617. *The Chemistry of Fluorene. Part III.* The Condensation of 9-Fluorenylsodium with Acid Chlorides and Anhydrides.*

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9-Fluorenylsodium with lower acyl halides and anhydrides yields 9-1′-acyloxyalkylidenefluorenes, unlike 9-fluorenyl-lithium which gives 9 : 9-diacylfluorenes. Phthalic anhydride or phthaloyl chloride yields fluorenylidene-phthalide and 2:5-difluorenylidene-2:5-dihydro-3:4-benzofuran, and succinic anhydride yields the corresponding compounds. Naphthalic anhydride and 9-fluorenylsodium give the mono-9-fluorenylidene analogue and fluorene-9′-*spiro*-2-perinaphthane-1 : 3-dione.

In Part I (*J.*, 1951, 2848) the production of 9-alkyl derivatives of fluorene by the condensation of 9-fluorenylsodium with alkyl halides was described. This condensation has now been extended to some acid chlorides and anhydrides.

The reaction of acetyl chloride or acetic anhydride with 9-fluorenylsodium yields, as the main product, 9-1′-acetoxyethylidenefluorene (I), identified by its preparation by the acetylation of 9-acetylfluorene (Von and Wagner, *J. Org. Chem.*, 1944, **9**, 155), by formation of a dibromide and a picrate, and by its ultra-violet spectrum which showed it to have a

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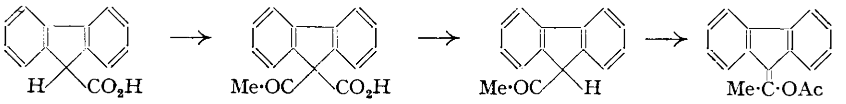
* Part II, *J.*, 1952, 986.

dibenzofulvene structure. It was identical with the compound prepared by Stollé and Ester (*J. pr. Chem.*, 1931, **132**, 14) from diphenyleneacetic acid, acetic anhydride, and sodium acetate and described by them as 9 : 9-diacetylfluorene. The following mechanism leading to (I) appears more probable than that put forward by these authors, and it is supported by the fact that 9-methylfluorene-9-carboxylic acid yields 9-methylfluorene as the sole product under their conditions.



(I)

The yields of (I) obtained from the chloride or anhydride were, at best, only about 33%. Condensation of trifluoroacetic anhydride with 9-fluorenylsodium gave 9-trifluoroacetylfluorene in low yield. The product in this case was not a dibenzofulvene derivative, presumably because the strong intermolecular hydrogen bonding between the 9-hydrogen atom of one molecule and the trifluoroacetyl group in another, which is indicated by the high molecular weight and high melting point, prevented enolisation.

Condensation of 9-fluorenyl-lithium with an acid chloride appears to yield the 9 : 9-diacyl derivative rather than a dibenzofulvene derivative (Kliegl, Weng, and Wiest, *Ber.*, 1930, **63**, 1262), and it therefore seemed probable that the so-called 9-acetylfluorene prepared by Miller and Bachman (*J. Amer. Chem. Soc.*, 1935, **57**, 766) is, in fact, 9 : 9-diacetylfluorene. Their structure is based on analysis of an oxime, m. p. 167°, which could quite readily be formed from the diacetyl compound by simultaneous hydrolysis of one acetyl group (cf. Kliegl *et al.*, *loc. cit.*). We found that both 9-acetylfluorene (m. p. 75—77°) and 9-1′-acetoxyethylidenefluorene yield 9-acetylfluorene oxime, m. p. 167°, which may be a stereoisomer of the oxime melting at 137° described by Von and Wagner (*loc. cit.*). On storage at 0° 9-acetylfluorene is converted into a crystalline hydroperoxide.

It might be expected that 9-methyl-9-fluorenylsodium would condense with acid chlorides or anhydrides to give good yields of 9-acyl-9-methylfluorenes. With acetyl chloride or acetic anhydride, however, an almost quantitative yield of 9-methylfluorene with a small amount of 9 : 9′-dimethyldi-9-fluorenyl was obtained.

Propionyl chloride condensed with 9-fluorenylsodium yielded 9-1′-propionoxypropylidenefluorene, analogous to (I). This compound has a typical dibenzofulvene ultra-violet spectrum and readily forms a picrate. 9-Mono- or 9 : 9-di-substituted fluorenes do not in general form molecular complexes with picric acid.

