	M. p.	Yield.	Formula.	%,	C.	H.	N.	Description.	Solvent.
1-p-*Tolyl*-1 : 4-*dihydro*-	237·5—238·5°	70%	$C_{23}H_{21}O_3N$	Found	77·1	5·9	4·0	Deep-red platelets	*b*
				Reqd.	76·9	5·9	3·9		
1-p-*Tolyl*-	118	—	$C_{23}H_{19}O_3N$	Found	77·2	5·1	4·0	Ivory-coloured needles	*f*
				Reqd.	77·3	5·3	3·9		
1-o-*Methoxyphenyl*-1 : 4-*dihydro*-	211·5—213	60	$C_{23}H_{21}O_4N$	Found	73·6	5·5	3·9	Plum-coloured crystals	*b*
				Reqd.	73·6	5·6	3·7		
1-o-*Methoxyphenyl*-	165·5—166	—	$C_{23}H_{19}O_4N$	Found	74·0	5·2	3·5	Pale-yellow warts	*f*
				Reqd.	74·0	5·1	3·8		
1-m-*Methoxyphenyl*-1 : 4-*dihydro*-	223—224	93	$C_{23}H_{21}O_4N$	Found	73·5	5·6	3·9	Scarlet small plates	*c*
				Reqd.	73·6	5·6	3·7		
1-m-*Methoxyphenyl*-	115—116	—	$C_{23}H_{19}O_4N$	Found	74·4	5·0	3·8	Pale-yellow crusts	*f*
				Reqd.	74·0	5·1	3·8		
1-p-*Methoxyphenyl*-1 : 4-*dihydro*-	253	74	$C_{23}H_{21}O_4N$	Found	73·4	5·6	4·0	Dark-red plates	*b*
				Reqd.	73·6	5·6	3·7		
1-p-*Methoxyphenyl*-	120·5	—	$C_{23}H_{19}O_4N$	Found	73·5	5·0	3·8	Bright-yellow prisms	*f*
				Reqd.	74·0	5·1	3·8		
1-(3′ : 4′-*Methylenedioxyphenyl*)-1 : 4-*dihydro*-	275	70	$C_{23}H_{19}O_5N$	Found	71·1	5·1	3·7	Deep-red plates	*b*
				Reqd.	71·0	4·9	3·6		
1-(3′ : 4′-*Methylenedioxyphenyl*)-	121·5	—	$C_{23}H_{17}O_5N$	Found	71·2	4·4	—	Mustard-coloured prisms	*f*
				Reqd.	71·3	4·4	—		
1-(4′-*Hydroxy*-3′-*methoxyphenyl*)-1 : 4-*dihydro*-	232·5—233	64	$C_{23}H_{21}O_5N$	Found	—	—	3·6	Deep-red needles	*a*
				Reqd.	—	—	3·6		
1-(4′-*Acetoxy*-3′-*methoxyphenyl*)-1 : 4-*dihydro*-	201—202	—	$C_{25}H_{23}O_6N$	Found	69·6	5·3	3·5	Scarlet platelets	*d*
				Reqd.	69·3	5·3	3·2		
1-(4′-*Acetoxy*-3′-*methoxyphenyl*)-	151	—	$C_{22}H_{21}O_6N$	Found	69·5	4·9	3·3	Fine cream-coloured needles	*e*
				Reqd.	69·6	4·9	3·3		
1-m-*Nitrophenyl*-1 : 4-*dihydro*-	241 (decomp.)	79	$C_{22}H_{16}O_5N_2$	Found	67·6	4·7	7·3	Flat dark-red needles	*b*
				Reqd.	67·7	4·6	7·2		
1-m-*Nitrophenyl*-	168	—	$C_{22}H_{16}O_5N_2$	Found	68·1	4·6	7·5	Felted ivory-coloured needles	*f*
				Reqd.	68·0	4·1	7·2		
1-m-*Aminophenyl*-	201—203	—	$C_{22}H_{18}O_3N_2$	Found	73·7	5·1	7·5	Ochre-coloured crystals	*e*
				Reqd.	73·7	5·0	7·8		
1-p-*Nitrophenyl*-1 : 4-*dihydro*-	226·5—227·5	84	$C_{22}H_{16}O_5N_2$	Found	67·4	4·5	6·8	Scarlet needles	*c*
				Reqd.	67·7	4·6	7·2		
1-p-*Nitrophenyl*-	201—201·5	—	$C_{22}H_{16}O_5N_2$	Found	67·8	3·1	7·5	Yellowish-green needles	*e*
				Reqd.	68·0	4·1	7·2		
1-p-*Aminophenyl*-	231—232	—	$C_{22}H_{18}O_3N_2$	Found	74·4	5·3	7·8	Deep-orange prisms	*e*
				Reqd.	73·7	5·0	7·8		
1-p-*Dimethylaminophenyl*-1 : 4-*dihydro*-	170	40	$C_{24}H_{24}O_3N_2$	Found	74·5	6·1	7·3	Orange needles	*a*
				Reqd.	74·2	6·2	7·2		
1-(3′-*Nitro*-4′-*dimethylaminophenyl*)-1 : 4-*dihydro*-	227·5—228·5	45	$C_{24}H_{23}O_5N_3$	Found	66·1	5·6	10·0	Scarlet needles	*c*
				Reqd.	66·5	5·3	9·7		
1-(3′-*Nitro*-4′-*dimethylaminophenyl*)-	210	—	$C_{24}H_{21}O_5N_2$	Found	66·5	4·6	9·9	Mustard-coloured prisms	*e*
				Reqd.	66·8	4·9	9·7		
1-2′-*Furyl*-1 : 4-*dihydro*-	249—251	71	$C_{20}H_{17}O_4N$	Found	71·3	4·9	4·1	Dark-red plates	*a*
				Reqd.	71·7	5·1	4·2		
1-2′-*Furyl*-	141—142	—	$C_{20}H_{15}O_4N$	Found	71·8	4·4	4·4	Straw-coloured needles	*f*
				Reqd.	72·1	4·5	4·2		

