614. *The Chemistry of Fluorene. Part V.* The Preparation of 9 : 9-Dialkylfluorenes and the Dehydrohalogenation of 9-Halogenoalkylfluorenes.*

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Reaction of alkyl sulphates or dichloroalkanes with 9-sodio-9-alkylfluorenes appears a convenient route to 9 : 9-dialkyl- and 9-alkyl-9-halogenoalkylfluorenes respectively.

Dehydrohalogenation of 9-halogenoalkylfluorenes yields an ethylidenefluorene or a *cyclo*propane*spiro*-9-fluorene derivative depending on the position of the halogen atom; 9-alkyl-9-halogenoalkylfluorenes are more difficult to dehydrohalogenate, those with a 1′-halogen atom undergoing an intramolecular change to 9 : 10-dialkylphenanthrenes in methanolic potassium hydroxide at 150° whereas under these conditions 9-2′-chloroethyl-9-methylfluorene yields a mixture of 9-2′-methoxyethyl-9-methyl- and 9-methyl-9-vinyl-fluorene. The latter is readily rearranged to 9 : 10-dimethylphenanthrene, and a similar rearrangement occurs with 9-allyl- and 9-allyl-9-methyl-fluorene.

The so-called 9-*iso*propenylfluorene[1] has been shown to be 2′-methyl*cyclo*propane*spiro*-9-fluorene.

IN Part II of this series[2] the preparation of 9-sodio-9-methylfluorene and its condensation with ethylene chlorohydrin and ethylene dichloride were described. This and the 9-ethyl analogue (conveniently prepared by the same technique) have been condensed with methyl and ethyl sulphate, and the former with allyl chloride, to yield the corresponding 9 : 9-dialkyl and alkenyl-alkyl derivatives. Although the yields are rather lower than in similar reactions with 9-sodiofluorene (Part I[3]), this method appears to furnish a convenient route to 9 : 9-disubstituted fluorenes.

9-Chloromethyl- and 9-1′-chloroethyl-9-ethylfluorene have been prepared by the reaction of 9-sodio-9-ethylfluorene with methylene and ethylidene chloride respectively. The dehydrohalogenation of these compounds and of 9-2′-chloroethyl-9-methyl-,[2] 9-(2-chloro-1-methylethyl)-, 9-1′-bromoethyl-, and 9-2′-bromoethyl-fluorene has been studied for comparison with that of 9-2′-chloroethylfluorene.[3] When heated with potassium hydroxide,

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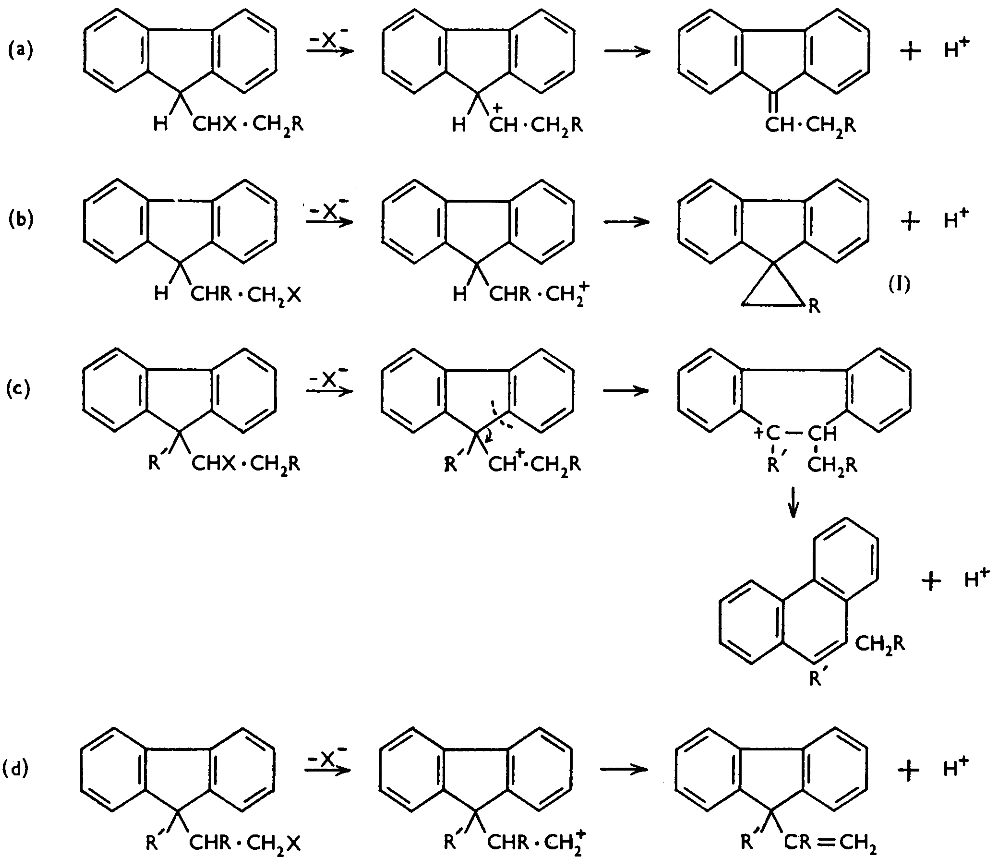
* Part IV, *J.*, 1954, 3116.