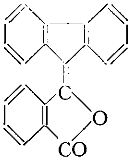
9-1′-Acetoxyethylidene- and 9-1′-propionoxypropylidene-fluorene formed dibromides which readily lost hydrogen bromide to yield monobromo-compounds whose ultra-violet spectra are similar to that of 9-bromofluorene.

With carbonyl chloride, 9-fluorenylsodium yielded an oil from which, after treatment with methanol, unchanged fluorene, di-9-fluorenyl ketone, and methyl fluorene-9-carboxylate were isolated. Under somewhat different conditions, di-9-fluorenyl-9-carboxylic acid was also isolated, its identity being proved by synthesis from difluorenyl by reaction with sodamide and subsequent carboxylation.

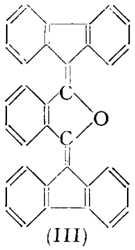
Dibasic acid chlorides or anhydrides yielded more complex products with 9-fluorenylsodium. Phthaloyl chloride or phthalic anhydride gave as a main product a yellow compound $C_{21}H_{12}O_2$, which forms a dibromide (whose ultra-violet spectrum is of the 9-bromofluorene type) and on hydrolysis yields a colourless acid. This product is therefore 3-9′-fluorenylidenephthalide (II) (Wislicenus and Neber, *Annalen*, 1919, **418**, 274). A second product of this reaction is a crystalline solid with a greenish metallic lustre which yields intensely red solutions. Its analysis and its ready formation of a colourless tetrabromide lead us to regard it as 2 : 5-di-9′-fluorenylidene-2 : 5-dihydro-3 : 4-benzofuran (III).

Succinic anhydride yields the corresponding γ-9-fluorenylidenebutyrolactone and 2 : 5-di-9′-fluorenylidenetetrahydrofuran. Naphthalic anhydride on the other hand gave in addition to (IV), which is analogous to (II), a product $C_{25}H_{14}O_2$ which forms a dioxime and whose infra-red spectrum indicates the presence of a ketone group. On treatment with phenylhydrazine it yields fluorene and *N*′-phenyl-*NN*-naphthalohydrazide. It is therefore fluorene-9′-*spiro*-2-perinaphthane-1 : 3-dione (V). After all condensations of dibasic acids or anhydrides with 9-fluorenylsodium bisdiphenylene-ethylene and/or difluorenyl were found among the products.

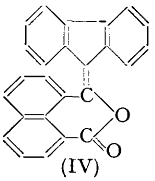
2 : 5-Di-9′-fluorenylidenetetrahydrofuran added bromine readily, to yield a colourless product which however on attempted purification evolved hydrogen bromide and bromine, to yield a bronze-green product, $C_{30}H_{18}O$, which is probably 2 : 5-difluorenylidene-2 : 5-dihydrofuran. It was hoped that this compound could be prepared by condensation of maleic anhydride with 9-fluorenylsodium but this gave a complex mixture, of which bisdiphenylene-ethylene was the only coloured ingredient.



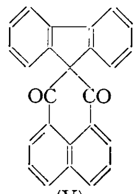
(II)



(III)



(IV)



(V)

Experimental

Silica gel used for chromatography was 100—120 mesh, 100 c.c. of gel being used for the treatment of 3·5 g. of material. Elution was carried out with, successively, light petroleum (b. p. 60—80°), benzene, chloroform, and chloroform–ethanol.

Bromides were prepared by adding to the unsaturated compound (0·5 g.) in carbon tetrachloride (20—80 c.c.) the theoretical amount of bromine as a 1% v/v solution in carbon tetrachloride. The mixture was stored overnight at 0° and was evaporated at about 40° under reduced pressure. The residue was crystallised from ethanol or light petroleum.

9-1′-*Acetoxyethylidenefluorene*.—(*a*) To 9-fluorenylsodium (from 100 g. of fluorene) (*J.*, 1951, 2848) suspended in light petroleum (b. p. 60—80°) (300 c.c.), acetyl chloride (100 c.c.) in light petroleum (b. p. 60—80°) (100 c.c.) was added slowly, with shaking, and the mixture stored overnight, evaporated, and extracted with ether. The extract on evaporation left a residue which on crystallisation gave fluorene (63 g.). The mother-liquor after evaporation and crystallisation of the residue from methanol gave a solid (10 g.), m. p. 74—75°. This gave a *picrate* (in acetic acid), m. p. 128° (Found: C, 57·2; H, 3·7; N, 8·6. $C_{23}H_{17}O_9N_3$ requires C, 57·6; H, 3·6; N, 8·8%), which on decomposition gave pale yellow 9-1′-*acetoxyethylidenefluorene* (5 g.), m. p. 97—98° (needles from light petroleum) (Found: C, 81·85; H, 5·7. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%).

