The Chemistry of Fluorene. Part IV. Some New Chloro- and Nitro-derivatives.*

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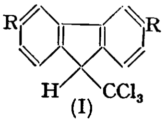
Attempts to synthesise 9-trichloromethylfluorene and 9-(1 : 1-dichloroethyl)fluorene were unsuccessful owing, it is believed, to the ease with which they lose hydrogen chloride to yield 9-dichloromethylenefluorene and 9-1′-chloroethylidenefluorene (or 9-1′-chlorovinylfluorene) respectively. 9-Dichloromethylfluorene and 9 : 10-dichlorophenanthrene were obtained from 9-formylfluorene and phosphorus pentachloride; the former product was readily dehydrochlorinated to 9-chloromethylenefluorene. With thionyl chloride 9-formylfluorene yielded 9 : 9′-diformyl-9 : 9′-difluorenyl and 9-acetylfluorene yielded 9-acetyl-9-chlorofluorene which was readily converted into 9 : 9′-diacetyl-9 : 9′-difluorenyl.

9 : 9-Dichlorofluorene was prepared from fluorene and carbon tetrachloride in the presence of benzyltrimethylammonium hydroxide, while 2 : 5 : 9 : 9-tetrachloro- and 5-nitro-2 : 9 : 9-trichloro-fluorene were obtained from 2 : 5-dinitrofluorenone and phosphorus pentachloride. Direct addition of chlorine to fluorene yielded a hexachloride and a complex mixture of polychlorofluorenes. Of these compounds, only 9 : 9-dichlorofluorene is active as an insecticide.

Although fluorene-9-carboxylic acid shows activity as a plant-growth promoter the 2 : 7-dichloro-derivative does not.



(I)

Although it is known that 1 : 3 : 6 : 8-tetranitro- and 1 : 8-dichloro-3 : 6-dinitro-carbazole are fungicidal (B.I.O.S. Final Report, No. 1480; F.I.A.T. Final Report, No. 949) and 1 : 1 : 1-trichloro-2 : 2-di-*p*-chlorophenylethane (D.D.T.) and "benzene hexachloride" (γ-isomer) are established insecticides, there is no record of the efficacy of the analogous fluorene derivatives. Indeed the fluorene analogues of D.D.T. (I; R= Cl) and benzene hexachloride are unknown and only a few polychloro-, polynitro- and chloronitro-fluorenes have been reported.

In attempts to synthesise 9-trichloromethylfluorene (I; R = H), chlorination of 9-methylfluorene in ultra-violet light gave, as the only substance isolated, poly-(9-methylenefluorene), presumably formed by way of 9-chloro-9-methylfluorene (cf. Wieland and Krause, *Annalen*, 1925, **443**, 135). In the absence of ultra-violet light, nuclear chlorination occurred to yield 2 : 7-dichloro-9-methylfluorene, the identity of which was established by oxidation to 2 : 7-dichlorofluorenone. No reaction occurred when 4 : 4′-dichlorodiphenyl was treated with chloral hydrate in the presence of sulphuric acid; with warm chlorosulphonic acid 2 : 7-dichlorodibenzothiophen dioxide was formed in a manner analogous to that used by Courtot and Lin (*Bull. Soc. chim.*, 1931, **49**, 1047) for the preparation of the corresponding dibromo-compound.

9-Dichloromethylenefluorene did not add hydrogen chloride in any conditions tried. The exocyclic double bond was very inert since bromination and chlorination yielded the corresponding 2 : 7-disubstituted derivatives and nitration gave 9-dichloromethylene-2-nitro-fluorene.

