176. *The Chemistry of Fluorene. Part II.* The Dehydration of 9-Hydroxyethylfluorenes.*

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The dehydration of 9-hydroxyethylfluorenes and 9-ethylfluoren-9-ol by phosphoric oxide in boiling decalin or by activated alumina in the vapour phase yields either ethylidenefluorene or a substituted phenanthrene depending on the conditions. The mechanism of these reactions is discussed and it is suggested that in one case fluorene-9-*spirocyclo*propane is an intermediate. This compound was prepared by the dehydrohalogenation of 9-2'-chloroethylfluorene and proof of its structure is given. 9-Vinylfluorene was not obtained by the dehydration of 9-hydroxyethylfluorenes under the conditions used, and it is suggested that this compound is either incapable of existence or is immediately isomerised.

IN Part I * one possible route to 9-vinylfluorene—the condensation of vinyl halides with 9-fluorenylsodium—was mentioned; this reaction resulted in the formation of fluorene, acetylene, and the sodium halide. Dehydration of 9-2'-hydroxyethylfluorene (Part I) offered an alternative route, but it was found that when this compound was passed over activated alumina at 350° or was heated with phosphoric oxide in boiling decalin it yielded products which were at first thought, on the evidence of mixed melting points and mixed melting points of picrates, to be identical with each other and with 9-ethylidenefluorene prepared by dehydration of 9-ethylfluoren-9-ol (Daupresne, *Bull. Soc. chim.*, 1907, **1**, 1236; Ullmann and Wurstemberger, *Ber.*, 1905, **38**, 4107).

It was later shown, however, that although the product obtained by dehydration over alumina was in fact 9-ethylidenefluorene, with an ultra-violet spectrum (Table 3) identical with that of the product obtained from the fluorenol, the dehydration product obtained from the liquid-phase reaction with phosphoric oxide in decalin was 9-methylphenanthrene.

Application of the two methods described above to the dehydration of 9-1'-hydroxyethylfluorene, which had previously been shown to yield 9-ethylidenefluorene on treatment with concentrated hydrochloric acid (Courtot, *Ann. Chim.*, 1915, **4**, 158, 220), gave 9-ethylidenefluorene (alumina at 350°) or a mixture of 9-ethylidenefluorene and 9-methylphenanthrene (phosphoric oxide in decalin).

* Part I, *J.*, 1951, 2848.

The effect of replacement of the remaining $C_{(9)}$-hydrogen atom has been studied; the dehydration results are summarised in the following table.

R．　　CHR'·CH₂R''

|	Dehydration conditions	
Substituents	Activated alumina at 350°	Phosphoric oxide in boiling decalin or xylene
R = OH; R' = R'' = H	9-Ethylidenefluorene	9-Ethylidenefluorene
R=R'=H; R'' = OH	9-Ethylidenefluorene	9-Methylphenanthrene
R = R'' = H; R' = OH	9-Ethylidenefluorene	Mixture of 9-ethylidenefluorene and 9-methylphenanthrene
R = Me; R' = H; R'' = OH ...	9 : 10-Dimethylphenanthrene	9 : 10-Dimethylphenanthrene
R = Me; R' = OH; R'' = H ...	9 : 10-Dimethylphenanthrene	9 : 10-Dimethylphenanthrene
R = Et; R' = OH; R'' = H ...	10-Ethyl-9-methylphenanthrene	

Thus, where there is a free $C_{(9)}$-hydrogen atom vapour-phase dehydration over alumina leads to the production of an ethylidenefluorene whereas the product obtained by use of phosphoric oxide in decalin may be 9-ethylidenefluorene, a substituted phenanthrene, or a mixture of both. Where there is no hydrogen atom on C_9, dehydration by either method is accompanied by the intramolecular change leading to a substituted phenanthrene.

