

7-, 8-, 9-, and 10-Methylbenzo[*a*]fluorene. Preparation of *o*-Iodotoluic Acids *via* the Thallium(III) Bistrifluoroacetates

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Iodination of *m*- and *p*-toluic acid by successive reaction with thallium(III) trifluoroacetate and aqueous potassium iodide afforded 2-iodo-5-methyl- and 2-iodo-4-methyl-benzoic acid respectively; with *o*-toluic acid 5- and 6-iodo-2-methylbenzoic acids were obtained. Reaction of the three *o*-iodo-acids with lithium diphenylcuprate and lithium di-(2-naphthyl)cuprate gave the corresponding aryltoluic acids. The naphthyl acids were used in the synthesis of 8-, 9-, and 10-methylbenzo[*a*]fluorene; the 7-methyl isomer was prepared by a separate procedure.

A PREVIOUS paper¹ described the synthesis of 1-, 3-, and 4-methylbenzo[*a*]fluorenes, which were required in connection with another investigation. We now report the synthesis of 7-methylbenzo[*a*]fluorene and a new and better route to the 8-, 9-, and 10-methyl isomers.

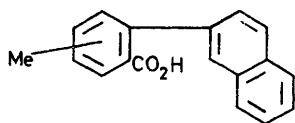
The 8-, 9-, and 10-methyl compounds were obtained through cyclisation of the appropriate 2-naphthyltoluic

acid (I). This route has been used to prepare benzo[*a*]fluorene itself² but has not been widely employed for the preparation of derivatives because of the inaccessibility of the naphthylbenzoic acids. We obtained the acids (I)

¹ W. Carruthers and H. N. M. Stewart, *J. Chem. Soc. (C)*, 1967, 556.

² C. Graebe, *Annalen*, 1904, **335**, 122; *Ber.*, 1900, **33**, 680.

conveniently from the corresponding iodotoluic acids which were themselves readily prepared from the toluic acids by the *ortho*-thallation procedure of McKillop and his co-workers.³ Thus, treatment of *p*-toluic acid with



(I)

thallium(III) trifluoroacetate in trifluoroacetic acid and reaction of the resulting arylthallium bistrifluoroacetate with aqueous potassium iodide gave 2-iodo-4-methylbenzoic acid exclusively in 75% yield. *m*-Toluic acid likewise gave only 6-iodo-3-methylbenzoic acid (80%) identified by conversion into 2-phenyl-3-methylbenzoic acid (below), and through the n.m.r. spectrum of the isolated arylthallium bistrifluoroacetate which showed $J_{\text{Ti},\text{ortho-H}}$ 990, $J_{\text{Ti},\text{meta-H}}$ 378 and 304, and $J_{\text{Ti},\text{H}(\text{CH}_3)}$ 56 Hz. None of the alternative *ortho*-iodo-compound was detected by g.l.c. of the methyl ester of the crude product. Intramolecular chelate-controlled *ortho*-thallation is reported³ to be very sensitive to steric hindrance, and it is no doubt this factor which prevents substitution at C-2 in the present case. *o*-Toluic acid gave two products in the ratio 2:1 (g.l.c.). The minor product was the desired 6-iodo-2-methylbenzoic acid; its structure was confirmed by its conversion into the corresponding phenyltoluic acid. The major product appears to be the 5-iodo-isomer, formed by initial *meta*-thallation of the toluic acid. This is supported by the n.m.r. spectrum⁴ which shows a doublet at τ 1.68 (1H, J 3 Hz, 6-H) and a quartet at τ 2.65 (2H, J 8 Hz), the lower field doublet of which at τ 2.65 is further split into doublets (J 3 Hz), and is confirmed by decarboxylation of the compound to *p*-iodotoluene. Presumably in this case formation of the complex necessary for *ortho*-thallation is hindered by the *ortho*-methyl substituent, and thallation thus takes place predominantly at the electronically most favourable position (*cf.* ref. 3). The four iodotoluic acids obtained in these experiments have all been made before by laborious procedures, and the present direct route is clearly advantageous.