Condensation of fluorene and 9-fluorenylsodium with carbon tetrachloride were also tried as a possible route to 9-trichloromethylfluorene. There was no reaction when fluorene, carbon tetrachloride, ethanol, and sodium ethoxide were refluxed but, after fluorene and benzyltrimethylammonium hydroxide in carbon tetrachloride had been exposed to daylight for three months, 9 : 9-dichlorofluorene and fluorenone were isolated. It is believed that the dichlorofluorene is formed by a free-radical photochemical reaction in the first stage of which carbon tetrachloride decomposes into chlorine radicals and trichloromethyl radicals. Bowen and Rohatgi (*Discuss. Faraday Soc.*, 1953, **14**, 146) obtained 9-chloro- and

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9 : 10-dichloro-anthracene on irradiation of anthracene in carbon tetrachloride with ultraviolet light, presumably by a similar mechanism. Condensation of carbon tetrachloride and 9-fluorenylsodium yielded 9-dichloromethylenefluorene in addition to fluorene and di-9-fluorenyl, which suggests that the trichloromethyl compound, if first formed, readily loses a molecule of hydrogen chloride. This view is consistent with the known stability of the dibenzofulvene structure and is supported by the fact that 9-dichloromethylfluorene and crude 9-(1 : 1-dichloroethyl)fluorene which were prepared by reaction of phosphorus pentachloride with 9-formyl- and 9-acetyl-fluorene were converted into 9-chloromethylenefluorene and 9-1′-chloroethylidenefluorene, respectively, when passed through activated alumina.

A minor product from the reaction of 9-formylfluorene and phosphorus pentachloride is 9 : 10-dichlorophenanthrene which must be formed either by a rearrangement during dehydrochlorination of 9-chloro-9-dichloromethylfluorene (cf. Wittig, Davis, and Koenig, *Ber.*, 1951, **84**, 627) or by chlorination of 9-chlorophenanthrene produced by a similar rearrangement during dehydrochlorination of 9-dichloromethylfluorene.

Distillation *in vacuo* of the product from 9-acetylfluorene and phosphorus pentachloride resulted in vigorous decomposition and gave 9-1′-chlorovinylfluorene in very low yield. This compound and 9-1′-chloroethylidenefluorene were identified by their infra-red and ultra-violet absorption spectra and by catalytic hydrogenation to 9-1′-chloroethylfluorene which was also prepared by the reaction of 9-1′-hydroxyethylfluorene with thionyl chloride.

It was expected that thionyl chloride would react with the enolic form of 9-acetylfluorene to yield 9-1′-chloroethylidenefluorene but the main product proved to be 9-acetyl-9-chlorofluorene which was readily converted by copper powder into 9 : 9′-diacetyl-9 : 9′-difluorenyl. The diacetyl compound ($C_{30}H_{24}O_2$) was identical with the alleged dimer of 9-acetylfluorene ($C_{30}H_{22}O_2$) described by Von and Wagner (*J. Org. Chem.*, 1944, **9**, 155). Both 9-acetyl-9-chlorofluorene and 9 : 9′-diacetyl-9 : 9′-difluorenyl were converted into 9 : 9′-difluorenyl by boiling alcoholic potassium hydroxide. With 9-formylfluorene thionyl chloride gave only 9 : 9′-diformyl-9 : 9′-difluorenyl.

When fluorene in carbon tetrachloride was treated with dry chlorine at 15° in sunlight or ultra-violet light, a clear viscous oil was obtained from which a crystalline hexachloride was isolated. This substance was readily oxidised to a hexachlorohexahydrofluorenone and its ultra-violet absorption spectrum showed it to have a non-aromatic structure; it forms a trichlorofluorene on dehydrohalogenation. The ether-soluble portion of the product was high-boiling and inseparable, probably composed of polychlorofluorenes.

2 : 5 : 9 : 9-Tetrachlorofluorene was prepared from 2 : 5-dinitrofluorenone and phosphorus pentachloride at 170—180° (see Schmidt and Wagner, *Annalen*, 1912, **387**, 159, for the similar synthesis of 2 : 7 : 9 : 9-tetrachlorofluorene). At a lower temperature both 9 : 9-dichloro-2 : 5-dinitrofluorene and a trichloromononitrofluorene were obtained. Since it is known that the 2-nitro-group of 2 : 5-dinitrofluorenone is more reactive than that in the 5-position, *e.g.*, partial reduction yields 2-amino-5-nitrofluorenone (Courtot and Moreaux, *Compt. rend.*, 1943, **217**, 453), the mononitro-compound is assumed to be 2 : 9 : 9-trichloro-5-nitrofluorene. Acid hydrolysis of the substituted 9 : 9-dichlorofluorenes gave the corresponding fluorenones.