[1] Badger, Cook, and Schwarz, *J.*, 1952, 117.

[2] Greenhow, McNeil, and White, *J.*, 1952, 986.

[3] Greenhow, White, and McNeil, *J.*, 1951, 2848.

9-1′-bromoethylfluorene yields, as expected, 9-ethylidenefluorene; 9-2′-bromoethylfluorene, like the chloro-analogue, gives *cyclo*propane*spiro*-9-fluorene; and 9-(2-chloro-1-methylethyl)-fluorene gives methyl*cyclo*propane*spiro*-9-fluorene (I; R = Me). The structure of this compound follows from the similarity of its infrared spectrum, which does not contain absorption peaks characteristic of an ethylenic linkage or a terminal methylene group, to that of *cyclo*propane*spiro*-9-fluorene,[2] and from formation of a picrate, which distinguishes it from 9-alkyl- and 9 : 9-dialkyl-fluorenes. Badger, Cook, and Schwarz [1] described the preparation of " 9-*iso*propenylfluorene " from 9-potassio-9-cyanofluorene and propylene oxide; a sample of this product, kindly supplied by Professor J. W. Cook, was found to be identical (m. p. and mixed m. p. 97—98° and identical infrared spectra) with the dehydrohalogenation product (I; R = Me).

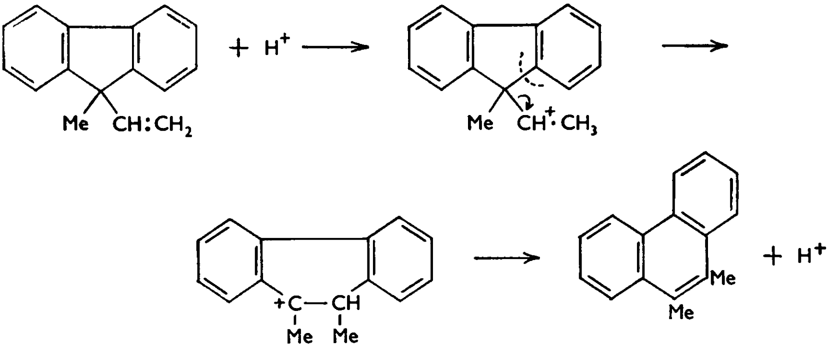


As already noted,[2] replacement of the remaining 9-hydrogen in 9-2′-chloroethylfluorene by an alkyl group prevents the formation of a *spirocyclo*propane derivative and renders elimination of hydrogen chloride much more difficult. Thus the 9-methyl derivative was unaffected by treatment with solid potassium hydroxide at 300° or refluxing alcoholic potassium hydroxide, although when refluxed with quinoline it gave a small amount of 9 : 10-dimethylphenanthrene. 9-Chloromethyl-9-ethyl-, 9-1′-chloroethyl-9-ethyl-, and 9-2′-chloroethyl-9-methylfluorene were almost quantitatively dehydrohalogened by methanolic potassium hydroxide under pressure, the products from the first two being 9-ethyl- and 9-ethyl-10-methylphenanthrene respectively. The product from the third was resolved by chromatography into a colourless oil and a solid. The infrared spectrum of the oil was similar to that of 9-allylfluorene (bands typical of an ethylenic linkage and a terminal methylene group); the oil readily formed a dibromide, and its ultraviolet spectrum was that of a substituted fluorene. It is, therefore, 9-methyl-9-vinylfluorene, the first example recorded of a fluorene derivative with a 9-vinyl group. The solid product proved to be 9-methyl-9-2′-methoxyethylfluorene.

The products formed on dehydrohalogenation of 9-halogenoalkylfluorenes are similar, with one exception, to those obtained by dehydration of the corresponding hydroxyalkylfluorenes over alumina,[2] and somewhat similar mechanisms (a—d) are proposed (R = H or alkyl; R′ = alkyl; X = halogen).

