Synthesis of Fluoranthenes. Part XII. Spectroscopic Examination of Fluoranthene Derivatives.*

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Ultra-violet spectra have been recorded of mono-, di-, and tri-methylfluoranthenes, and of the methoxyfluoranthenes. For this purpose, 3 : 4-dimethyl- and 2-, 4-, and 10-methoxy-fluoranthene have been synthesised.

FEW ultra-violet absorption spectra of compounds containing the fluoranthene ring system have been recorded. (For references, see Tucker and Whalley, *Chem. Reviews*, 1952, **50**, 484; Friedel and Orchin, "Ultra-violet Spectra of Aromatic Compounds," 1951, Nos. 439—444; Stubbs and Tucker, *J.*, 1951, 2936; Tucker and Whalley, *J.*, 1952, 3187). Since absorption spectra are being increasingly used not only for characterisation of isomers, but also for their identification in mixtures (cf. Jones, *Chem. Reviews*, 1943, **32**, 1; *J. Amer. Chem. Soc.*, 1945, **67**, 2127) we have examined the ultra-violet absorption spectra of a number of fluoranthene derivatives prepared in this series of researches (see Table, and Figs. 1—2). Replacement of a hydrogen atom by a methyl group in an aromatic

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hydrocarbon has only slight effect on the general outline of the absorption curve : any shift of the main absorption bands is to longer wave-lengths (cf. Jones, *locc. cit.* ; Brode and Patterson, *J. Amer. Chem. Soc.*, 1941, **63**, 3252). It will be seen (Table and Fig. 1) that the substitution of one or more methyl groups in fluoranthene has practically no effect on the shape of the curve but produces a slight progressive shift of most of the absorption maxima towards the red end of the spectrum. The absorption curve of 2-methoxyfluoranthene (Fig. 2, apart from the prominent α-band at 327·5 mμ) is remarkably like the

Ultra-violet absorption spectra of fluoranthene and its derivatives. (Solvent, ethanol; max. in mμ.)

Fluoranthene derivative			*p*-Bands [a]			
Fluoranthene [b]	Fig. 1	$\lambda_{max.}$	358·5	342	323	309
	,,	log ε	3·92	3·87	3·78	3·57
2-Methyl	,,	$\lambda_{max.}$	364	348	327	313
	,,	log ε	3·88	3·89	3·87	3·62
3-Methyl	,,	$\lambda_{max.}$	362	346	326·5	311·5
	,,	log ε	3·92	3·90	3·82	3·58
4-Methyl	,,	$\lambda_{max.}$	364	348	327·5	312
	,,	log ε	3·96	4·95	3·77	3·55
10-Methyl [c]	,,	$\lambda_{max.}$	366	350	324	309
	,,	log ε	3·93	3·94	3·77	3·54
11-Methyl	,,	$\lambda_{max.}$	362	346	326	310
	,,	log ε	3·91	3·89	3·78	3·53
2 : 4-Dimethyl	Fig. 1	$\lambda_{max.}$	368	352	328	314
	,,	log ε	3·96	3·96	3·85	3·60
3 : 4-Dimethyl	,,	$\lambda_{max.}$	366	350	329	314
	,,	log ε	3·96	3·94	3·78	3·57
2 : 3 : 4-Trimethyl	,,	$\lambda_{max.}$	367	352, 341	330	315
	,,	log ε	3·96	3·96, 3·83	3·88	3·62
2-Methoxy	Fig. 2	$\lambda_{max.}$	372	—	327·5	312
	,,	log ε	3·96	—	3·91	3·65
4-Methoxy	,,	$\lambda_{max.}$	363·5	—	323	—
	,,	log ε	4·06	—	3·79	—
10-Methoxy	,,	$\lambda_{max.}$	380, 363	352	—	303
	,,	log ε	3·92, 4·11	4·05	—	3·55
11-Methoxy	,,	$\lambda_{max.}$	361	344	324	310
	,,	log ε	3·80	3·73	3·72	3·62