Wain (Roy. Inst. Chem. Monograph, 1953, No. 2, p. 7) has reported that whereas fluorene-9-carboxylic acid is a plant-growth hormone, its 9-methyl derivative is inactive and he suggests that activity is associated with the presence of a $C_{(9)}$-hydrogen atom. As certain ring-chlorinated phenoxyacetic acids are highly active plant-growth hormones although the parent phenoxyacetic acid is inactive (Wain, *ibid*, p. 5), 2 : 7-dichlorofluorene-9-carboxylic acid was prepared for evaluation. It was obtained by chlorination of fluorene-9-carboxylic acid in chloroform, but could not be prepared by carboxylation of 9-(2 : 7-dichlorofluorenyl)sodium since 2 : 7-dichlorofluorene did not react with sodamide in decalin. This failure to form a sodio-derivative and the inactivity of 2 : 7-dichlorofluorene-9-carboxylic acid as a plant-growth promoter are no doubt due to deactivation of the 9-hydrogen atoms by the chlorine in the 2- and the 7-position.

Of the chloro- and nitro-fluorenes described above, only 9 : 9-dichlorofluorene was active against *Calliphora.* 2 : 7 : 9 : 9-Tetrachloro- and 9 : 9-dichloro-fluorene were nontoxic to the grain weevil (*Calandra granara*) and locust (*Locusta migratoria*), and the latter compound was also inactive against the mosquito (*Aedis aegypti*) and housefly (*Musca domestica*).

EXPERIMENTAL

2 : 7-Dichloro-9-methylfluorene.—A slow stream of chlorine was passed for 2 hr. through a solution of 9-methylfluorene (5 g.) in carbon tetrachloride (50 c.c.) at room temperature. Evaporation *in vacuo* gave a viscous oil from which 2 : *7-dichloro-9-methylfluorene* slowly crystallised. After it had been freed from oil by washing with cold light petroleum (b. p. 40—60°), the compound crystallised from ethanol as white plates, m. p. 132—133° (Found : C, 67·2; H, 4·0; Cl, 28·2. $C_{14}H_{10}Cl_2$ requires C, 67·5; H, 4·0; Cl, 28·5%). Oxidation with chromic oxide in acetic acid gave 2 : 7-dichlorofluorenone, m. p. and mixed m. p. with a specimen prepared from 2 : 7-dichlorofluorene, 190°.

Experiments with 9-Dichloromethylenefluorene.—(*a*) 9-Dichloromethylenefluorene (Staudinger, *Helv. Chim. Acta*, 1920, **3**, 840) (0·5 g.) in carbon tetrachloride (5 c.c.) was treated with bromine (0·5 g.) and iodine (0·1 g.) in carbon tetrachloride (20 c.c.). Rapid bromination occurred on gentle warming and 2 : *7-dibromo-9-dichloromethylenefluorene* gradually crystallised. After being filtered off, washed with carbon tetrachloride, and crystallised from acetic acid, the compound formed yellow needles (0·5 g.), m. p. 237—238° (Found: C, 41·7; H, 1·6. $C_{14}H_6Cl_2Br_2$ requires C, 41·5; H, 1·5%). In the absence of iodine only unchanged 9-dichloromethylenefluorene was obtained.