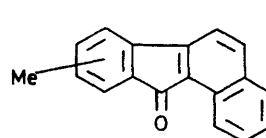
Reaction of 2-iodo-6-methyl-, 2-iodo-5-methyl-, and 2-iodo-4-methylbenzoic acids with lithium di-(2-naphthyl)cuprate⁵ afforded the corresponding 2-naphthyltoluic acids [as (I)] in 20–30% yield. The reason for the uncharacteristically low yields obtained in these reactions is not clear; it may be inefficient conversion of the 2-naphthyl-lithium into the cuprate reagent or the low reactivity of the latter. Much higher yields of the corresponding phenyltoluic acids, comparable to those obtained in other cases,⁵ were obtained by reaction of the iodotoluic acids with lithium diphenylcuprate. In large scale preparations the 2-, 3-, and 4-methyl-6-(2-naph-

³ E. C. Taylor, F. Kienzle, R. L. Robey, A. McKillop, and J. D. Hunt, *J. Amer. Chem. Soc.*, 1971, **93**, 4845.

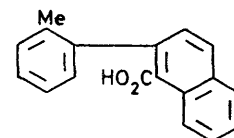
⁴ *Cf.* A. McKillop, J. D. Hunt, M. J. Zelesko, J. S. Fowler, E. C. Taylor, G. McGillivray, and F. Kienzle, *J. Amer. Chem. Soc.*, 1971, **93**, 4841.

thyl)benzoic acids (I) were more conveniently obtained by a mixed Ullmann reaction from the iodotoluic esters and 2-iodonaphthalene. This gave only marginally better yields than the reaction with lithium dinaphthylcuprate but was less wasteful of material since the cuprate has to be employed in large excess. In both reactions the yield of 2-methyl-6-(2-naphthyl)benzoic acid was considerably less than that of the other two isomers, presumably because of the steric effect of the methyl group. This is probably also responsible for the fact that 10-methylbenzo[*a*]fluorenone [as (II)] is formed in considerable amount during the Ullmann reaction with methyl 2-iodo-6-methylbenzoate.

Cyclisation of the acids (I) with polyphosphoric acid afforded the benzo[*a*]fluorenones (II) whence 8-, 9-, and 10-methylbenzo[*a*]fluorenes were obtained by reduction



(II)



(III)

with hydriodic acid and phosphorus. The 9-methyl isomer obtained by us is apparently identical with that previously made by Gross and Lankelma⁶ about which there was some ambiguity.

For the synthesis of 7-methylbenzo[*a*]fluorene the naphthoic acid (III) seemed a suitable starting material. The 2-iodo-1-naphthoic acid required for the preparation of (III) has been obtained previously by a lengthy route⁷ and it was thought that it might be more accessible from 1-naphthoic acid by the thallation procedure. In the event reaction of 1-naphthoic acid with thallium(III) trifluoroacetate in trifluoroacetic acid followed by treatment with aqueous potassium iodide gave an intractable tar (*cf.* ref. 3); with iodine and thallium(III) trifluoroacetate in carbon tetrachloride, however, a mixture was obtained from which the main product was isolated by crystallisation. The m.p. (245 °C) of this product showed, however, that it was not the desired 2-iodo-1-naphthoic acid (m.p. 192 °C) and suggested that it might be the 3-iodo-isomer. In agreement, decarboxylation gave 2-iodonaphthalene and reaction with lithium diphenylcuprate gave a product with m.p. the same as that of 3-phenyl-1-naphthoic acid. This iodination procedure is reported⁴ to lead to 1-iodonaphthalene from naphthalene; the orientation of the product obtained in the present reaction is surprising and difficult to account for.

7-Methylbenzo[*a*]fluorene was eventually obtained by the method of Orchin and Reggel⁸ from *m*-toluoyl

⁵ *Cf.* G. M. Whitesides, W. F. Fischer, J. San Filippo, R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, 1969, **91**, 4871; H. O. House, D. G. Koepsell, and W. J. Campbell, *J. Org. Chem.*, 1972, **37**, 1003.