This intramolecular change was first demonstrated by Werner and Grob (*Ber.*, 1904, **37**, 2984) and more clearly by Bachmann (*J. Amer. Chem. Soc.*, 1933, **55**, 3857) who showed that dehydration of 9-α-hydroxybenzyl-9-phenylfluorene yielded 9 : 10-diphenylphenanthrene and not 9-diphenylmethylenefluorene. Brown and Bluestein (*J. Amer. Chem. Soc.*, 1940, **62**, 3256) have prepared phenanthrene by the action of phosphoric oxide on 9-hydroxymethylfluorene and Wittig, Davis, and Koenig (*Ber.*, 1951, **84**, 627) have obtained 9-benzylphenanthrene by the action of phosphorus tribromide on 9-benzyl-9-fluorenylmethanol. We have repeated Brown and Bluestein's experiment and confirmed that 9-hydroxymethylfluorene yields phenanthrene when refluxed with phosphoric oxide in xylene, but when it is passed over alumina at 350° the product is a mixture of 9-methylenefluorene and its polymers, no phenanthrene being detected. 9-Hydroxymethyl-9-methylfluorene was found to undergo rearrangement to 9-methylphenanthrene with both dehydrating agents.

This intramolecular change of a 9-hydroxyalkylfluorene to a phenanthrene derivative is generally regarded as an example of the Wagner rearrangement, proceeding by a mechanism involving a carbonium ion thus :
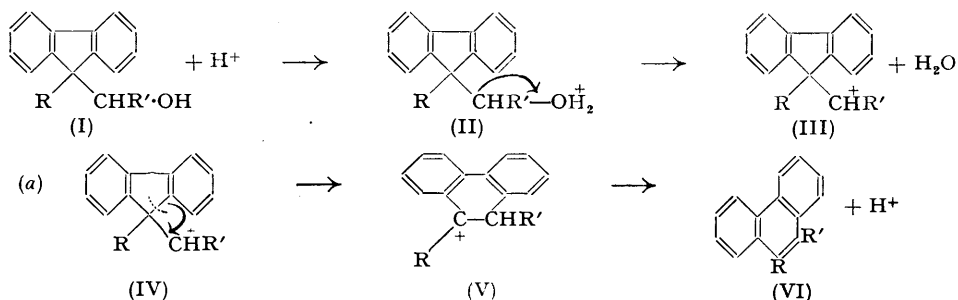
When R = H the ion (III) may stabilise itself in two ways, either by rearrangement as shown in (*a*), or by the formation of a methylenefluorene (*b*).
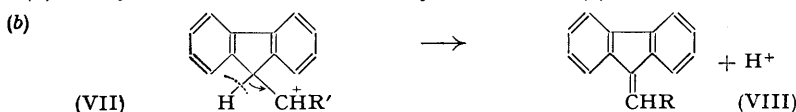

It would be expected that in an alkaline (proton-accepting) environment in which the $C_{(9)}$-hydrogen atom is known to be labile, this second mode of stabilisation would

predominate, and the production of ethylidenefluorene only by the dehydration of 9-1′-hydroxyethylfluorene over alumina and of a mixture of ethylidenefluorene and 9-methyl-phenanthrene when phosphoric oxide is used is consistent with this view.

To explain the reactions of 9-2′-hydroxyethylfluorene the mechanism shown below (IX—XIV) might be postulated, but in this case one would expect that the products from both hydroxyethylfluorenes when dehydrated in the liquid phase with phosphoric oxide would be the same; no ethylidenefluorene could, however, be isolated from the product obtained from the 2-hydroxyethyl compound.

It is therefore suggested that the ion (XI) formed by proton addition and removal of the elements of water from the 9-2′-hydroxyethylfluorene under the influence of alumina forms the *spirocyclo*propane compound which isomerises to ethylidenefluorene and that, under the more acidic conditions when phosphoric oxide is used, the changes leading to (XIV) from (XI) occur synchronously rather than as distinct stages.