(*b*) Chlorine was passed through 9-dichloromethylenefluorene (2 g.) in chloroform (50 c.c.) at 18—22° for 10 hr. 2 : *7-Dichloro-9-dichloromethylenefluorene* was deposited as a yellow solid which crystallised from toluene as needles (0·8 g.), m. p. 242—244° (Found : C, 52·7; H, 2·05; Cl, 44·4. $C_{14}H_6Cl_4$ requires C, 53·1; H, 1·9; Cl, 44·9%). The ultra-violet absorption spectrum, like that of the corresponding dibromo-compound, is of the 9-ethylidenefluorene type (see Table). Oxidation with chromic oxide in acetic acid gave 2 : 7-dichlorofluorenone, m. p. and mixed m. p. 189—190°).

(*c*) 9-Dichloromethylenefluorene (2 g.) was added portionwise to nitric acid (7·5 c.c.; *d* 1·42) and acetic acid (15 c.c.). After it had been stirred for 1 hr., the mixture was stored for 24 hr. and the yellow solid was then filtered off (2·3 g.). Chromatography on alumina gave *9-dichloromethylene-2-nitrofluorene* (0·8 g.), yellow needles (from acetic acid), m. p. 199—200° (Found: C, 57·1; H, 2·5; Cl, 24·6; N, 4·6. $C_{14}H_7O_2NCl_2$ requires C, 57·5; H, 2·4; Cl, 24·3; N, 4·8%). Oxidation with chromic acid gave 2-nitrofluorenone, m. p. and mixed m. p. 222—223°.

Attempt to Condense 4 : 4′-Dichlorodiphenyl and Chloral Hydrate.—Chlorosulphonic acid (3·5 c.c.) was slowly added to 4 : 4′-dichlorodiphenyl (5·6 g.) and chloral hydrate (4·1 g.), and the mixture was stirred for 5 hr. at 80°, then diluted with water. The insoluble material was filtered off and crystallised from acetic acid to give 2 : 7-dichlorodibenzothiophen 9 : 9-dioxide (2·2 g.), m. p. 295—296° (Found : C, 50·6; H, 2·2. Calc. for $C_{12}H_6O_2SCl_2$: C, 50·5; H, 2·1%).

Reaction of Fluorene and Carbon Tetrachloride.—Fluorene (10 g.), benzyltrimethylammonium hydroxide (10 c.c. of a 40% solution in *n*-butanol), and carbon tetrachloride (100 c.c.) were stored for 3 months at room temperature in daylight. After it had been washed with dilute hydrochloric acid and water, the solution was dried and evaporated, to give an orange solid (9·2 g.). Crystallisation from ethanol gave fluorene (4·5 g.) and 9 : 9-dichlorofluorene (3·2 g.), m. p. and mixed m. p. 98—100°. The filtrate, after evaporation, was chromatographed on alumina to give fluorenone (1·1 g.).

Condensation of 9-Fluorenylsodium and Carbon Tetrachloride.—9-Fluorenylsodium (70 g.), carbon tetrachloride (100 c.c.), and light petroleum (b. p. 60—80°; 300 c.c.) were refluxed for 60 hr. The product was filtered to remove sodium chloride (23 g.), and the filtrate evaporated to leave a dark oil (56 g.). The latter when chromatographed on alumina (30 × 1¼ in.) yielded successively fluorene (21 g.), 9-dichloromethylenefluorene (4·3 g.), 9 : 9′-difluorenyl (5·4 g.), and an amorphous brown powder (22 g.) which could not be purified further. The dichloro-compound crystallised from methanol as needles, m. p. and mixed m. p. 127—128°, and formed a picrate (in acetic acid), m. p. 172—173°. The ultra-violet spectrum (Table) is similar to that of 9-ethylidenefluorene.

Reaction of 9-Formylfluorene and Phosphorus Pentachloride.—Freshly prepared 9-formylfluorene (10 g.) and phosphorus pentachloride (11 g.) were heated at 150° for 2 hr. Phosphorus oxychloride was distilled off continuously and its removal completed at reduced pressure. The residue distilled as a yellow viscous oil (5 g.), b. p. 175—180°/5 mm., which slowly solidified.