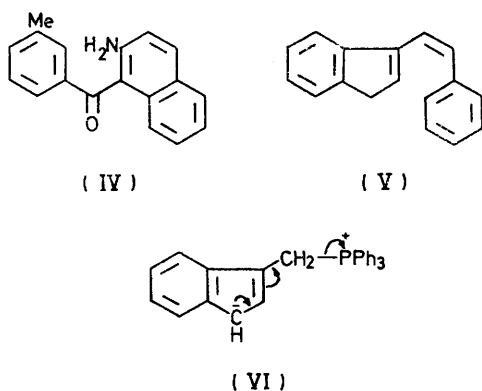
⁶ M. E. Gross and H. P. Lankelma, *J. Amer. Chem. Soc.*, 1951, **73**, 3439.

⁷ T. Fujita, T. Komazawa, K. Koshimizu, and T. Mitsui, *Agric. Biol. Chem. (Japan)*, 1961, **25**, 719.

⁸ M. Orchin and L. Reggel, *J. Amer. Chem. Soc.*, 1951, **73**, 436.

chloride and 2-naphthylamine. The derived amino-ketone (IV) was diazotised and cyclised by reaction with copper powder and the hydrocarbon was isolated from the resultant mixture of fluorenones by reduction and chromatography.

N.m.r. spectroscopy has been used in a number of cases⁹ for determining the position of a methyl substituent on an aromatic nucleus, but it is less helpful in differentiating the above four methylbenzo[*a*]fluorenones. The protons of the 8-, 9-, and 10-methyl substituents show almost identical chemical shifts (τ 7.52–7.56) and only the 7-methyl group (τ 7.19) is easily distinguishable.



The comparative downfield shift of the signal of the 7-methyl protons is analogous to those shown in the spectra of 4-methyl derivatives of phenanthrene, fluorene, and carbazole, which have been attributed to the shielding effect of the neighbouring benzene ring.

We considered the possibility of synthesising benzo[*a*]fluorene derivatives by photocyclisation of (*Z*)-3-styrylindenes [as (V)],¹⁰ but this design has been frustrated by our inability, in model experiments, to prepare 3-styrylindene. Thus, attempted Wittig condensation by addition of lithium ethoxide to a mixture of benzaldehyde and inden-3-ylmethyltriphenylphosphonium bromide led to rapid elimination of triphenylphosphine from the bromide [*cf.* (VI)] and very little of the styrylindene was obtained. The alternative Wittig procedure was precluded by the very poor yields of indene-3-carbaldehyde obtained by reduction of the acid chloride with lithium hydridotri-*t*-butoxyaluminate¹¹ or by reaction of indenylmagnesium bromide with ethyl orthoformate. Again, (*E*)-1-styrylindan-1-ol, obtained from indanone by reaction with phenylethynylmagnesium bromide and reduction of the product with lithium aluminium hydride,¹² on dehydration under various conditions gave not the desired styrylindene, but dimeric and polymeric products which were not further investigated.

⁹ W. Carruthers and N. Evans, *J.C.S. Perkin I*, 1974, 421; W. Carruthers and D. Whitmarsh, *ibid.*, 1973, 1511; I. Puskas and E. J. Fields, *J. Org. Chem.*, 1968, **33**, 4237; A. D. Cross and L. J. Durham, *ibid.*, 1965, **30**, 3200.

¹⁰ *Cf.* E. V. Blackburn and C. J. Timmons, *Quart. Rev.*, 1969, 482.

¹¹ H. C. Brown and R. F. McFarlin, *J. Amer. Chem. Soc.*, 1958, **80**, 5372, 5377.

EXPERIMENTAL

U.v. spectra were measured with a Unicam SP 800 spectrometer for solutions in 95% ethanol unless otherwise stated. Routine i.r. spectra were measured with a Perkin-Elmer Infracord. Mass spectra were recorded with a Hitachi RMU 60 instrument and ¹H n.m.r. spectra with a Perkin-Elmer R 10 spectrometer at 60 MHz or a JEOL MH-100 instrument at 100 MHz, for solutions in deuteriochloroform, with tetramethylsilane as internal reference. G.l.c. experiments were run on a Pye 104 instrument. Light petroleum refers to the fraction b.p. 60–80 °C.