Some support for the view that the *spiro*-compound is an intermediate when 9-ethylidenefluorene is formed from 9-2′-hydroxyethylfluorene is furnished by its ready formation from 9-2′-chloroethylfluorene and its almost quantitative isomerisation to 9-ethylidenefluorene under both sets of dehydration conditions.
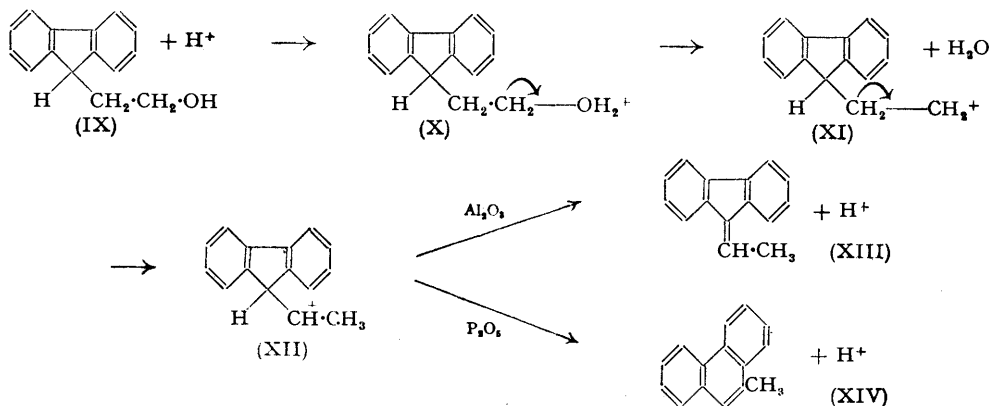
The identity of the *spiro*-compound has been established as follows. Analysis shows it to be isomeric with 9-ethylidenefluorene, and its ultra-violet spectrum (Table 3) and the fact that it is oxidised by chromic acid to fluorenone prove it to be a 9-substituted fluorene. Examination of its infra-red spectrum showed no absorption band attributable to either a monosubstituted ethylene (1650 cm.$^{-1}$) or a vinyl group (910 cm.$^{-1}$ and 990 cm.$^{-1}$) (Thompson and Torkington, *Proc. Roy. Soc.*, 1945, *A*, **184**, 3), thus eliminating the only other possible structure, 9-vinylfluorene. Our material agrees in melting point with that produced from 9-methylenefluorene and diazomethane by Wieland and Probst (*Annalen*, 1937, **530**, 274) who, however, gave no evidence of structure.

As a further confirmation it was hoped that bromine would split the *cyclo*propane ring symmetrically to yield 9 : 9-bisbromomethylfluorene. The addition product, however, lost hydrogen bromide spontaneously to form 9-2′-bromoethylidenefluorene [ultra-violet spectrum (Table 3)], which, of course, could also be derived from 9-vinylfluorene.

The replacement of the remaining $C_{(9)}$-hydrogen atom in 9-2′-chloroethylfluorene prevents formation of a *spirocyclo*propane derivative. 9-2′-Chloroethyl-9-methylfluorene is resistant to both dehydrohalogenation and hydrolysis, and is recovered unchanged when heated with potassium hydroxide to 300° or after prolonged refluxing with alcoholic potassium hydroxide. Dehydrohalogenation in the presence of an acid catalyst by Charlton, Dostrovsky, and Hughes's method (*Nature*, 1951, **167**, 986) also did not result in any change. Reaction does take place when the chloro-compound is refluxed in quinoline for several hours, and a small amount of 9 : 10-dimethylphenanthrene can be isolated from the product. The major product, however, appears to be a salt since it is soluble in dilute aqueous acid and not extracted therefrom by chloroform.