Several crystallisations from light petroleum (b. p. 60—80°) gave 9-*dichloromethylfluorene* as white plates, m. p. 106° (Found : C, 67·5; H, 4·2; Cl, 28·0. $C_{14}H_{10}Cl_2$ requires C, 67·5; H, 4·0; Cl, 28·5%). The compound did not form a picrate and when refluxed with alcoholic potassium hydroxide was converted into fluorene. When 9-dichloromethylfluorene in light petroleum (b. p. 60—80°) was adsorbed on activated alumina it was quantitatively dehydrochlorinated to 9-*chloromethylenefluorene* which crystallised from ethanol or light petroleum as white needles, m. p. 74—75° (Found : C, 78·9; H, 4·2; Cl, 17·0. $C_{14}H_9Cl$ requires C, 79·1; H, 4·2; Cl, 16·7%). The infra-red spectrum shows a band due to a trisubstituted ethylene and the ultra-violet spectrum is of the 9-ethylidenefluorene type (see Table). The *picrate*, orange needles (from benzene), had m. p. 141—142° (Found : C, 54·1; H, 2·8; N, 9·4. $C_{20}H_{12}O_7N_3Cl$ requires C, 54·4; H, 2·7; N, 9·5%). Concentration of the light petroleum filtrate from the first crystallisation of 9-dichloromethylfluorene led to the isolation of 9 : 10-dichlorophenanthrene (0·2 g.), white needles, m. p. and mixed m. p. 165° (Found : C, 68·1; H, 3·2; Cl, 28·5. Calc. for $C_{14}H_8Cl_2$: C, 68·0; H, 3·3; Cl, 28·7%).

Reaction of 9-*Acetylfluorene and Phosphorus Pentachloride.*—Freshly prepared 9-acetylfluorene (10 g.) and phosphorus pentachloride (10 g.) were heated at 150° for 1½ hr. and phosphorus oxychloride was continuously distilled from the mixture. The residue started to distil at 170—180°/5 mm., but when only a small amount of distillate had been collected a vigorous decomposition occurred and the mixture after foaming considerably formed a soft coke. The distillate (2 g.), which solidified on cooling, was crystallised from light petroleum (b. p. 60—80°), to give 9-1′-*chlorovinylfluorene* as white needles, m. p. 81—82° (Found : C, 79·6; H, 5·0; Cl, 15·4. $C_{15}H_{11}Cl$ requires C, 79·5; H, 4·9; Cl, 15·6%). The compound did not form a picrate and was not changed by chromatography on activated alumina. Infra-red examination showed the presence of the $CH_2{:}C{<}$ group; the ultra-violet spectrum is similar to that of fluorene (Table).

In a further experiment the products from the reaction of 9-acetylfluorene and phosphorus pentachloride were passed in benzene through a small alumina column to remove coloured impurities. Evaporation of the eluate gave a pale brown oil which was partly soluble in light petroleum (b. p. 60—80°). The soluble portion was adsorbed on an alumina column (20 × 1 in.). A mixture of benzene and light petroleum eluted 9-1′-*chloroethylidenefluorene* (2·5 g.) which crystallised from light petroleum as white needles, m. p. 91·5—92·5° (Found : C, 79·6; H, 4·9; Cl, 15·5. $C_{15}H_{11}Cl$ requires C, 79·5; H, 4·9; Cl, 15·6%). A methyl group and a fully substituted ethylene structure were shown to be present by infra-red examination. The compound formed a *picrate*, orange needles (from benzene), m. p. 181—182° (Found : C, 55·2; H, 3·3; N, 9·0. $C_{21}H_{14}O_7N_3Cl$ requires C, 55·3; H, 3·1; N, 9·2%). No 9-1′-chlorovinylfluorene was isolated from the chromatographic fractions.