Fluoranthene derivative			β-Bands							β′-Bands	
Fluoranthene [b] ...	Fig. 1	$\lambda_{max.}$	287	282	276	271·5	261·5	252·5	245	236	—
	,,	log ε	4·49	4·23	4·34	4·04	4·13	4·20	4·32	4·73	—
2-Methyl	,,	$\lambda_{max.}$	286·5	—	276·5	—	—	—	—	239	—
	,,	log ε	4·43	—	4·29	—	—	—	—	4·70	—
3-Methyl	,,	$\lambda_{max.}$	289·5	—	279	—	262	253·5	—	236·5	—
	,,	log ε	4·40	—	4·31	—	4·19	4·24	—	4·69	—
4-Methyl	,,	$\lambda_{max.}$	290·5	285	280	—	264	—	239	230	—
	,,	log ε	4·48	4·26	4·33	—	4·03	—	4·70	4·47	—
10-Methyl [c]	,,	$\lambda_{max.}$	288	—	277	269	265	257	—	235	—
	,,	log ε	4·34	—	4·28	4·18	4·16	4·17	—	4·64	—
11-Methyl	,,	$\lambda_{max.}$	290	284	279	266	—	—	—	236	—
	,,	log ε	4·55	4·34	4·40	4·06	—	—	—	4·61	—
2 : 4-Dimethyl......	Fig. 1	$\lambda_{max.}$	290·5	—	279·5	—	263	—	242	—	—
	,,	log ε	4·48	—	4·29	—	4·05	—	4·67	—	—
3 : 4-Dimethyl......	,,	$\lambda_{max.}$	293	281·5	—	268	—	255	241	—	—
	,,	log ε	4·44	4·29	—	4·17	—	4·22	4·68	—	—
2 : 3 : 4-Trimethyl	,,	$\lambda_{max.}$	292·5	281	—	264	—	—	243	—	—
	,,	log ε	4·45	4·28	—	4·17	—	—	4·67	—	—
2-Methoxy	Fig. 2	$\lambda_{max.}$	285·5	—	276	—	—	—	246·5	—	—
	,,	log ε	4·36	—	4·23	—	—	—	4·74	—	—
4-Methoxy	,,	$\lambda_{max.}$	296	285	—	—	—	—	240	—	220
	,,	log ε	4·62	4·34	—	—	—	—	4·74	—	4·59
10-Methoxy	,,	$\lambda_{max.}$	290	282	—	—	—	—	246	230	222
	,,	log ε	3·71	3·67	—	—	—	—	4·31	4·55	4·64
11-Methoxy-	,,	$\lambda_{max.}$	295	285	—	—	—	—	—	236	—
	,,	log ε	4·59	4·35	—	—	—	—	—	4·55	—

[a] For classification of bands see Clar, *J. Chem. Phys.*, 1949, **17**, 741; *Chem. Ber.*, 1949, **82**, 495; *Spectrochim. Acta*, 1950, **4**, 116; Clar and Stewart, *J. Amer. Chem. Soc.*, 1952, **74**, 6235. [b] Clar, Stubbs, and Tucker, *Nature*, 1950, **166**, 1075. [c] Tucker and Whalley, *J.*, 1952, 3187. Reinvestigation has shown that there is no max. at 374 mμ, and that there is one at 309 mμ (log ε 3·54) [J. WILLIAMSON].

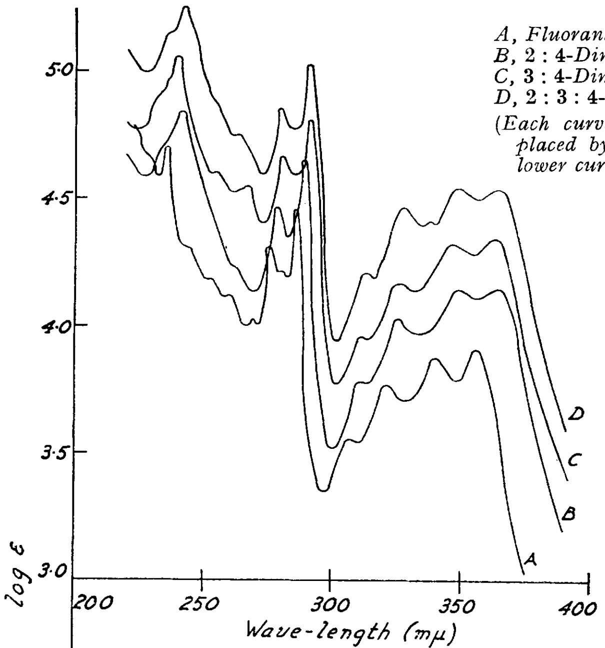


FIG. 1.