It seemed surprising that Courtot (*loc. cit.*) should have obtained 9-ethylidenefluorene from 9-1′-hydroxyethylfluorene under acid conditions (concentrated hydrochloric acid in acetic acid solution), which would be expected to promote the Wagner change. We have therefore repeated Courtot's experiments and, although the time of reaction was increased from 1 to 3 hours, the product obtained contained no picrate-forming material—indicating the absence of both 9-ethylidenefluorene and 9-methylphenanthrene. Chromatography of the oily product gave 9-1′-acetoxyethylfluorene and starting material. The ester on distillation at atmospheric pressure decomposed to acetic acid and 9-ethylidenefluorene. This is in accord with Hurd and Blunck's views (*J. Amer. Chem. Soc.*, 1938, **60**, 2419) that pyrolysis of esters gives rise to the simple dehydration product of the alcohol.

It may be concluded from these results that 9-vinylfluorene is an unstable structure which is either incapable of existence or immediately isomerised under the experimental conditions used.

EXPERIMENTAL

9-Acetylfluorene and 9-Formylfluorene.—These were prepared, in 57% and 80% yield, respectively, by Von and Wagner's methods (*J. Org. Chem.*, 1944, **9**, 155).

9-Hydroxymethylfluorene.—This was prepared from 9-formylfluorene by Brown and Bluestein's method (*J. Amer. Chem. Soc.*, 1940, **62**, 3256). Our product had m. p. 107° (Brown and Bluestein record m. p. 99·5—100°).

9-Ethylfluoren-9-ol.—This was obtained in 78% yield by Ullmann and Wurstemberger's method (*Ber.*, 1905, **38**, 4107).

9-Acyl-9-alkylfluorenes.—9-Acylfluorene (0·1 mole) was added to a cooled solution of sodium (0·1 mole) in dry ethanol (40 c.c.), and alkyl halide (0·11 mole) then slowly added with frequent shaking. The mixture was heated under reflux on a water-bath for 2 hours, the ethanol evaporated *in vacuo*, the residue extracted with ether, and the product obtained by evaporation of the ether from the dried (MgSO₄) solution. The following were so obtained : 9-formyl-9-methylfluorene (0·1 mole) [*oxime*, m. p. 175° (Found : C, 81·0; H, 5·9; N, 6·25. C₁₅H₁₃ON requires C, 80·7; H, 5·8; N, 6·3%), and *semicarbazone*, m. p. 227—228° (Found : C, 72·6; H, 5·8; N, 16·1. C₁₆H₁₅ON₃ requires C, 72·5; H, 5·7; N, 15·85%)]; 9-acetyl-9-methylfluorene (0·055 mole), m. p. 85—86°, as needles from light petroleum (b. p. 40—60°) [semicarbazone, m. p. 249—250° (cf. Meerwein, *Annalen*, 1913, **396**, 241)]; and 9 acetyl-9-ethylfluorene (0·08 mole), m. p. 70°, as plates from light petroleum (b. p. 40—60° [*semicarbazone*, m. p. 222° (Found : C, 73·5; H, 6·7; N, 14·3. C₁₈H₁₉ON₃ requires C, 73·7; H, 6·5; N, 14·3%)].

9-1′-Hydroxyalkylfluorenes.—9-Acylfluorene (0·1 mole) in *iso*propanol (50 c.c.) was heated with a solution of aluminium *iso*propoxide (0·1 mole) in *iso*propanol (50 c.c.) on a water-bath at 85° ± 5°, and the acetone which was formed was distilled off. The residue was cooled, decomposed with cold dilute hydrochloric acid (200 c.c.; 6·5% wt./vol.), and extracted with ether. The product was obtained by evaporation of this dried extract (MgSO₄). The following were obtained by this method : 9-1′-hydroxyethylfluorene (0·077 mole), m. p. 103—104°, as needles from light petroleum (b. p. 60—80°) [Courtot (*Ann. Chim.*, 1915, **4**, 159) records m. p. 102—103°]; 9-hydroxymethyl-9-methylfluorene (0·062 mole), m. p. 148—149°, as prisms from benzene (Found : C, 85·4; H, 6·7%; *M*, 205. C₁₅H₁₄O requires C, 85·7; H, 6·7%; *M*, 210); 9-1′-hydroxyethyl-9-methylfluorene (0·085 mole), m. p. 81°, as needles from light petroleum (b. p. 60—80°) (Found : C, 85·4; H, 7·0; OH, 7·4%; *M*, 229. C₁₆H₁₆O requires C, 85·7; H, 7·1; OH, 7·6%; *M*, 224); and 9-ethyl-9-1′-hydroxyethylfluorene (0·076 mole), m. p. 83°, from light petroleum (b. p. 60—80°) (Found : C, 85·3; H, 7·4; OH, 7·5. C₁₇H₁₈O requires C, 85·7; H, 7·6; OH, 7·1%).