9-1′-*Chloroethylfluorene.*—(*a*) 9-1′-Hydroxyethylfluorene (1 g.) and thionyl chloride (10 c.c.) were heated under reflux for 1 hr. Unchanged thionyl chloride was distilled off, the residue was dissolved in ether, and the solution washed with water, dried, and evaporated. The residual oil was freed from traces of unchanged hydroxyethylfluorene by chromatography on activated alumina, light petroleum eluting the less strongly adsorbed *chloroethyl* compound which was obtained as a colourless oil, n_D^{25} 1·630 (Found : C, 78·9; H, 5·5; Cl, 15·4. $C_{15}H_{13}Cl$ requires C, 78·8; H, 5·7; Cl, 15·5%).

(*b*) 9-1′-Chlorovinylfluorene (0·5 g.) in acetic acid (20 c.c.) was shaken with hydrogen in the presence of pre-reduced Adams's catalyst (0·1 g.). When 1 mol. of hydrogen had been absorbed, the mixture was filtered and crude 9-1′-chloroethylfluorene was obtained by evaporation of the filtrate. Impurities were removed by chromatography on activated alumina to give a colourless oil (0·4 g.), the infra-red absorption spectrum of which was identical with that of the compound prepared by method (*a*).

(*c*) 9-1′-Chloroethylidenefluorene was hydrogenated in the same way as the chlorovinyl compound. Infra-red spectroscopy showed that the product was again 9-1′-chloroethylfluorene.

9-*Acetyl*-9-*chlorofluorene.*—9-Acetylfluorene (5 g.) and thionyl chloride (20 c.c.) were heated under reflux for 4 hr. Excess of thionyl chloride was distilled off under reduced pressure and the residue extracted with light petroleum (b. p. 60—80°). The extract was washed with water, dried, and evaporated to give an oil which slowly solidified. Crystallisation from ethanol (charcoal) gave 9-*acetyl*-9-*chlorofluorene* as white needles (1·5 g.), m. p. 100° (Found : C, 74·1; H, 4·8; Cl, 14·5. $C_{15}H_{11}OCl$ requires C, 74·2; H, 4·6; Cl, 14·6%). When the compound was heated under reflux with alcoholic potassium hydroxide it was converted into 9 : 9′-difluorenyl, m. p. 245—246°.

9 : 9′-*Diacetyl*-9 : 9′-*difluorenyl.*—9-Chloro-9-acetylfluorene (0·25 g.) and copper powder

(0·4 g.) were heated in boiling benzene (30 c.c.) for 6 hr. The solution was filtered and the filtrate evaporated, to give the *diacetyl*-compound (quantitative yield), white prisms (from benzene–light petroleum), m. p. 241—242° (Found: C, 87·2; H, 5·4; $C_{30}H_{24}O_2$ requires C, 86·9; H, 5·35%). This was converted by boiling alcoholic potassium hydroxide into 9 : 9′-difluorenyl, m. p. 245—246°.

9 : 9′-*Diformyl*-9 : 9′-*difluorenyl*.—9-Formylfluorene (3 g.), thionyl chloride (5 c.c.), and dry ether (20 c.c.) were heated under reflux for 1 hr. On cooling, the diformyl derivative separated as a white solid (1·6 g.) which crystallised from benzene as prisms, m. p. 217—218° (Found: C, 86·7; H, 4·7. Calc. for $C_{28}H_{18}O_2$: C, 87·0; H, 4·7%), converted by boiling alcoholic potassium hydroxide into 9 : 9′-difluorenyl, m. p. 245—246°.

Chlorination of Fluorene.—Dry chlorine was passed into fluorene (50 g.) in carbon tetrachloride (800 c.c.) at 15° for 9 hr. in bright sunlight. After it had been freed from chlorine by bubbling of air through it, the solution was evaporated *in vacuo* on the water-bath, to leave a clear viscous oil (101 g.) which was dissolved in ether and stored at 0°. The white precipitate (20·5 g.) was filtered off and crystallised from acetic acid, to give *fluorene hexachloride*, prisms, m. p. 215—217° (Found: C, 41·4; H, 2·65; Cl, 56·5. $C_{13}H_{10}Cl_6$ requires C, 41·1; H, 2·6; Cl, 56·2%).