2-Iodo-4-methylbenzoic Acid.—*p*-Toluic acid (5 g) was stirred at 68–73 °C for 48 h with a solution prepared from thallium(III) oxide (15 g), trifluoroacetic acid (60 ml), and water (7.5 ml).⁴ A solution of potassium iodide (15 g) in water (50 ml) was added and the mixture was maintained at 45 °C with stirring for 0.5 h. Aqueous sodium metabisulphite was added to destroy the free iodine and the reaction mixture was basified with 15% sodium hydroxide solution and precipitated thallium(II) iodide was filtered off. The filtrate was acidified with hydrochloric acid and the 2-iodo-4-methylbenzoic acid was collected. Crystallisation from benzene gave plates (6.9 g), m.p. 126–127 °C (lit.,¹³ 127 °C) (Found: C, 36.5; H, 2.9%; *M*⁺, 262. Calc. for C₈H₇IO₂: C, 36.7; H, 2.7%; *M*, 262).

2-Iodo-5-methylbenzoic Acid.—This was prepared in the same way from *m*-toluic acid (5 g). Crystallisation from benzene–light petroleum gave needles, m.p. 119–120 °C (lit.,¹⁴ 118 °C) (8.2 g) (Found: C, 36.8; H, 2.8%; *M*⁺, 262).

5- and 6-Iodo-2-methylbenzoic Acid.—Iodination of *o*-toluic acid (5 g) as in the foregoing experiments gave a crude product (8.7 g) shown by g.l.c. (15% SE 30 on Chromosorb W at 170 °C) of the methyl esters to contain two products in the ratio 2 : 1. Crystallisation from benzene afforded the major product, 5-iodo-2-methylbenzoic acid (3.2 g), as plates, m.p. 178 °C (lit.,¹⁵ 180 °C) (Found: C, 36.7; H, 2.7%; *M*⁺, 262, τ 7.45 (3H, s), 3.05 (d, *J* 8 Hz, H-3), 2.3 (d, *J* 8 Hz, H-4; each peak split into d, *J* 2 Hz), and 1.65 (d, *J* 2 Hz, H-6). The methyl ester had m.p. 58–60 °C (lit., 60 °C). The mother liquors afforded 2-iodo-6-methylbenzoic acid (2.3 g), by crystallisation and mechanical separation, as prisms, m.p. 115–116 °C (lit.,¹⁵ 115 °C) (Found: C, 36.3; H, 2.6%; *M*⁺, 262, τ 7.6 (3H, s), 2.8–3.2 (m, H-3 and H-4), and 2.36 (d, *J* 8 Hz, H-5).

Decarboxylation of the 5-iodo-2-methylbenzoic acid (0.5 g) with copper powder (0.1 g) in quinoline (15 ml) at 200 °C for 3 h and chromatography of the product gave *p*-iodotoluene (0.21 g), m.p. and mixed m.p. 35–37 °C.

3-Iodo-1-naphthoic Acid.—Thallium(III) trifluoroacetate, prepared from thallium(III) oxide (7 g), trifluoroacetic acid (28 ml), and water (3.5 ml),⁴ was rinsed thoroughly with dichloromethane and added to a solution of 1-naphthoic acid (2 g) in carbon tetrachloride (60 ml). The stirred mixture was heated to boiling and iodine (3.2 g) was added in portions as quickly as it was decolourised. Heating was continued for 1 h and the solution was cooled, filtered and evaporated to dryness. The residue was digested with ether (50 ml) and water (50 ml), and the ether layer washed with

¹² J. D. Chanley and H. Sabotka, *J. Amer. Chem. Soc.*, 1949, **71**, 4140; E. B. Bates, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1954, 1854.

¹³ E. Kloeppel, *Ber.*, 1893, **26**, 1733.

¹⁴ D. Peltier and A. Pichevin, *Compt. rend.*, 1957, **245**, 436; R. G. Hinton, F. G. Mann, and I. T. Millar, *J. Chem. Soc.*, 1958, 4704.