9-Methyl-9-sodiofluorene.—9-Methylfluorene (50 g.) and powdered sodamide (11 g.) were heated at 180—190° in decalin (150 c.c.) with stirring for 4 hours in an atmosphere of dry nitrogen. The sodio-derivative separated as a heavy dark oil which cooled to a red solid. This was washed with light petroleum and used immediately in the following preparations. The yield is approximately quantitative.

9-2′-Hydroxyethyl-9-methylfluorene.—9-Methyl-9-sodiofluorene (from 50 g. of 9-methylfluorene) and ethylene chlorohydrin (80 c.c.) were heated under reflux for 6 hours in light petroleum (b. p. 40—60°; 200 c.c.), and the sodium chloride was filtered off. Evaporation of the filtrate *in vacuo* gave 9-*2′-hydroxyethyl-9-methylfluorene*, crystallising from benzene in

needles (42·6 g.), m. p. 105—107° (Found : C, 85·3; H, 7·0. $C_{16}H_{16}O$ requires C, 85·7; H, 7·1%).

9-2′-Chloroethyl-9-methylfluorene.—9-Methyl-9 sodiofluorene (from 50 g. of 9 methylfluorene) was added in portions to a solution of ethylene dichloride (50 g.) in light petroleum (b. p. 40—60°; 300 c.c.), and the mixture heated under reflux for 4 hours, cooled, and filtered to remove sodium chloride. Evaporation of the filtrate gave 9-2′-*chloroethyl-9-methylfluorene*, crystallising in needles (67·5 g.), m. p. 100—101°, from *n*-propanol (Found : C, 78·8; H, 6·2; Cl, 14·4. $C_{16}H_{15}Cl$ requires C, 79·0; H, 6·2; Cl, 14·65%).

Fluorene-9-spirocyclopropane.—9-2′-Chloroethylfluorene (5 g.) was heated to 200° with potassium hydroxide (1·5 g.) with slow stirring; an exothermic reaction took place and the temperature rose to 270°. Heating was continued for 4 minutes and mixture was then cooled, extracted with water, and acidified (HCl). The oily spiro-*compound* solidified and was crystallised from *n*-propanol, forming needles (3·2 g.), m. p. 71·5° (Found : C, 93·6; H, 6·4%; *M*, 190. Calc. for $C_{15}H_{12}$: C, 93·7; H, 6·2%; *M*, 192). The picrate, prepared in acetic acid, formed orange needles, m. p. 139·5°.

9-2′-Bromoethylidenefluorene.—A solution of bromine in carbon tetrachloride (1% vol./vol.; 27·8 c.c.) was added slowly with shaking to one of fluorene-9-*spirocyclo*propane (1 g.) in the same solvent (10 c.c.). The bromine was absorbed in a few minutes, and a small quantity of hydrogen bromide was evolved. The solution, after storage for 20 hours at 0°, was concentrated at 50° (stream of air) to an oil, which, after being boiled with charcoal (1 g.) and light petroleum (b. p. 60—80°; 20 c.c.), crystallised as pale yellow needles, m. p. 90—91° (0·7 g.). The ultra-violet absorption spectrum of this product (Table 3) together with elementary analysis indicates that it was 9-2′-*bromoethylidenefluorene* (Found : C, 66·4; H, 4·15; Br, 28·7%; *M*, 280. $C_{15}H_{11}Br$ requires C, 66·4; H, 4·05; Br, 29·5%; *M*, 276).