a, Alcohol. *b*, Acetic acid. *c*, Aqueous acetic acid. *d*, Benzene. *e*, Benzene–ligroin. *f*, Light petroleum.

product formed cream-coloured needles, identical in m. p. and mixed m. p. with the compound obtained by method (*a*).

2-*Cyano*-1 : 3-*diphenyl*-1 : 4-*dihydro*-4-*azafluorenone*.—This compound, fine orange-red needles, m. p. 251° (Found : N, 7·6. $C_{25}H_{16}ON_2$ requires N, 7·4%), from acetic acid, was prepared (40%) by heating benzylideneindane-1 : 3-dione (4 g.), 2-aminocinnamonitrile (5 g.), and acetic acid (40 ml.) under reflux for 30 minutes. 2-*Cyano*-1 : 3-*diphenyl*-4-*azafluorenone* separated in felted cream needles, m. p. 273·5°, from pyridine–ligroin (Found : C, 83·4; H, 4·1; N, 8·1. $C_{25}H_{14}ON_2$ requires C, 83·8; H, 3·9; N, 7·8%).

2-*Anilomethylindane*-1 : 3-*dione*.—Indane-1 : 3-dione (2·1 g.) and diphenylformamidine (3·2 g.) were fused together at 145° for 45 minutes. The crystalline product was washed free from a blue impurity with cold alcohol, and the residue recrystallised from alcohol. 2-*Anilomethylindane*-1 : 3-*dione* (60%) separated in olive-green plates, m. p. 197—198° (Found : C, 77·1; H, 4·4; N, 5·6. $C_{16}H_{11}O_2N$ requires C, 77·1; H, 4·4; N, 5·6%).

TABLE III.

2-Acetyl-3-methyl-4-azafluorenones.

Substituent.	M. p.	Yield.	Formula.	%,	C.	H.	N.	Description.	Solvent.*
1-*Phenyl*-1 : 4-*dihydro*-	246—247°	60%	$C_{21}H_{17}O_2N$	Found	79·9	5·2	4·3	Scarlet needles	
				Reqd.	80·0	5·4	4·4		
1-*Phenyl*-	167·5—168	—	$C_{21}H_{15}O_2N$	Found	80·1	5·0	4·6	Long cream-coloured needles	*f*
				Reqd.	80·5	4·8	4·5		
1-m-*Nitrophenyl*-1 : 4-*dihydro*-	232	88	$C_{21}H_{16}O_4N_2$	Found	69·6	4·7	7·9	Vermilion needles	*a*
				Reqd.	70·0	4·4	7·8		
1-m-*Nitrophenyl*-	224	—	$C_{21}H_{14}O_4N_2$	Found	70·0	4·3	7·8	Ochre-coloured plates	*c*
				Reqd.	70·4	3·9	7·8		
1-m-*Aminophenyl*-	216·5—217·5	—	$C_{21}H_{16}O_2N_2$	Found	76·6	5·2	8·6	Ochre-coloured crystals	*e*
				Reqd.	76·8	4·9	8·5		
1-p-*Nitrophenyl*-1 : 4-*dihydro*-	242·5—243	77	$C_{21}H_{16}O_4N_2$	Found	70·0	4·6	7·9	Strawberry-coloured plates	*b*
				Reqd.	70·0	4·4	7·8		
1-p-*Nitrophenyl*-	238	—	$C_{21}H_{14}O_4N_2$	Found	70·3	4·2	7·6	Pale-yellow needles	*c*
				Reqd.	70·4.	3·9	7·8		
1-p-*Aminophenyl*-	253—254	—	$C_{21}H_{16}O_2N_2$	Found	76·8	5·4	8·2	Flame-coloured needles	*a*
				Reqd.	76·8	4·9	8·5		

* See footnote to Table II.

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