¹⁵ D. Peltier, *Compt. rend.*, 1954, **238**, 357.

aqueous sodium metabisulphite. The recovered product, after decolourisation with activated charcoal in methanol, was a yellow solid (1.9 g). G.l.c. analysis of a portion which was esterified with diazomethane (15% SE 30 on Chromosorb W at 190 °C) showed three peaks in the ratio 1 : 6 : 1. Crystallisation of the crude product from glacial acetic acid gave the idonaphthoic acid as pale brown needles, m.p. 245—247 °C (lit.,⁷ 245 °C) (Found: C, 44.8; H, 2.4%; M^+ , 298. Calc. for $C_{11}H_7IO_2$: C, 44.3; H, 2.4%; M , 298). Decarboxylation of this acid as described above for 5-iodo-2-methylbenzoic acid gave 2-iodonaphthalene, m.p. and mixed m.p. 54—55 °C.

Reaction of the idonaphthoic acid with lithium diphenylcuprate by the method described below gave 3-phenyl-1-naphthoic acid, m.p. 221—223 °C (lit.,¹⁶ 221—222 °C; lit.,² m.p. for 2-phenyl-1-naphthoic acid, 114 °C).

Reaction of Iodotoluic Acids with Lithium Diphenylcuprate.—Typically,⁵ a solution of the iodotoluic acid (0.15 g) in ether (10 ml) was added to a solution of lithium diphenylcuprate, prepared from lithium (0.15 g), bromobenzene (1.5 g), and copper(I) bromide (0.75 g) in ether (30 ml), and the mixture was stirred at room temperature for 16 h. It was then cooled to 0 to -5 °C, nitrobenzene (1.5 ml) in ether (5 ml) was added, and the mixture was stirred for a further 1 h. The mixture was acidified with dilute hydrochloric acid and the ethereal extract extracted with sodium hydrogen carbonate. Crystallisation of the recovered acids from benzene gave 5-methyl-2-phenylbenzoic acid (64%), m.p. 151—153 °C (lit.,¹⁷ 152 °C), 4-methyl-2-phenylbenzoic acid (88%), m.p. 163 °C (lit.,¹⁸ 165 °C), and 2-methyl-6-phenylbenzoic acid (52%), m.p. 133 °C (lit.,¹⁷ 132 °C).

5-Methyl-2-(2-naphthyl)benzoic Acid.—(a) 2-Naphthyllithium, prepared from 2-bromonaphthalene (4.4 g) and lithium (0.3 g) in ether (50 ml) as described by Gilman, Zoellner, and Selby,¹⁹ was added to a stirred suspension of freshly prepared copper(I) bromide²⁰ (1.4 g) in ether (20 ml) at 0 to -5 °C. After 1 h a solution of 2-iodo-5-methylbenzoic acid (0.19 g) in ether (10 ml) was added and stirring was continued for 16 h at room temperature. The mixture was cooled to 0 °C, nitrobenzene (4 ml) in ether (10 ml) was added, and reaction was continued for 0.5 h. Water was added and the solution was carefully acidified. The product was worked up as described above for the phenyltoluic acids. The carboxylic acid mixture was esterified with diazomethane and the crude ester mixture chromatographed on acid-washed alumina. Elution with benzene afforded first methyl 2-iodo-5-methylbenzoate and then methyl 5-methyl-2-naphthylbenzoate (83 mg), b.p. 170—175 °C at 0.08 mmHg (Found: C, 82.1; H, 6.1%; M^+ , 276. $C_{18}H_{16}O_2$ requires C, 82.6; H, 5.8%; M , 276). Hydrolysis gave the acid, m.p. 176 °C (prisms from benzene-light petroleum) (Found: C, 81.9; H, 5.3%; M^+ , 262. $C_{18}H_{14}O_2$ requires C, 82.4; H, 5.4%; M , 262).

(b) A solution of methyl 2-iodo-5-methylbenzoate (1.5 g) and 2-iodonaphthalene (4.5 g) in dimethylformamide²¹ (50 ml) was boiled with copper bronze (4 g) for 6 h; a further portion of copper bronze (4 g) was added and the mixture was boiled for a further 6 h. The cooled solution was filtered, the residue washed with ether, and the combined organic layers evaporated to dryness. The residue was boiled with alcoholic sodium hydroxide (10%; 50 ml) and

the recovered acidic material esterified with diazomethane and chromatographed on acid washed alumina. Elution with light petroleum containing increasing amounts of toluene afforded methyl *m*-toluate and 2-iodo-5-methylbenzoate (0.45 g), identified by comparison with the material obtained above. Continued elution gave finally dimethyl 4,4'-dimethylbiphenyl-2,2'-dicarboxylate (0.98 g), m.p. 87—88 °C (Found: M^+ , 298. Calc. for $C_{18}H_{18}O_4$: M , 298).