A, Fluoranthene.
B, 2 : 4-*Dimethylfluoranthene.*
C, 3 : 4-*Dimethylfluoranthene.*
D, 2 : 3 : 4-*Trimethylfluoranthene.*
(*Each curve, except that of A, displaced by* + 0·3 (log ε) *above the lower curve.*)

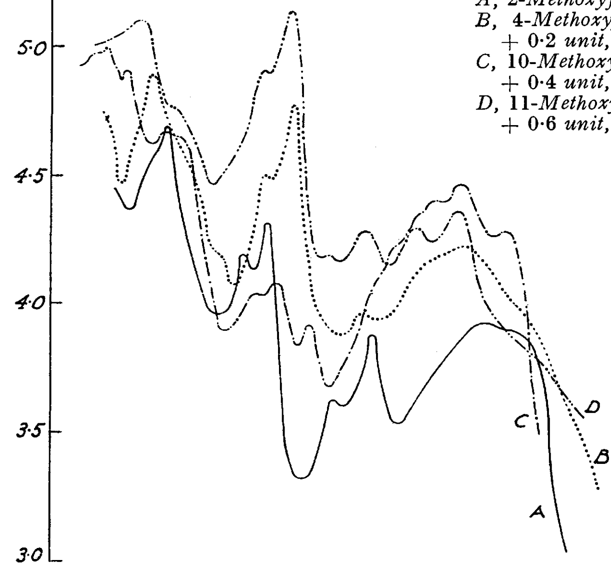
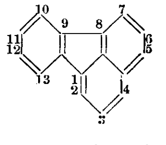


FIG. 2.

A, 2-*Methoxyfluoranthene.*
B, 4-*Methoxyfluoranthene* (*displaced* + 0·2 *unit,* log ε).
C, 10-*Methoxyfluoranthene* (*displaced* + 0·4 *unit,* log ε).
D, 11-*Methoxyfluoranthene* (*displaced* + 0·6 *unit,* log ε).

very flat one of 4-phenylfluoranthene (Stubbs and Tucker, *J.*, 1951, 2937), and similar to that of 4-methoxyfluoranthene (Fig. 2) (for numbering see inset) In these three compounds electronic interaction between the substituent methoxyl or phenyl group and the naphthalene nucleus is probable. If, as already suggested (Clar, Stubbs, and Tucker, *loc. cit.*), "*p*-absorption in fluoranthene is located in the naphthalene ring system," one would expect these three compounds to have spectra varying similarly from that of fluoranthene. On the other hand, since the benzene ring in fluoranthene, on the above assumption, has very little effect on *p*-absorption, 10- and 11-methoxyfluoranthene should have spectra closely related to that of fluoranthene. This is seen to be so (Fig. 2). Clearly, since the spectra of 2- and 10-methoxyfluoranthene are so different, there is no justification



for assuming that methoxyl groups in these two compounds have any steric effect on planarity of the molecule.

For these investigations several fluoranthene derivatives had to be synthesised, *viz.*, 2-, 4-, and 10-methoxy-fluoranthene (3-methoxyfluoranthene has not yet been prepared). 1-*o*-Methoxyphenylnaphthalene was also needed for comparison. 3 : 4-Dimethylfluoranthene was easily prepared.

The method successfully adopted for the synthesis of 11-methoxyfluoranthene failed when applied to the synthesis of the 10-methoxy-isomer (Hawkins and Tucker, *J.*, 1950, 3286). Another attempt, herein described, also failed since, although 3-bromo-2-nitroanisole reacts with 1-iodonaphthalene, by the Ullmann method, to give the expected 1-(3-methoxy-2-nitrophenyl)naphthalene which can be reduced to the corresponding amine, cyclisation to give 10-methoxyfluoranthene failed. These two failures are surprising since this compound has been synthesised without difficulty by a new route: 1-bromo-8-nitronaphthalene + *o*-iodoanisole ⟶ 1-*o*-methoxyphenyl-8-nitronaphthalene ⟶ amine ⟶ 10-methoxyfluoranthene. It might have been expected that ring closure on the benzene ring, as effected in the last synthesis, would have been less easy than at the α-position of the naphthalene nucleus.