With 1 mol. of bromine 9-1′-acetoxyethylidenefluorene (0·5 g.) gave a mixture containing 9-(1-*acetoxy*-1-*bromoethyl*)-9-*bromofluorene* (0·4 g.), m. p. 91° (needles from light petroleum, b. p. 60—80°) (Found: C, 49·3; H, 3·3; Br, 39·7. $C_{17}H_{14}O_2Br_2$ requires C, 49·7; H, 3·4; Br, 39·2%), and 9-1′-*acetoxyvinyl*-9-*bromofluorene* (0·1 g.), m. p. 109—110° (needles from light petroleum, b. p. 60—80°) (Found: C, 62·3; H, 4·0; Br, 24·8. $C_{17}H_{13}O_2Br$ requires C, 62·0; H, 3·95; Br, 24·3%).

The structures of these three compounds were confirmed by resemblance of their ultraviolet spectra with those of 9-ethylidene- (see Table) and 9-bromo-fluorene.

(*b*) 9-Fluorenylsodium (from 40 g. of fluorene) was suspended in light petroleum (b. p. 100—120°) (250 c.c.), and acetic anhydride (60 c.c.) added with shaking. The mixture was heated under reflux for 3 hr. and the sodium acetate filtered off. Evaporation and crystallisation from methanol gave fluorene (11·6 g.) and 9-1′-acetoxyethylidenefluorene, m. p. 98—99° (15·9 g.). The methanol filtrates with picric acid afforded 9-1′-acetoxyethylidenefluorene picrate (10·1 g.), which on decomposition gave a further 4·0 g. of product.

(*c*) 9-Acetylfluorene (3 g.), acetic anhydride (8 c.c.), and pyridine (15 c.c.) were heated under reflux for 4 hr. and the cooled mixture poured into water. The precipitate was filtered off and recrystallised from light petroleum (b. p. 60—80°) as needles (2·3 g.), m. p. 97—98°. The picrate, m. p. 128°, on decomposition gave a purer product, crystallising from light petroleum as prisms, m. p. 98·5—99·5°.

9-*Acetylfluorene oxime* was obtained from 9-acetylfluorene or 9-1′-acetoxyethylidenefluorene and crystallised from ethanol as needles, m. p. 167—168° [Found (product from 9-acetylfluorene): C, 81·0; H, 5·8; N, 6·1. $C_{15}H_{13}ON$ requires C, 80·6; H, 5·8; N, 6·3%].

9-*Acetylfluorenyl* 9-*Hydroperoxide*.—On storage, in darkness at 0°, with access to air, 9-acetylfluorene was gradually converted into 9-*acetylfluorenyl* 9-*hydroperoxide* (95% in 12 months). This crystallised from methanol as white prisms, m. p. 123—124° (decomp.) (Found: C, 75·5; H, 5·1; peroxide-O, 6·4. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0; peroxide-O, 6·7%). (Peroxide-oxygen was determined by titration of the iodine liberated from potassium iodide in methanol–acetic acid with 0·1N-sodium thiosulphate.)

9-*Methylfluorene*-9-*carboxylic Acid*.—Through 9-methyl-9-sodiofluorene (from 20 g. of 9-methylfluorene) (Part II, *J.*, 1952, 986) suspended in dry ether (500 c.c.) was passed dry carbon dioxide gas for 5 hr. The precipitated sodium salt, on acidification, gave 9-methylfluorene-9-carboxylic acid (4·5 g.), m. p. 170—171° (flat needles from acetic acid) (Wieland and Probst, *Annalen*, 1937, **530**, 274, give m. p. 168°). 9-Methylfluorene (12 g.), m. p. and mixed m. p. 45—46°, was recovered from the ethereal solution.