9-1′-Acetoxyethylfluorene.—(*a*) 9-1′-Hydroxyethylfluorene (1 g.), acetic acid (10 c.c.), and concentrated hydrochloric acid (1 c.c.) were heated under reflux for 3 hours, more concentrated hydrochloric acid (2 c.c.) was added, and heating was continued for 1 hour. The cooled solution was diluted with water and extracted with chloroform; the extract, after being washed with sodium carbonate solution and water, was dried and evaporated. The oily product in benzene was passed through a column (8 in. × ½ in.) of alumina, giving two fractions : (i) 9-1′-*acetoxyethylfluorene* (0·57 g.) as a viscous, non-picrate-forming oil (Found : C, 80·9; H, 6·7. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8%), and (ii) 9-1′-hydroxyethylfluorene (0·38 g.), m. p. 104°. Distillation of fraction (i) at atmospheric pressure caused its decomposition to acetic acid and 9-ethylidenefluorene, plates (from ethanol), m. p. and mixed m. p. 104° (picrate, m. p. and mixed m. p. 157—158°). (*b*) 9-1′-Hydroxyethylfluorene (1 g.) and acetic anhydride (10 c.c.) were refluxed for 3 hours, a stream of dry hydrogen chloride being bubbled through the solution. The cooled solution gave 9-1′-acetoxyethylfluorene (0·90 g.) and 9-1′-hydroxyethylfluorene (0·08 g.).

Dehydrations over Activated Alumina at 350°.—The apparatus consisted of an electrically heated hard-glass tube, 16 in. long and 1¼ in. in diameter. This reactor tube, shielded by an outer glass jacket, was clamped vertically and packed with activated alumina (Peter Spence 666, type A, mesh 4—8) to a length of 13 in. A liquid-feed device, controlled by a metal-in-glass needle valve, was fitted to the top of the tube, and a glass receiver, immersed in a solid carbon dioxide–ethanol mixture, connected to the bottom. This receiver was connected through a second outlet, a reflux condenser, and cooling traps to a vacuum gauge and pump.

The compound for dehydration (10 g.) dissolved in benzene (150—500 c.c.) was passed through the alumina, maintained at 350° ± 10°, at approximately 10 c.c./min., at 20 mm. pressure. Results are given in Table 1.

The identity of the dehydration products was established by comparison with known compounds, by comparison of ultra-violet spectra, and by examination of the products of bromination at 0° [1·0 g. of dehydration product in 10 c.c. of carbon tetrachloride was treated with a molecular proportion of bromine in the same solvent (1% v/v); the product was stored for 2 days at 0°, and the residue, obtained by evaporation of the solvent in a stream of air, recrystallised from light petroleum (b. p. 60—80°)].

Dehydrations with Phosphoric Oxide.—The method is that described by Brown and Bluestein (*J. Amer. Chem. Soc.*, 1940, **62**, 3256), except that in certain experiments decalin was used in place of xylene.

The hydroxy-compound (5 g.) was heated with phosphoric oxide (5 g.) and the solvent (20 c.c.); the solvent was decanted, the residual solid washed with light petroleum (b. p. 100—120°). the solvent and washings were evaporated, and the residue was recrystallised from

ethanol, except for 9-1'- and 9-2'-hydroxyethylfluorene where the residue was converted directly, in ethanol, into a picrate, and the picrate, in benzene, decomposed on an alumina column (30 in. × 1 in.).   Results are given in Table 2.

TABLE 1.