For comparison, 1-*o*-methoxyphenylnaphthalene was synthesised by an Ullmann reaction from *o*-iodoanisole and 1-iodonaphthalene, and two forms, m. p. 91—93° and 98—99°, respectively, were isolated. It was later learned that Dr. Orchin had previously isolated these (m. p. 91·2—92·6° and 98·6—99·8°), starting from *o*-methoxyphenylmagnesium bromide and α-tetralone (Orchin, *J. Amer. Chem. Soc.*, 1948, **70**, 495). We have repeated and confirmed his work. A sample (m. p. 98·6—99·8°) which he kindly supplied, has proved identical in properties with our material. He states that the lower- is slowly transformed into the higher-melting form. We have found that 1 : 2 : 3 : 4-tetrahydro-1-hydroxy-1-*o*-methoxyphenylnaphthalene can be dehydrated and dehydrogenated in one stage to 1-*o*-methoxyphenylnaphthalene by boiling its solution in xylene with iodine and magnesia. This dehydrogenation process would appear to be restricted in scope to dihydro-compounds since tetralin was unaffected under comparable conditions (cf. Potter and Taylor, *J.*, 1953, 1320, and references therein).

These syntheses of 1-*o*-methoxyphenylnaphthalene throw light on the work of Hönigschmidt (*Monatsh.*, 1902, **23**, 823) who, by the action of diazotised 1-naphthylamine on phenol, obtained 1-*x*-hydroxyphenylnaphthalene (cf. Hodgson and Foster, *J.*, 1942, 581). This on methylation gave a methoxyphenylnaphthalene, m. p. 90·7—91·2°, assumed by van Alphen and Drost (*Rec. Trav. chim.*, 1950, **69**, 284) to be 1-*o*-methoxyphenylnaphthalene. The above syntheses prove that this is correct. These authors mentioned the possibility of dimorphism (cf. van Alphen, *Ber.*, 1928, **61**, 276; 1938, **71**, 491; 1930, **63**, 94; 1931, **64**, 1819; *Rec. Trav. chim.*, 1932, **51**, 179, 361, 453), but had obviously overlooked Orchin's paper (*loc. cit.*).

1-*o*-Methoxyphenylnaphthalene gives a picrate with the somewhat unusual proportion of 0·5 mol. of picric acid.

For synthesis of 2-methoxyfluoranthene, 1-iodo-2-methoxynaphthalene was prepared by iodination of 2-methoxynaphthalene (Jurd, *Austral. J. Sci. Res.*, 1949, **2**, *A*, 246). An Ullmann reaction with this iodo-compound and *o*-bromonitrobenzene, with subsequent procedure as in this series of papers, led to 2-methoxyfluoranthene. The possibility that ring closure had involved the methoxyl group was excluded by a Zeisel estimation on the product (2-methoxyfluoranthene) which gave the expected result. 4-Methoxyfluoranthene was synthesised similarly from 1-iodo-4-methoxynaphthalene (cf. Forrest and Tucker, *J.*, 1948, 1139).

3 : 4-Dimethylfluoranthene has been synthesised by a straightforward Grignard reaction on 1 : 2 : 3 : 4-tetrahydro-3-methyl-4-oxofluoranthene, followed by dehydration–dehydrogenation.

EXPERIMENTAL

Ultra-violet absorption spectra were recorded on the Unicam spectrophotometer, ethanol being used as solvent.

10-Methoxyfluoranthene.—8-Nitro-1-naphthylamine (Hodgson and Crook, *J.*, 1936, 1845;

Hodgson and Ratcliffe, *J.*, 1949, 1314) was converted into 1-bromo-8-nitronaphthalene (m. p. 99—100°) as for the corresponding iodo-compound (Hodgson and Crook, *J.*, 1937, 572). *o*-Iodoanisole (2·34 g., 2 mols.), 1-bromo-8-nitronaphthalene (2·52 g., 1 mol.), and copper bronze (1·0 g.) were heated at 224° (methyl salicylate bath) (Tucker, *J. Chem. Educ.*, 1953, in the press) for 1·5 hr., and stirred (tantalum-wire stirrer). The product was extracted with benzene, the solution evaporated, and the black residue so obtained extracted with cold benzene. Insoluble 8 : 8′-dinitro-1 : 1′-dinaphthyl (0·1 g.), recrystallised from acetic anhydride diluted with acetone, had m. p. 290° (decomp.) (Found: C, 69·8; H, 3·4; N, 7·9. Calc. for $C_{20}H_{12}O_4N_2$: C, 69·8; H, 3·5; N, 8·1%). The benzene solution was chromatographed on alumina. The first portion (*ca.* 10 ml.) of the eluate, after removal of benzene, gave a pale yellow oil; a solution of this in excess of methanol slowly gave crystals of the desired product (see below), and *o*-iodoanisole remained in solution. The next portion of eluate (*ca.* 50 ml.), treated similarly, gave at once pale greenish-yellow rectangular lathes, m. p. 135—136°, of 1-*o*-*methoxyphenyl*-8-*nitronaphthalene* (1·01 g., 35%) (Found: C, 73·1; H, 4·6; N, 5·1. $C_{17}H_{13}O_3N$ requires C, 73·1; H, 4·7; N, 5·0%). It crystallised also from benzene–light petroleum (b. p. 60—80°) but the crystals became opaque on storage, presumably owing to loss of solvent of crystallisation.