The hexachloride (0·5 g.) was oxidised with chromic oxide (1·0 g.) in boiling acetic acid (10 c.c.) to a *hexachlorohexahydrofluorenone* (0·2 g.), prisms (from acetic acid), m. p. 193—194° (Found: C, 39·6; H, 2·1; Cl, 53·8. $C_{13}H_8OCl_6$ requires C, 39·7; H, 2·0; Cl, 54·2%). The infra-red spectrum showed the presence of a carbonyl group.

The fluorene hexachloride (1 g.) was treated for 3 hr. with potassium hydroxide (5 g.) in boiling ethanol (50 c.c.). The brown solid product, chromatographed on alumina, gave a *trichlorofluorene* (0·1 g.), white needles (from ethanol), m. p. 102—103° (Found: C, 57·3; H, 2·4; Cl, 39·0. $C_{13}H_7Cl_3$ requires C, 57·8; H, 2·6; Cl, 39·6%). The ultra-violet spectrum resembles that of fluorene (Table).

Reaction of 2 : 5-*Dinitrofluorenone and Phosphorus Pentachloride*.—(*a*) 2 : 5-Dinitrofluorenone (5 g.) and phosphorus pentachloride (12·5 g.) were heated at 170—180° for 6 hr. in a sealed tube. The cooled product was treated with ice and water, and the insoluble material filtered off, washed, and dried. Crystallisation from ethanol gave 2 : 5 : 9 : 9-*tetrachlorofluorene* (3·2 g.), white needles, m. p. 148—149° (Found: C, 50·8; H, 2·05; Cl, 47·2. $C_{13}H_6Cl_4$ requires C, 51·3; H, 2·0; Cl, 46·7%).

2 : 5 : 9 : 9-Tetrachlorofluorene (0·4 g.), acetic acid (5 c.c.), concentrated hydrochloric acid (1 c.c.), and water (15 c.c.) were heated under reflux for 4 hr. The product was extracted with ether, and the extract washed with sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and evaporated to yield 2 : 5-*dichlorofluorenone* (0·24 g.); recrystallisation from *n*-propanol gave yellow needles, m. p. 151—152° (Found: C, 62·3; H, 2·3; Cl, 29·2. $C_{13}H_6OCl_2$ requires C, 62·65; H, 2·4; Cl, 28·6%). The *phenylhydrazone* crystallised from ethanol as needles, m. p. 162—163° (Found: C, 66·8; H, 3·4; Cl, 21·2; N, 7·9. $C_{19}H_{12}N_2Cl_2$ requires C, 67·3; H, 3·5; Cl, 20·9; N, 8·3%).

(*b*) 2 : 5-Dinitrofluorenone (9·5 g.) and phosphorus pentachloride (15 g.) were heated at 140° for 20 hr. in a sealed tube. The product was cooled and poured into ice and water, and the insoluble brown solid (10 g.) was filtered off, washed with water, and dried at 100°. Chromatography on alumina (30 × 1¼ in.) gave 2 : 9 : 9-*trichloro*-5-*nitrofluorene* (3·6 g.), yellow needles (from *n*-propanol), m. p. 170—171° (Found: C, 49·9; H, 2·0; Cl, 33·3. $C_{13}H_6O_2NCl_3$ requires C, 49·6; H, 1·9; Cl, 33·8%), followed by 9 : 9-*dichloro*-2 : 5-*dinitrofluorene* (3·2 g.), yellow prisms (from acetic acid), m. p. 212—213° (Found: C, 48·5; H, 1·9; Cl, 21·2; N, 8·3. $C_{13}H_6O_4N_2Cl_2$ requires C, 48·0; H, 1·85; Cl, 21·8; N, 8·6%).