The exception is 9-2′-chloromethyl-9-methylfluorene which yields 9-methyl-9-vinylfluorene, whereas 9-2′-hydroxymethyl-9-methylfluorene gives 9 : 10-dimethylphenanthrene. The ready conversion of the methylvinylfluorene into 9 : 10-dimethylphenanthrene on treatment with phosphoric oxide at 180° and the formation of a small amount of the latter from 9-2′-chloromethyl-9-methylphenanthrene when refluxed with quinoline might suggest that the vinyl compound is an intermediate in the fluorene–phenanthrene change. 9-Hydroxymethyl- and 9-chloromethyl-fluorene, however, both yield methylphenanthrene on elimination of water or hydrogen chloride, and the intermediate formation of a vinyl compound is not possible in these cases; it clearly is not a necessary intermediate in the intramolecular change.

It is probable that the formation of 9 : 10-dimethylphenanthrene when 9-2′-chloromethyl-9-methylfluorene is refluxed with quinoline is due to the decomposition of an intermediate quinolinium salt. The addition of a proton under acid conditions explains the isomerisation of 9-methyl-9-vinylfluorene to 9 : 10-dimethylphenanthrene when heated with phosphoric oxide, and this change also occurs with 9-allyl-9-methylfluorene which, when heated with phosphoric oxide at 200°, give a good yield of 9-ethyl-10-methylphenanthrene.



EXPERIMENTAL

9-Sodio-9-methyl- and 9-2′-chloroethyl-9-methyl-fluorene were prepared as described earlier.[2]

9-*Sodio*-9-*ethylfluorene*.—9-Ethylfluorene (40 g.) and powdered sodamide (8·5 g.) were heated at 190—200° in decahydronaphthalene (150 c.c.) with stirring for 4 hr. in dry nitrogen, giving 9-*sodio*-9-*ethylfluorene* as a brown solid (yield was ~100%) (Found : Na, 10·3. $C_{15}H_{13}Na$ requires Na, 10·7%). The sodio-compound was washed with light petroleum before use.

9 : 9-*Dimethylfluorene*.—9-Sodio-9-methylfluorene (45 g.), methyl sulphate (50 c.c.), and benzene (200 c.c.) were refluxed for 16 hr. The product was filtered and the filtrate evaporated at reduced pressure. The residual oil, fractionated *in vacuo*, gave 9 : 9-dimethylfluorene, b. p. 158—160°/15 mm. (33 g.) (Found : C, 92·4; H, 7·3. Calc. for $C_{15}H_{14}$: C, 92·8; H, 7·2%). The dimethylfluorene crystallised from light petroleum as prisms, m. p. 72—74°. Chromatography through alumina gave a product which crystallised from light petroleum as prisms of the same m. p. but repeated recrystallisation from ethanol raised it to 96°.