Use of 1-iodo-8-nitronaphthalene in place of the bromo-analogue in the above preparation gave relatively more dinitrodinaphthyl and less of the desired compound.

1-*o*-Methoxyphenyl-8-nitronaphthalene (0·93 g.) was reduced at room temperature and pressure by hydrogen (theoretical absorption in 1 hr.) in presence of Raney nickel (*ca.* 1 g.), in ethanol (50 ml.), to give stout, pale brown prisms (from light petroleum, b. p. 60—80°), m. p. 106—107° (0·65 g., 78%), of 8-*o*-*methoxyphenyl*-1-*naphthylamine* (Found: C, 81·7; H, 6·0; N, 5·6. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·1; N, 5·6%). This amine (0·49 g.) in glacial acetic acid (5 ml.) was added to a solution prepared by dissolving sodium nitrite (0·2 g.) in concentrated sulphuric acid (2 ml.) and then diluting it with glacial acetic acid (5 ml.). The black solution was diluted with water (10 ml.) and then treated with sulphamic acid to destroy excess of nitrous acid. Addition of copper bronze and warming caused effervescence and formation of a tar. It was extracted with hot benzene, and the benzene extract, after extraction with hot 20% potassium hydroxide solution, was washed, dried, and passed through a chromatographic column (alumina). A continuous band, fluorescing brilliant violet in ultra-violet light, was eluted, leaving a canary-yellow band surmounted by green and red-brown bands. The violet-fluorescing benzene solution, on evaporation, gave pale yellow crystals (0·14 g.). These were only partly soluble in ethanol. The insoluble pale green residue crystallised from benzene in light green rosettes, m. p. 290°. On combustion, a residue was left. Analysis, allowing for residue, indicated that the substance may be 1 : 1′-(di-*o*-methoxyphenyl)-8 : 8′-dinaphthyl. The above ethanol filtrate from these gave pale green prisms, which after recrystallisation (from benzene, then ethanol) gave material, m. p. 106—108°. This was converted in ethanol into 10-*methoxyfluoranthene picrate*, deep magenta prisms, m. p. 123° (Found: C, 59·7; H, 3·2; N, 9·0. $C_{17}H_{12}O,C_6H_3O_7N_3$ requires C, 59·9; H, 3·3; N, 9·1%). Chromatography of this picrate in benzene, as above, gave, from ethanol, pale green prisms, m. p. 106—108°, of 10-*methoxyfluoranthene* (Found: C, 88·1; H, 5·2. $C_{17}H_{12}O$ requires C, 87·9; H, 5·2%). The 2 : 4 : 7-*trinitrofluorenone* complex gave (from acetic acid) black needles with a purple reflex, m. p. 211—212° (Found: C, 65·6; H, 3·1; N, 7·7. $C_{17}H_{12}O,C_{13}H_5O_7N_3$ requires C, 65·8; H, 3·1; N, 7·7%). The fluoroborate method for cyclisation, as developed by Heacock and Hey (*J.*, 1952, 1508), gave a small yield of 10-methoxyfluoranthene, identified as such and as its picrate.

The following nitro- and amino-compounds were prepared; but cyclisation to give 10-methoxyfluoranthene failed.

1-(3-*Methoxy*-2-*nitrophenyl*)*naphthalene*.—3-Bromo-2-nitroanisole (0·6 g.), 1-iodonaphthalene (0·7 g.), and copper bronze (0·5 g.; washed with carbon tetrachloride) were heated at 220—230° for 2 hr., with frequent stirring. The benzene extract of the product was chromatographed on alumina and gave 1-(3-*methoxy*-2-*nitrophenyl*)*naphthalene* (0·49 g., 55%) as yellow needles (from ethanol), m. p. 154—155° (Found: C, 73·1; H, 4·5; N, 5·0. $C_{17}H_{13}O_3N$ requires C, 73·1; H, 4·7; N, 5·0%). Reduction of this nitro-compound in ethanol by hydrogen in presence of Raney nickel at room temperature and pressure gave prisms (from ethanol), m. p. 86—88°, with softening at 84° (yield, *ca.* 100%) of 1-(2-*amino*-3-*methoxyphenyl*)*naphthalene* (Found: C, 81·7; H, 5·9; N, 5·6. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·1; N, 5·6%).