4-Methyl-2-(2-naphthyl)benzoic Acid.—This was obtained similarly from lithium di-(2-naphthyl)cuprate and 2-iodo-4-methylbenzoic acid (27% yield) or from methyl 2-iodo-4-methylbenzoate and 2-iodonaphthalene (38%). It formed needles from light petroleum-toluene, m.p. 144—146 °C (Found: C, 82.7; H, 5.6%; M^+ , 262).

2-Methyl-6-(2-naphthyl)benzoic Acid.—Reaction of lithium di-(2-naphthyl)cuprate and 2-iodo-6-methylbenzoic acid as described above gave 2-methyl-6-(2-naphthyl)benzoic acid as microcrystals, m.p. 212 °C (from methanol-light petroleum). Because of the tendency of this acid to cyclise to the benzofluorenone during crystallisation a satisfactory analysis could not be obtained. The methyl ester had b.p. 185—190 °C at 0.05 mmHg (Found: C, 82.4; H, 6.0%; M^+ , 276. $C_{18}H_{16}O_2$ requires C, 82.6; H, 5.9%; M , 276).

Similarly, Ullmann reaction of methyl 2-iodo-6-methylbenzoate and 2-iodonaphthalene as described above gave the acid in only 7% yield. From the neutral fraction 10-methylbenzo[*a*]fluoren-11-one, m.p. and mixed m.p. 157 °C, was isolated in 30% by chromatography on alumina.

Cyclisation of Methyl-naphthylbenzoic Acids.—A solution of the acid (150 mg) in polyphosphoric acid (10 ml) was heated at 85—90 °C for 4 h. The solution was poured into water, extracted with ether, and the extracts washed with sodium carbonate. The benzofluorenones were purified by chromatography on alumina (average yield 75—85%). Details are recorded in the Table.

Properties of methylbenzo[*a*]fluoren-11-ones

Benzo[<i>a</i>]fluoren-11-one	M.p. (°C)	Found (%)		Required (%)	
		C	H	C	H
8-Methyl- Yellow needles	168	88.0	4.8	88.5	5.0
9-Methyl- Yellow needles	136	88.2	5.1		
10-Methyl- Yellow needles	157	88.2	5.1		

2-Amino-1-naphthyl *m*-Tolylketone.—This compound was prepared from 2-naphthylamine and *m*-toluoyl chloride by the procedure of Orchin and Reggel,⁸ by way of 2-*m*-toluoylaminonaphthalene, m.p. 124—125 °C, and 2-*m*-toluoylamino-1-naphthyl *m*-tolyl ketone, m.p. 133 °C. It formed yellow needles in ethanol, m.p. 162 °C (Found: C, 82.9; H, 6.0; N, 6.0%; M^+ , 261. $C_{18}H_{15}NO$ requires C, 82.7; H, 5.8; N, 5.4%; M , 261).

7-Methylbenzo[*a*]fluorene.—A solution of pentyl nitrite (1.1 ml) in glacial acetic acid (5 ml) was added in portions to a stirred solution of the foregoing amino-ketone (1 g) in glacial acetic acid (30 ml) and concentrated sulphuric acid (0.5 ml). The mixture was stirred for 0.5 h, during which the solid completely dissolved. The red solution was cooled in ice, and copper powder (0.5 g) was added. The mixture was stirred for 3 h at room temperature and then for a further 3 h on a steam-bath. The mixture was worked up as described for a similar case.⁸ G.l.c. of the mixture of

¹⁶ F. G. Baddar, A. M. Fleifel, and S. Sherif, *J. Chem. Soc.*, 1959, 1009.