Fluorene	Product	Yield, g.*	M. p. (mixed m. p.)	
9-Hydroxy-methyl-	9-Methylene-fluorene	4·1	48—49° (49—50)	Dibromide, m. p. 140—141° (lit., 142—143°); picrate, m. p. 149—151° (lit., 152°).
	Poly-(9-methyl-enefluorene)	1·4	—	
9 : 1'-Hydroxy-ethyl-	9-*Ethylidene-fluorene*	7·1 †	102—103 (102—104)	(Found : C, 93·5; H, 6·3%; bromine val., 79·8. C₁₅H₁₂ requires C, 93·8; H, 6·2%; bromine val., 83·3); dibromide, m. p. and mixed m. p. 93·5°.
9 : 2'-Hydroxy-ethyl-	9-Ethylidene-fluorene	6·8 †	102—103	(Found : C, 93·6; H, 6·1%); dibromide, m. p. 93·5°.
9-Ethyl-9-hydr-oxy-	9-Ethylidene-fluorene	6·9 †	102—103	(Found : C, 93·6; H, 6·2%; dibromide, m. p. 93·5°.
9-Hydroxy-methyl-9-methyl-	9-Methylphen-anthrene	7·2	92—93 (92—93)	Mixed m. p. with 9-ethylidenefluorene, 95—97°; bromine slowly gives 9-bromo-10-methylphenanthrene, m. p. 121·5—122·5°.
9 : 1'-Hydroxy-ethyl-9-methyl-	9 : 10-Dimethyl-phenanthrene	7·0	143—144 (lit., 142·5—143)	(Found : C, 93·0; H, 6·75%; *M*, 208. Calc. for C₁₆H₁₄ : C, 93·2; H, 6·8%; *M*, 206); picrate, m. p. 196° (lit., 193—194°).
9 : 2'-Hydroxy-ethyl-9-methyl-	9 : 10-Dimethyl-phenanthrene	7·2	143—144	(Found : C, 93·1; H, 6·7%;) picrate, m. p. 198°.
9-Ethyl-9 : 1'-hydroxyethyl-	9-Ethyl-10-methylphen-anthrene	6·2	85° (lit., 85)	Picrate, m. p. 150° (lit., 150°).

   * From 10 g. of the fluorene.
   † In the dehydration of 9-1'- and 9-2'-hydroxyethylfluorene and 9-ethylfluoren-9-ol the filtrate after recrystallisation of the products from *n*-propanol gave, on evaporation, viscous oils amounting to approximately 30% of the original yields.   The oils contained traces of fluorene and fluorenone which were removed.   The filtered oils have not yet been identified; they are not picrate-forming and have negligible bromine values, and infra-red examination indicates that they are identical.

TABLE 2.

Fluorene	Medium *	Time, h.	Product	Yield, g.†	M. p. (mixed m. p.)	Bromination
9 : 1'-Hydroxy-ethyl	A	2	9-Methylphenan-threne; 9-ethyl-idenefluorene	2·2	93—95°	On addition of bromine in CCl₄, approx. ½ is absorbed rapidly; two products : (*a*) 9-bromo-10-methylphenanthrene (0·53 g.), m. p. 120—120·5°; (*b*) 9-ethylidene-fluorene dibromide (0·64 g.), m. p. 92·5—93·5°.
9 : 2'-Hydroxy-ethyl	B	3	9-Methylphenan-threne	2·1	92—93 (92—93)	9-Bromo-10-methyl-phenanthrene (0·8 g.), m. p. 120—120·5.
9-Hydroxy-methyl-9-methyl-	A	1	9-Methylphenan-threne	3·0	91—93° (92—93)	9-Bromo-10-methylphen-anthrene (0·87 g.), m. p. 120—120·5°.
9 : 1'-Hydroxy-ethyl-9-methyl-	A	2	9 : 10-Dimethyl-phenanthrene	4·3	143—144 (143—144)	—
9 : 2'-Hydroxy-ethyl-9-methyl-	B	2	9 : 10-Dimethyl-phenanthrene	4·0	143—144 (143—144)	—

   * A, xylene at 140—160°; B, decalin at 180—190°.   † From 5 g. of the fluorene.