1-*o*-*Methoxyphenylnaphthalene*.—*o*-Iodoanisole (2·3 g.), 1-iodonaphthalene (2·5 g.), and copper bronze (2·5 g.) were heated at 240° (diethylene glycol) for ¾ hr. The product was extracted with acetone, the solution evaporated, and the oil obtained dissolved in light petroleum (b. p. 60—80°). Black crystals separated (shown to be 2 : 2′-dimethoxydiphenyl, m. p. 152—

154°) (Found: C, 78·4; H, 6·3. Calc. for $C_{14}H_{14}O_2$: C, 78·5; H, 6·6%). The petroleum filtrate was distilled, finally in a vacuum, until only a high-boiling oil was left. This was chromatographed (light petroleum, b. p. 60—80°; alumina). The first part (25 ml.) of eluate gave uncrystallisable oil; the second portion (100 ml.) gave on evaporation an oil which dissolved in methanol and gave thick rosettes of faintly yellow crystals, which recrystallised from light petroleum (b. p. 40—60°) in colourless bulky rosettes (0·05 g.), m. p. 91—93°, of 1-*o*-methoxyphenylnaphthalene (Found: C, 87·0; H, 6·0. Calc. for $C_{17}H_{14}O$: C, 87·15; H, 6·0%). The *hemipicrate* (prepared in ethanol) separated from methanol in bright yellow, rectangular laths, m. p. 106—108° (Found: C, 68·9; H, 4·5; N, 6·1. $2C_{17}H_{14}O,C_6H_3O_7N_3$ requires C, 68·9; H, 4·5; N, 6·0%). Excess of picric acid (1·1 mols.) was required in the preparation of this picrate; when proportions were those of the above complex the starting material separated. Chromatography of this picrate gave 1-*o*-methoxyphenylnaphthalene, m. p. 91—93°, as above, but, when the picrate was washed with sodium hydrogen carbonate solution and the residue crystallised from light petroleum (b. p. 40—60°), 1-*o*-methoxyphenylnaphthalene, m. p. 98—99° (Orchin, *loc. cit.*, gives m. p. 98·6—99·8°), was isolated. This could not be repeated. But a sample, m. p. 98—99°, supplied by Dr. Orchin, when mixed with our crystals, m. p. 91—93°, melted at 91—98°. A solution in ethanol of our crystalline form, m. p. 91—93°, after being seeded with Dr. Orchin's sample, gave crystals, m. p. 97—99°.

The ultra-violet absorption spectrum of 1-*o*-methoxyphenylnaphthalene (in ethanol) had maxima at 284 (log ε 3·99) and 223 mμ (log ε 4·86), as found by Friedel and Orchin (*op. cit.*, No. 293) for a *cyclo*hexane solution.

1-o-*Methoxyphenylnaphthalene.*—This was prepared in one step from 1 : 2 : 3 : 4-tetrahydro-1-hydroxy-1-*o*-methoxyphenylnaphthalene (cf. Orchin, *loc. cit.*) (0·25 g.), iodine (0·25 g., 1 mol.) and magnesia (0·5 g.) in boiling xylene (10 ml.). The iodine was added as the colour was discharged during 45 min. More magnesia (0·5 g.) was added, the mixture boiled for a further 30 min., and the deep red liquor was distilled, finally under vacuum, to remove xylene only. The residue was extracted with light petroleum (b. p. 60—80°), the extract evaporated, and the residual dark oil dissolved in ethanol. Addition of picric acid (0·25 g.) to the hot solution gave the picrate (0·35 g.; m. p. 102—105°). It was chromatographed [benzene–light petroleum (2 : 1) and finally benzene; alumina, 1 × 10 cm.] and the first eluate (*ca.* 200 ml.) evaporated to give a pale yellow oil, which, after crystallisation from ligroin (b. p. 40—60°), gave 1-*o*-methoxyphenylnaphthalene, m. p. 91—93° (0·19 g., 81%).