9-*Ethyl*-9-*methylfluorene*.—9-Sodio-9-ethylfluorene (10 g.), methyl sulphate (30 c.c.), and benzene (100 c.c.) were refluxed for 10 hr., then filtered, and the filtrate evaporated to an oil which was then boiled with 20% w/w sodium hydroxide solution (150 c.c.) to decompose excess of methyl sulphate. The mixture was extracted with ether, and the ether layer washed, dried

($MgSO_4$), filtered, and evaporated to a clear oil (7·8 g.), which, fractionated *in vacuo*, gave *9-ethyl-9-methylfluorene*, b. p. 156—161°/12·5 mm. (6·8 g.), plates (from ethanol), m. p. 61—62° (Found : C, 92·1; H, 7·7. $C_{16}H_{16}$ requires C, 92·3; H, 7·7%).

9 : *9-Diethylfluorene*.—9-Sodio-9-ethylfluorene (10 g.), ethyl sulphate (30 c.c.), and benzene (100 c.c.) gave, as above, crude 9 : *9-diethylfluorene* (7·7 g.), b. p. 159—163°/11·5 mm. (6·4 g.) which did not solidify. When this was boiled with a small quantity of sodamide in light petroleum (b. p. 100—120°) for 10 min. (to remove traces of ethyl sulphate and 9-ethylfluorene), the recovered diethylfluorene solidified and crystallised from ethanol as needles m. p. 29—30° (Found : C, 91·6; H, 8·0. $C_{17}H_{18}$ requires C, 91·9; H, 8·1%).

9-Allyl-9-methylfluorene.—9-Sodio-9-methylfluorene (10 g.), allyl chloride (20 c.c.), and benzene (50 c.c.) were refluxed for 6 hr. Sodium chloride (3·0 g.) was filtered off and the filtrate evaporated under reduced pressure to a yellow oil (12·5 g.), giving *9-allyl-9-methylfluorene* (7·8 g.), b. p. 143—150°/3 mm. (Found : C, 92·3; H, 7·4%; *M*, 215. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%; *M*, 220).

9-Chloromethyl-9-ethylfluorene.—9-Sodio-9-ethylfluorene (20 g.), methylene chloride (50 c.c.), and light petroleum (b. p. 40—60°; 150 c.c.) were heated under reflux for 6 hr., then filtered, and the filtrate was evaporated on the water-bath to a viscous oil which, fractionated *in vacuo*, gave *9-chloromethyl-9-ethylfluorene*, b. p. 128—132°/1 mm. (16·4 g.) (Found : C, 79·7; H, 6·3; Cl, 14·1. $C_{16}H_{15}Cl$ requires C, 79·2; H, 6·2; Cl, 14·6%).

9-1′-Chloroethyl-9-ethylfluorene.—9-Sodio-9-ethylfluorene (40 g.), ethylidene chloride (30 c.c.), and light petroleum (b. p. 60—80°; 200 c.c.) were heated under reflux for 8 hr. They afforded *9-1′-chloroethyl-9-ethylfluorene*, b. p. 126—130°/1 mm. (42 g.) (Found : C, 80·0; H, 6·7; Cl, 13·4. $C_{17}H_{17}Cl$ requires C, 79·5; H, 6·6; Cl, 13·8%).

9-(2-Chloro-1-methylethyl)fluorene.—9-Sodiofluorene (60 g.), heated under reflux with 1 : 2-dichloropropane (50 c.c.) and light petroleum (b. p. 60—80°; 200 c.c.) for 10 hr., gave fluorene (31 g.) and an oil, b. p. 180—190°/6 mm. (28 g.). The latter was diluted with light petroleum (b. p. 40—60°) and cooled and the methyl*cyclo*propane*spiro*-9-fluorene (4·1 g.) filtered off. The filtrate was evaporated to a clear oil (22 g.) which, when fractionated in a vacuum through a column (5″ × ½″) packed with stainless-steel gauze rings, gave *9-(2-chloro-1-methylethyl)-fluorene* (17·6 g.), b. p. 184—188°/4 mm. (Found : C, 79·5; H, 6·1; Cl, 13·7. $C_{16}H_{15}Cl$ requires C, 79·1; H, 6·2; Cl, 14·6%).