The products were identified by the methods indicated above for dehydration over alumina.

Dehydrohalogenation of 9-2'-Chloroethyl-9-methylfluorene.—9-2'-Chloroethyl-9-methylfluorene (3 g.) and quinoline (10 c.c.) were heated under reflux in an atmosphere of nitrogen for 6 hours. The dark product was then distilled at 25 mm. pressure until approximately one-third had distilled, and the combined residue and distillate washed with dilute hydrochloric acid and extracted with chloroform. The washed and dried extract, on evaporation, gave a sticky solid (0·8 g.), which formed a picrate, m. p. 192—196°. Decomposition of this gave 9 : 10-dimethylphenanthrene (0·4 g.), m. p. 143—144°.

9-Bromo-10-methylphenanthrene.—To 9-methylphenanthrene (1 g.) in carbon tetrachloride (10 c.c.) was added a cold solution of bromine (0·83 g.) in carbon tetrachloride (50 c.c.), and the mixture was stored for 2 days at 0°. On evaporation a solid was obtained which crystallised from light petroleum (b. p. 60—80°) in needles (0·93 g.), m. p. 121—122·5° (Found : Br, 28·7. $C_{15}H_{11}Br$ requires Br, 29·5%). *9-Bromo-10-methylphenanthrene* was confirmed by comparison of its ultra-violet spectrum with that of 9 : 10-dimethylphenanthrene.

Absorption Spectra.—Ultra-violet absorption spectra were determined in absolute ethanol, with a Hilger " Uvispek " spectrophotometer. The infra-red absorption spectrum was measured with a modified Hilger D.209 spectrophotometer working as a single-beam instrument, the powdered specimen being suspended in " Nujol."

TABLE 3.—*Absorption spectra.*

9-Ethylidenefluorene	$\lambda_{max.}$, Å	2300	2465	2555	2710	2800	2970	3110			
	log ε	4·61	4·46	4·60	4·13	4·15	4·03	4·00			
9 : 2'-Bromoethylidene-fluorene	$\lambda_{max.}$, Å	2280	2520	2610	2790	2870	3120				
	log ε	4·50	4·50	4·61	4·10	4·11	4·14				
9-Methylphenanthrene	$\lambda_{max.}$, Å	2520	2770	2840	2970	3170	3250	3310	3400	3490	
	log ε	4·79	4·13	4·00	4·07	2·5	2·45	2·63	2·41	2·64	
Fluorene	$\lambda_{max.}$, Å	2260 *	2545 *	2610	2710 *	2885	3000				
	log ε	3·86	4·20	4·24	4·10	3·78	3·94				
9-Methylfluorene	$\lambda_{max.}$, Å	2280	2580 *	2650	2730 *	2900	3010				
	log ε	3·80	4·20	4·23	4·11	3·77	3·95				
Fluorene-9-*spirocyclo*-propane	$\lambda_{max.}$, Å	2260 *	2590 *	2680	2750 *	2915	3025				
	log ε	4·30	4·15	4·20	4·07	3·90	4·04				
9 : 10-Dimethylphen-anthrene	$\lambda_{max.}$, Å	2225	2550	2700 *	2800	2870	3000	3200	3275	3360	3525
	log ε	4·34	4·75	4·47	4·28	4·05	4·11	2·53	2·40	2·64	2·63
9-Bromo-10-methyl-phenanthrene	$\lambda_{max.}$, Å	2240	2560	2725 *	2800	2900	3015	3200 *	3275	3350	3425	3520
	log ε	4·23	4·72	4·35	4·20	4·07	4·10	2·37	2·29	2·40	2·30	2·16

* Inflection.