9-*Trifluoroacetylfluorene*.—9-Fluorenylsodium (from 21 g. of fluorene), trifluoroacetic anhydride (26 g.), and benzene (50 c.c.) were refluxed for 2 hr. The product was filtered from sodium trifluoroacetate (16·0 g.), and the filtrate evaporated to a viscous oil (22·4 g.), which on repeated crystallisation from light petroleum (b. p. 60—80°) gave fluorene (11·5 g.) and 9-*trifluoroacetylfluorene* (4·85 g.), m. p. 188—189° (hexagonal prisms from light petroleum) [Found: C, 69·0; H, 3·5; F, 20·1%; *M* (Rast), 484. $C_{15}H_9OF_3$ requires C, 68·7; H, 3·4; F, 21·7%; *M*, 262]. Hydrolysis with aqueous-alcoholic N-potassium hydroxide gave a "saponification value" 213 ($C_{15}H_9OF_3$ requires "saponification value" 215); the theoretical amount of fluorene was isolated from the acidified mixture.

Reaction of 9-*Methyl*-9-*sodiofluorene with Acetic Anhydride*.—9-Methyl-9-sodiofluorene (from 20 g. of 9-methylfluorene), acetic anhydride (12·5 g.), and benzene (250 c.c.) were mixed at room temperature and refluxed for 4 hr. The product was filtered and the filtrate evaporated. The residual oil, on distillation *in vacuo*, gave 9-methylfluorene (14 g.) and from the residue was obtained by crystallisation from light petroleum (b. p. 60—80°) 9 : 9′-dimethyldi-9-fluorenyl, prisms, m. p. 209—210° (Found: C, 93·5; H, 6·0. Calc. for $C_{28}H_{22}$: C, 93·85; H, 6·15%) (Vansheidt and Moldavskii, *Ber.*, 1931, **64**, 917, give m. p. 209°).

9-1′-*Propionoxypropylidenefluorene*.—Propionyl chloride (35 c.c.) reacted similarly, giving with 9-fluorenylsodium (from 60 g. of fluorene) a viscous oil (71 g.) which after crystallisation several times from light petroleum (b. p. 60—80°) gave fluorene (25 g.) and 9-1′-*propionoxypropylidenefluorene* (28 g.). The latter, after three crystallisations from light petroleum, had m. p. 69·5—70·5° (pale yellow prisms) (Found: C, 82·1; H, 6·6. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%). It gave a *picrate* (from acetic acid), m. p. 86—87° (Found: C, 58·7; H, 4·1; N, 8·1. $C_{25}H_{21}O_9N_3$ requires C, 59·2; H, 4·2; N, 8·3%). With 1 mol. of bromine it (1 g.) gave a bromide which decomposed on recrystallisation from light petroleum with the evolution of hydrogen bromide to form 9-*bromo*-9-1′-*propionoxypropenylfluorene* (0·6 g.), m. p. 145·5—146·5° (colourless needles) (Found: C, 63·3; H, 4·7; Br, 22·9. $C_{19}H_{17}O_2Br$ requires C, 63·7; H, 4·8; Br, 22·4%).

Reaction of 9-*Fluorenylsodium with Carbonyl Chloride*.—(*a*) 9-Fluorenylsodium (from 60 g. of fluorene) was added portionwise to a solution of carbonyl chloride in benzene (1 l.), cooled in ice water whilst carbonyl chloride was still passing into the solution. The mixture was stored overnight, gradually attaining room temperature, and was then filtered to remove sodium chloride (22 g.). The degassed filtrate on evaporation gave an oil (63·4 g.) which on dilution with light petroleum (b. p. 40—60°) (200 c.c.) deposited a brown solid (10 g.), m. p. 200—220°. The latter on extraction with hot *n*-propanol left a colourless solid which on recrystallisation from benzene gave prisms (5 g.), m. p. 242—243·5°. The propanol solution slowly deposited fluorene-9-carboxylic acid as needles (4 g.), m. p. 231·5—233°. The light petroleum solution (after removal of the brown solid), on evaporation and crystallisation from light petroleum, gave fluorene and an oil (26 g.) which could not be obtained crystalline. The oil, which was probably mainly fluorenyl-9-carbonyl chloride was treated with methanol (50 c.c.) and distilled *in vacuo*, to give methyl fluorene-9-carboxylate (21 g.), m. p. 65—66° (Found: C, 80·7; H, 5·4. Calc. for $C_{15}H_{12}O_2$: C, 80·3; H, 5·4%).