9-1′-Bromoethylfluorene.—9-1′-Hydroxyethylfluorene (2 g.) and phosphorus tribromide (2·8 g.) were heated at 140° in a sealed tube for 15 hr. The product was treated with acetic acid, and water, then extracted with ether, and the ether layer washed with aqueous sodium carbonate, filtered, dried, and evaporated. The residue, *9-1′-bromoethylfluorene* (2·1 g.), crystallised from ethanol–water as needles, m. p. 58° (Found : C, 65·7; H, 4·7; Br, 29·5. $C_{15}H_{13}Br$ requires C, 65·9; H, 4·8; Br, 29·3%).

9-2′-Bromoethylfluorene.—9-2′-Hydroxyethylfluorene (2 g.) and phosphorus tribromide (2·8 g.) were heated at 140° (sealed tube) for 28 hr. The product was diluted with water and extracted with ether, and the ether extract neutralised with solid sodium hydrogen carbonate, filtered, and evaporated. The residual *product* (2·2 g.) solidified and crystallised from light petroleum (b. p. 40—60°) as needles, m. p. 49·5° (Found : C, 65·6; H, 4·8; Br, 29·6. $C_{15}H_{13}Br$ requires C, 65·9; H, 4·8; Br, 29·3%). With bromine in carbon tetrachloride at 0° it slowly gave *9-bromo-9-2′-bromoethylfluorene*, m. p. 80° (hexagonal crystals from light petroleum) (Found : C, 50·7; H, 3·5; Br, 45·7. $C_{15}H_{12}Br_2$ requires C, 51·1; H, 3·4; Br, 45·5%), whose ultraviolet spectrum is similar to that of 9-bromo-9-bromoethylfluorene.

Dehydrohalogenations with Solid Potassium Hydroxide.—The halogen compound (5 g.) was heated with potassium hydroxide (1·5 g.) with slow stirring for 4 min. at 200°. The mixture was then cooled, extracted with water, and acidified. The oily product solidified and was crystallised from propan-1-ol. Results are given in Table 1.

Dehydrohalogenations with Methanolic Potassium Hydroxide at 150°.—The halogen compound (4 g.), potassium hydroxide (5 g.), and methanol (60 c.c.) were heated (sealed tube) at 150° for 30 hr. The product was diluted with water and extracted with ether. The ether extract was dried, filtered, and evaporated and the oily residue was dissolved in light petroleum and chromatographed through alumina (20″ × 1″). Results are shown in Table 2.

9-(1 : 2-Dibromoethyl)-9-methylfluorene.—9-Methyl-9-vinylfluorene (1·85 g.) and bromine in carbon tetrachloride (1% v/v; 48 c.c.) were mixed and stored at 0° for 20 hr., then evaporated under reduced pressure and the residue crystallised from ethanol, to yield the *dibromide* (1·72 g.), prisms, m. p. 120·5—121·0 (Found : C, 52·4; H, 3·8; Br, 43·7. $C_{16}H_{14}Br_2$ requires C, 52·5; H, 3·8; Br, 43·8%).

TABLE 1.

Fluorene	Product	Yield (g. from 5 g.)	M. p.	Analysis, etc.
9-1′-Bromoethyl	9-Ethylidenefluorene (see Part II)	3·4	102—103° (mixed m. p. 102—104)	(Found : C, 93·5; H, 6·3%). Dibromide, m. p. and mixed m. p. 93·5°
9-2′-Bromoethyl	*cyclo*Propane*spiro*-9-fluorene (see Part II)	3·1	70·5 (mixed m. p. 70—71)	(Found : C, 93·6; H, 6·4%; *M*, 190. Calc. for $C_{15}H_{12}$: C, 93·7; H, 6·2%; *M*, 192). Picrate (from acetic acid), needles, m. p. 139·5°
9-(2-Chloro-1-methylethyl)	Methyl*cyclo*propane-*spiro*-9-fluorene	3·6	97—98	(Found : C, 93·1; H, 6·9. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%). Picrate (prepared in ethanol), yellow needles, m. p. 108—109°

TABLE 2.