3 : 4-*Dihydro*-1-o-*methoxyphenylnaphthalene.*—A mixture of 1 : 2 : 3 : 4-tetrahydro-1-hydroxy-1-*o*-methoxyphenylnaphthalene (0·25 g.) and 90% formic acid (2·5 ml.) was boiled for 1 hr. Instead of the product being distilled (Orchin, *loc. cit.*), the mixture was diluted with water, and the precipitated oil washed with water, dried in a current of air, and dissolved in light petroleum (b. p. 40—60°). On cooling, the dihydro-compound (0·20 g., 84%), m. p. 65—66°, separated (Orchin gives m. p. 66·6—67·6° for the pure compound). Addition of toluene-*p*-sulphonic acid to the formic acid solution seemed to facilitate dehydration.

Dehydrogenation of this dihydro-compound was accomplished in two ways: (*A*) By the method described above for dehydration-dehydrogenation of 1 : 2 : 3 : 4-tetrahydro-1-hydroxy-1-*o*-methoxyphenylnaphthalene. (*B*) 3 : 4-Dihydro-1-*o*-methoxyphenylnaphthalene (0·12 g.) was heated with chloranil (0·13 g.) in boiling xylene (2 ml.) for 1 hr. Dilution with hot benzene, extraction of the solution with alkaline sodium pyrosulphite, and evaporation of the xylene–benzene extract (finally in a vacuum) left a red oil. The picrate therefrom gave 1-*o*-methoxyphenylnaphthalene in poor yield.

2-*Methoxyfluoranthene.*—2-*Methoxy*-1-o-*nitrophenylnaphthalene.* 1-Iodo-2-methoxynaphthalene (Jurd, *Austral. J. Sci. Res.*, 1949, **2**, *A*, 246) (2 g.) and *o*-bromonitrobenzene (1·6 g.) were heated to 220—230°, and copper bronze (2·4 g.) was added with stirring during 30 min. Heating was continued with occasional stirring for a further 90 min. The mass was extracted with benzene, and the solution chromatographed on alumina. The first brown band gave a yellow eluate, which on evaporation gave yellow needles (from ethanol) (1 g., 50%), m. p. 133—134°, of 2-*methoxy*-1-o-*nitrophenylnaphthalene* (Found: C, 72·9; H, 4·7; N, 5·1. $C_{17}H_{13}O_3N$ requires C, 73·1; H, 4·7; N, 5·0%). Reduction of this nitro-compound with hydrogen in presence of Raney nickel in ethanol gave 1-*o*-aminophenyl-2-methoxynaphthalene as an oil. In ethanol it gave a *picrate*, crystallising from benzene in globular clusters of yellow needles, m. p. 205° (decomp.) (Found: C, 57·7; H, 4·0; N, 11·7. $C_{17}H_{15}ON,C_6H_3O_7N_3$ requires C, 57·7; H, 3·8; N, 11·7%). The *acetyl* derivative of the amine gave plates (from benzene–light petroleum), m. p. 135—136° (Found: C, 77·7; H, 5·9; N, 5·0. $C_{19}H_{17}O_2N$ requires C, 78·3; H, 5·9; N, 4·8%).

The above picrate was shaken with a mixture of ammonia solution and ether, the recovered 1-*o*-aminophenyl-2-methoxynaphthalene (1·9 g.) was dissolved in warm dilute sulphuric acid, and the solution cooled to 0° and diazotised (sodium nitrite, 0·6 g.). Urea was added, then copper bronze (washed with carbon tetrachloride), and the scarlet diazo-solution was stirred (45 min.) at room temperature, then warmed on the steam-bath (30 min.) to complete discharge of the colour. Filtration, extraction with benzene, and chromatography (from light petroleum, b. p. 60—80°; alumina) gave a colourless eluate with a blue fluorescence. This solution gave faintly green feather-like crystals, m. p. 111—113°, of 2-*methoxyfluoranthene* (Found: C, 88·0; H, 5·4; OMe, 13·8. $C_{17}H_{12}O$ requires C, 87·9; H, 5·2; OMe, 13·4%).