¹⁷ R. D. Haworth, and P. B. Tinker, *J. Chem. Soc.*, 1955, 911.

¹⁸ K. Alder, K.-H. Decker, and R. Lienau, *Annalen*, 1950, 570, 214.

¹⁹ H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Amer. Chem. Soc.*, 1933, 55, 1252.

²⁰ G. F. Kauffman and R. P. Pinnell, *Inorg. Synth.*, 1960, 6, 3.

²¹ N. Kornblum and D. L. Kendall, *J. Amer. Chem. Soc.*, 1952, 74, 5782.

methylbenzofluorenes obtained by reduction of a sample of the crude product showed the presence of the two methylbenzofluorenes in approximately equal amounts. The crude mixture of methylbenzo[*a*]fluorenones was chromatographed on alumina; elution with toluene–light petroleum (3 : 1) afforded first the 9-methyl-isomer (108 mg) and then a mixture of the 9- and 7-methyl compounds from which the 9-methyl compound could not be completely removed by further chromatography or by crystallisation.

This mixture (95 mg) and hydriodic acid (*d* 1.94; 1.6 ml) in propionic acid (30 ml) was refluxed with red phosphorus (140 mg) for 60 h. The cooled solution was poured into water and extracted with ether and the recovered products chromatographed on alumina. Careful elution with light petroleum afforded first 9-methylbenzo[*a*]fluorene and then the 7-methyl isomer (22 mg) as plates, m.p. 162–163 °C (from ethanol–benzene) (Found: C, 93.6; H, 6.3%; M^+ , 230. $C_{18}H_{14}$ requires C, 93.9; H, 6.1%; M , 230), λ_{max} 226, 237, 246.5, 255, 260, 264, 296inf, 301, 306.5, 314, 319.5inf, 328, and 344 nm ($\log \epsilon$ 4.46, 4.31, 4.49, 4.84, 4.68, 5.07, 4.21, 4.17, 4.22, 4.13, 4.15, 3.48, and 2.87).

8-, 9-, and 10-Methylbenzo[*a*]fluorene.—These were prepared in the same way from the corresponding fluorenone; 8-methylbenzo[*a*]fluorene, blades from ethanol–benzene, m.p. 183–185 °C (lit.,⁶ 184 °C) (Found M^+ , 230. Calc. for $C_{18}H_{14}$: M , 230); 9-methylbenzo[*a*]fluorene, m.p. 178–180 °C (lit.,⁶ 175–176 °C) (Found: M^+ , 230), and 10-methyl-

benzo[*a*]fluorene, m.p. 124–126 °C (lit.,⁶ 121–122.5 °C) (Found: M^+ , 230). The u.v. spectra were similar to those recorded.

1-Phenylethynylindan-1-ol.—A solution of phenylacetylene (5.2 g) in ether (20 ml) was added slowly to a stirred solution of ethylmagnesium bromide [from ethyl bromide (5.4 g) and magnesium (1.2 g) in ether (30 ml)] and the solution was refluxed for 2 h. The solution was cooled, a solution of indan-1-one (7.0 g) in ether (50 ml) was added and the mixture was refluxed for 5 h. The complex was decomposed with aqueous ammonium chloride and the recovered product (9.8 g) distilled at 150–155 °C at 0.08 mmHg (Found: C, 87.7; H, 6.2%; M^+ , 234. $C_{17}H_{14}O$ requires C, 87.2; H, 6.0%; M , 234).

(*E*)-1-Styrylindan-1-ol.—The foregoing alcohol (5 g) in ether (50 ml) was added to a stirred suspension of lithium aluminium hydride (0.9 g) in ether (60 ml) and the mixture was boiled for 2 h. The recovered allylic alcohol (4.1 g) had b.p. 160–165 °C at 0.08 mmHg. Because of the tendency of the alcohol to dehydrate during distillation a correct elemental analysis could not be obtained (Found: M^+ , 236; $C_{17}H_{16}O$ requires M , 236), ν_{max} (film) 3380 and 965 cm^{-1} , τ 7.6 (2H, q), 6.9 (2H, q), 3.62 (1H, d, J 16 Hz), and 3.31 (1H, d, J 16 Hz).

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