The product, m. p. 242—243·5°, was identified as di-9-fluorenyl ketone (Found: C, 90·1; H, 5·1. Calc. for $C_{27}H_{18}O$: C, 90·5; H, 5·0%) (Blum-Bergmann, *Annalen*, 1930, **484**, 47, gives m. p. 230—232°). Its *oxime* (prepared by Bachmann and Boatner's method, *J. Amer. Chem. Soc.*, 1936, **58**, 2097) had m. p. 230·5—231·5° (Found: C, 86·4; H, 5·2; N, 3·5. $C_{27}H_{19}ON$ requires C, 86·8; H, 5·1; N, 3·7%).

Infra-red examination indicated presence of :CO groups in both high-melting products.

(*b*) 9-Fluorenylsodium (from 60 g. of fluorene) in toluene (400 c.c.) was cooled in ice, and carbonyl chloride (approx. 60 g.) passed through the solution for 6 hr. The mixture was allowed to warm to room temperature overnight, methanol (300 c.c.) added, and the solution stored for a further 20 hr. and filtered. The filtrate, after degassing, was washed with 10% sodium carbonate solution and water and dried. The alkaline washings, on acidification, gave 0·8 g. of *di-*9-*fluorenyl-*9-*carboxylic acid*, m. p. (prisms; two crystallisations from acetic acid) 258—259° (decomp.) (Found: C, 86·3; H, 4·8%; equiv., 372. $C_{27}H_{18}O_2$ requires C, 86·5; H, 4·8%; equiv., 374). The ultra-violet spectrum is of the fluorene type (Table).

The filtrate, on evaporation at 100°/20 mm., gave a dark oil (68·5 g.). This was extracted with light petroleum (b. p. 60—80°), the extract evaporated, and the semisolid product (54 g.) distilled *in vacuo*, to give fluorene (16 g.), di-9-fluorenyl (8·4 g.), and methyl fluorene-9-carboxylate (22·5 g.), m. p. 64·5—66° (pale yellow prisms from methanol).

The material (14·2 g.) insoluble in light petroleum was chromatographed to give three products: a solid (4·6 g.) crystallising from benzene as prisms m. p. 160—161° (decomp.), having an ultra-violet spectrum of the fluorene type and giving di-9-fluorenyl ketone on treatment with alcoholic potassium hydroxide; a viscous oil (7 g.); and di-9-fluorenyl ketone (0·5 g.).

*Di-*9-*fluorenyl-*9-*carboxylic Acid.*—Di-9-fluorenyl (1·35 g.), sodamide (1·0 g.), and decahydronaphthalene (20 c.c.) were heated under reflux for 4 hr. and the precipitated 9-sodiodi-9-fluorenyl (approx. 1·5 g.) filtered off. Carbon dioxide was passed through a suspension of this in light petroleum (b. p. 100—120°) for 5 hr. and the precipitate filtered off, washed with light petroleum (b. p. 40—60°), dried, and extracted with water. The portion insoluble in water (0·9 g.) was di-9-fluorenyl, and the aqueous solution on acidification gave di-9-fluorenyl-9-carboxylic acid (0·4 g.), m. p. (after two crystallisations from acetic acid) and mixed m. p. 257—259° (decomp.) (Found: C, 86·4; H, 4·7%).

Reaction of 9-*Fluorenylsodium with* s-*Phthaloyl Chloride.*—9-Fluorenylsodium (from 60 g. of fluorene) and *s*-phthaloyl chloride (55 c.c.) in benzene (400 c.c.) were refluxed for 12 hr. The filtered solution was extracted with 10% aqueous sodium hydroxide (100 c.c.), and the alkaline extract acidified, to give phthalic acid (16·6 g.). The washed and dried benzene solution on evaporation gave a dark residue (74 g.). Crystallised from light petroleum (b. p. 60—80°; 400 c.c.) this gave a red solid (40 g.), and fluorene (33·1 g.) was recovered from the filtrate. The red solid on chromatography on silica gel gave bisdiphenylene-ethylene (0·5 g.), a lustrous green solid (5·3 g.), and a bright yellow solid (18 g.). The green compound, crystallising from toluene as green prisms, m. p. 264—265°, was 2 : 5-*di-*9′-*fluorenylidene-*2 : 5-*dihydro-*3 : 4-*benzofuran* (Found: C, 91·5; H, 4·7%; *M*, 452. $C_{34}H_{20}O$ requires C, 91·9; H, 4·5%; *M*, 444). Oxidation with hot chromic acid (CrO_3 1·5 g., H_2O 1·5 c.c., and AcOH 1 c.c.) gave fluorenone, m. p. 79—80° (yellow prisms from benzene). The di-9-fluorenylidene compound (0·9 g.) in carbon tetrachloride (80 c.c.) gave with bromine (1·9 g.) in carbon tetrachloride (60 c.c.) a *tetrabromide*, crystallising from toluene as colourless plates, m. p. 422—425° (Found: C, 54·0; H, 2·7; Br, 42·6. $C_{34}H_{20}OBr_4$ requires C, 53·5; H, 2·6; Br, 42·0%). The ultra-violet spectrum of the tetrabromide was similar in general shape to those of other 9-bromofluorenes.