Fluorene	Product	Yield (g. from 4 g.)	M. p.	Analysis, etc.
9-2′-Chloroethyl-9-methyl-	9-*Methyl*-9-*vinylfluorene*	2·6	Oil	(Found : C, 93·1; H, 6·9. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%). Bromide, see text
	9-2′-*Methoxyethyl*-9-*methylfluorene*	0·9	74—75°	(Found : C, 85·3; H, 7·6. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%)
9-Chloromethyl-9-ethyl-	9-Ethylphenanthrene	2·2	62—63 [a]	(Found : C, 92·8; H, 6·7. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%). Picrate, m. p. 121—123°
9-1′-Chloroethyl-9-ethyl-	9-Ethyl-10-methylphenanthrene	2·8	85	M. p. 84—85°, mixed m. p. 83—85°. Picrate, m. p. 150°

[a] Pschorr (*Ber.*, 1906, **39**, 3129) gives m. p. 61—63° (picrate, m. p. 124°).

TABLE 3. *Absorption spectra* [$\lambda_{max.}$ (mμ) *and* log ε].

Fluorenes									
9 : 9-Dimethyl	228	264	—	296	—	$301._5$			
	3·85	4·25	—	3·84	—	4·05			
9-Ethyl-9-methyl	229	263	—	291	—	302			
	3·77	4·23	—	3·82	—	4·05			
9 : 9-Diethyl	222	229	—	264	292	—	303		
	4·17	3·81	—	4·22	3·82	—	4·05		
9-Methyl-9-vinyl	230	265	—	290_5	—	302			
	3·91	4·22	—	3·75	—	4·06			
9-Allyl	228_5	257	—	290_5	—	301_5			
	3·76	4·21	—	3·70	—	3·86			
Methyl*cyclo*propane*spiro*-9-fluorene	267_5	292	—	302_5					
	4·21	3·93	—	4·04					
Phenanthrenes									
9-Ethyl-10-methyl	255	270	277_5	288	300	320	327_5	336	352_5
	4·69	4·25	4·11 *	4·00	4·03	2·51	2·45	2·64	2·66
9-Ethyl	252	274	284	296	310	325	332_5	340	350
	4·81	4·18	4·02	4·12	2·79 *	2·65	2·65	2·41	2·70

* Inflection.

Rearrangement of 9-*Methyl*-9-*vinylfluorene*.—9-Methyl-9-vinylfluorene (0·48 g.), phosphoric oxide (1 g.), and decahydronaphthalene (10 c.c.) were boiled together for 1 hr., then extracted with hot light petroleum (b. p. 100—120°), and the light petroleum solution was evaporated *in vacuo*. The residual 9 : 10-dimethylphenanthrene (0·48 g.) crystallised from propan-1-ol as needles, m. p. and mixed m. p. 147·5—148·5°.

Rearrangement of 9-*Allylfluorene*.—9-Allylfluorene (9 g.), phosphoric oxide (10 g.), and light petroleum (b. p. 100—120°; 40 c.c.) were heated at 200° for 15 hr., then filtered. The filtrate was treated with charcoal (1 g.), filtered, and evaporated. The oily product (8·6 g.) with picric acid in methanol gave a picrate (6·5 g.) and this was decomposed on alumina (20″ × ¾″) to give a solid (2·8 g.) which crystallised from light petroleum (b. p. 40—60°) as needles, m. p.

59—61°, mixed m. p. with 9-ethylphenanthrene 61—63°. The picrate (orange needles from methanol) had m. p. and mixed m. p. 121—123°.

Rearrangement of 9-*Allyl*-9-*methylfluorene*.—This fluorene (4·3 g.), phosphoric oxide (4·7 g.), and light petroleum (b. p. 100—120°; 20 c.c.) were heated at 200° for 12 hr., then filtered, and the filtrate was evaporated to a solid (3·8 g.), which crystallised from methanol as plates, m. p. 80—81°, mixed m. p. with 9-ethyl-10-methylphenanthrene 81—83°. The picrate (orange needles from acetic acid) had m. p. and mixed m. p. 150°.

Absorption Spectra (see Table).—Ultraviolet absorption spectra were determined in absolute ethanol with a Hilger " Uvispek " spectrophotometer. The infrared absorption spectra were measured with a Grubb-Parsons S.3A single-beam spectrometer, the powdered specimens being suspended in " Nujol."

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