2 : 9 : 9-Trichloro-5-nitrofluorene (0·6 g.), acetic acid (7·5 c.c.), concentrated hydrochloric acid (1·5 c.c.), and water (22·5 c.c.) were heated under reflux for 4 hr. 2-*Chloro*-5-*nitrofluorenone* was filtered off, washed with water, and dried at 100°. It crystallised from *n*-propanol as yellow needles (0·4 g.), m. p. 174—175° (Found: C, 59·7; H, 2·4; Cl, 13·5; N, 5·2. $C_{13}H_6O_3NCl$ requires C, 60·2; H, 2·3; Cl, 13·7; N, 5·4%).

9 : 9-Dichloro-2 : 5-dinitrofluorene (1 g.), when hydrolysed similarly, gave 2 : 5-dinitrofluorenone (0·7 g.), yellow needles (from acetic acid), m. p. and mixed m. p. 241—243° (Found: C, 58·2; H, 2·3; N, 10·1. Calc. for $C_{13}H_6O_5N_2$: C, 57·8; H, 2·2; N, 10·4%).

2 : 7-*Dichlorofluorene*-9-*carboxylic Acid*.—Dry chlorine was passed into fluorene-9-carboxylic acid (6 g.) in chloroform (150 c.c.) at 20° for 6 hr. The solution was evaporated under nitrogen, and the oily residue diluted with light petroleum (b. p. 40—60°; 100 c.c.) to give 2 : 7-*dichlorofluorene*-9-*carboxylic acid* (3·3 g.). Crystallisation from acetic acid yielded white prisms, m. p. 253—254° (decomp.) (Found: C, 60·1; H, 3·0; Cl, 24·8. $C_{14}H_8O_2Cl_2$ requires C, 60·2; H, 2·9;

Cl, 25·4%). Oxidation with sodium dichromate in acetic acid gave 2 : 7-dichlorofluorenone, m. p. and mixed m. p. 190—190·5°. The ultra-violet spectrum of the acid was similar to that of fluorene (Table).

Absorption spectra (*maxima, in* Å, *followed by log* ε).

9-Ethylidenefluorene	2300	2465	2555	2710	2800	2970	3110
	4·61	4·46	4·60	4·13	4·15	4·03	4·00
9-1′-Chloroethylidenefluorene	2300	2500	2575	2700	2800	3025	3150
	4·47	4·49	4·59	4·20	4·20	4·09	4·11
9-Chloromethylenefluorene	2300	2475	2575	2700	2800	3000	3125
	4·45	4·52	4·66	4·13	4·13	4·04	4·00
9-Dichloromethylenefluorene	2275	2500	2600	2700	2800	3050	3175
	4·37	4·50	4·66	4·19	4·20	4·12	4·17
2 : 7-Dichloro-9-dichloromethylenefluorene	2300	2575	2650	2750	2850	3050	3200
	4·43	4·57	4·69	4·34	4·37	4·25	4·21
2 : 7-Dibromo-9-dichloromethylenefluorene	2300	2575	2675	2750 *	2875	3075	3200
	4·43	4·58	4·75	4·36	4·36	4·29	4·20
Fluorene	2260 *	2545 *	2610	2710 *	2885	3000	
	3·86	4·20	4·24	4·10	3·78	3·94	
Trichlorofluorene	2300	2625	2700	2825 *	2950	3075	
	4·40	4·20	4·27	4·07	3·89	3·45	
9-1′-Chlorovinylfluorene	2280 *	2580 *	2650	2750	2900	3025	
	3·97	4·18	4·25	4·10	3·61	3·68	
2 : 7-Dichlorofluorene-9-carboxylic acid	—	2650 *	2750	2825 *	3000	3100	
	—	4·28	4·35	4·24	3·87	3·89	

* Inflection.

Absorption Spectra.—Ultra-violet absorption spectra (shown above) were determined in absolute ethanol with a Hilger " Uvispek " spectrophotometer. Infra-red absorption spectra were measured with a Grubb Parsons S3A single-beam spectrometer, the powdered specimens being suspended in " Nujol."

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