4-*Methoxyfluoranthene*.—4-*Iodo*-1-*naphthyl methyl ether*. 1-Naphthyl methyl ether (2 g.), potassium iodide (2·1 g.), potassium nitrate (2 g.), and acetic acid (40 ml.) were boiled till all the potassium iodide had reacted (15 min.). The mixture was poured into water, and the precipitate crystallised from methanol in leaflets, m. p. 52—55° (2·9 g., 81%), of 4-*iodo*-1-*naphthyl methyl ether* (Found: C, 46·6; H, 3·4; I, 44·8. $C_{11}H_9OI$ requires C, 46·5; H, 3·2; I, 44·7%). The use of iodine in place of potassium iodide gave an inferior result. The use of potassium iodide (1·42 g.) and potassium iodate (2 g.) gave 4-iodo-1-naphthyl methyl ether, but the reaction period was considerably longer (6—7 hr.) and the yield lower (63%).

1-*Methoxy*-4-o-*nitrophenylnaphthalene*.—4-Iodo-1-naphthyl methyl ether (2·8 g.) and *o*-bromonitrobenzene (2·2 g.) were heated to 220°, and copper powder (3·5 g.; washed with carbon tetrachloride) added, with stirring. After 2 hours' heating the cooled mass was extracted with benzene and the solution chromatographed on alumina. The first eluate (orange) gave on evaporation a red oil, trituration of which with ethanol followed by crystallisation from light petroleum (b. p. 60—80°) gave clusters of golden prisms, m. p. 113—115°, of 1-*methoxy*-4-o-*nitrophenylnaphthalene* (1·7 g., 62%) (Found: C, 73·1; H, 4·95; N, 5·0. $C_{17}H_{13}O_3N$ requires C, 73·1; H, 4·7; N, 5·0%). Reduction of this nitro-compound with hydrogen in presence of Raney nickel in ethanol gave 4-o-*aminophenyl*-1-*methoxynaphthalene*, m. p. 93—95° (from methanol), (*ca.* 100%) (Found: C, 81·7; H, 5·9; N, 5·6. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·1; N, 5·6%). This amine was dissolved in excess of hot dilute sulphuric acid, and the solution cooled with stirring, to give the sulphate as a white crystalline precipitate, which was diazotised at room temperature, giving a red solution. Urea was added, then copper powder. After 30 minutes at room temperature the mixture was heated on the steam-bath with frequent stirring, until it became colourless. The filtered and dried residue was extracted with benzene, and the solution chromatographed on alumina. The yellow eluate (strong blue fluorescence) gave 4-*methoxyfluoranthene* (48%), which crystallised from ethanol in green nacreous leaflets, m. p. 156—157° (Found: C, 87·8; H, 5·3; OMe, 13·3. $C_{17}H_{12}O$ requires C, 87·9; H, 5·2; OMe, 13·4%).

3 : 4-*Dimethylfluoranthene*.—1 : 2 : 3 : 4-Tetrahydro-3-methyl-4-oxofluoranthene (0·78 g., 1 mol.), dissolved in dry benzene (10 ml.), was added to a solution of methylmagnesium iodide (from magnesium, 0·25 g., 3 atoms; methyl iodide, 1·4 g., 3 mols; ether, 5 ml.), and the mixture boiled for 1 hr. Treatment with dilute hydrochloric acid, and distillation of the benzene, gave (colour change, red to yellow-green) a yellow, oily residue which was dissolved in light petroleum (b. p. 60—80°) and chromatographed on alumina. The pale green (blue-fluorescent) eluate gave, on evaporation, a green, strongly fluorescent oil, which was essentially 1 : 2-dihydro-3 : 4-dimethylfluoranthene since it gave a 2 : 4 : 7-*trinitrofluorenone* complex (in glacial acetic acid) crystallising from ethyl acetate in orange needles, m. p. 177—178° (softening at 170°) (Found: C, 68·1; H, 4·0; N, 7·8. $C_{18}H_{16},C_{13}H_5O_7N_3$ requires C, 68·0; H, 3·9; N, 7·7%). The oily 1 : 2-dihydro-3 : 4-dimethylfluoranthene was readily dehydrogenated by chloranil in xylene (1·5 hr.), and chromatography of the product (light petroleum, b. p. 60—80°; alumina) gave a green (blue-fluorescent) solution which, on evaporation, gave pale green needles, m. p. 83—85° (softening at 81°) (84%) of 3 : 4-*dimethylfluoranthene* (Found: C, 93·9; H, 5·9. $C_{18}H_{14}$ requires C, 93·9; H, 6·1%). It gave a *picrate*, orange needles (from benzene), m. p. 181—182° (softening at 150°) (Found: C, 63·05; H, 4·0; N, 9·2. $C_{18}H_{14},C_6H_3O_7N_3$ requires C, 62·7; H, 3·7; N, 9·15%).

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