The bright yellow solid, 3-9′-fluorenylidenephthalide, crystallised from *n*-propanol as bright yellow needles, m. p. 212—214° (Found: C, 85·0; H, 4·1%; sap. val., 195. Calc. for $C_{21}H_{12}O_2$: C, 85·1; H, 4·1%; sap. val. 189) (Wislicenus and Neber, *loc. cit.*, give m. p. 204—206°). Hydrolysis with alcoholic potassium hydroxide gave an acid which on recrystallisation from acetic acid gave 9-1′-*o*-carboxybenzoylfluorene prisms, m. p. 201—202° (decomp.) (Found: C, 79·7; H, 4·5%, equiv., 320. Calc. for $C_{21}H_{14}O_3$: C, 80·0; H, 4·5%; equiv., 314) (Wislicenus and Neber, *loc. cit.*, give m. p. 188—189°). 3-9′-Fluorenylidenephthalide (0·5 g.) gave a *dibromide* (0·4 g.) which crystallised from benzene as prisms, m. p. 199—200° (decomp.) (Found: C, 55·7; H, 2·7; Br, 34·7. $C_{21}H_{12}O_2Br_2$ requires C, 55·3; H, 2·6; Br, 35·1%).

Reaction of 9-*Fluorenylsodium with Phthalic Anhydride.*—9-Fluorenylsodium (from 60 g. of fluorene) and phthalic anhydride (57 g.) in benzene (400 c.c.) were refluxed for 12 hr. The product, worked up as in the previous experiment, gave fluorene (36 g.), bisdiphenylene-ethylene (0·5 g.), 2 : 5-di-9′-fluorenylidene-2 : 5-dihydro-3 : 4-benzofuran (2 g.), and 3-9′-fluorenylidenephthalide (12 g.).

Reaction of 9-*Fluorenylsodium with Naphthalic Anhydride.*—9-Fluorenylsodium (from 40 g. of fluorene) and naphthalic anhydride (50 g.) in benzene (500 c.c.) were refluxed for 8 hr. The product was filtered, to remove disodium naphthalate (40 g.) and other insoluble material (28 g.). The filtrate on evaporation left an oil (26·5 g.). The last two materials were combined and chromatographed on silica gel, to give fluorene (22 g.), naphthalic anhydride (5·5 g.), 3-9′-*fluorenylidenenaphthalide* (IV) (Found: C, 87·2; H, 4·1%; *M*, 340. $C_{25}H_{14}O_2$

requires C, 86·7; H, 4·0%; *M*, 346), deep red, m. p. 256—257° (prisms from benzene) (1·9 g.), and a colourless *fluorene*-9′-spiro-2-*perinaphthane*-1 : 3-*dione* (Found : C, 87·1; H, 4·1. $C_{25}H_{14}O_2$ requires C, 86·7; H, 4·0%), m. p. 282—284° (recrystallised from benzene as white needles) (10·4 g.).

The red solid had an infra-red spectrum showing a band due to the C=O group in the region expected for a lactone or a saturated or unsaturated ester. This substance in carbon tetrachloride absorbed 1 mol. of bromine, the solution losing its colour; evaporation followed by crystallisation gave pale yellow prisms, m. p. 210—212°, which contained bromine but did not give correct analyses for the dibromide and have not been identified.

The spiran had infra-red bands due to the C=O group in the region expected for ketones. It gave a *dioxime*, m. p. 287—287·5° (Found : N, 7·2. $C_{25}H_{16}O_2N_2$ requires N, 7·4%). With boiling phenylhydrazine fission occurred, to give *N*′-phenyl-*NN*-naphthalohydrazide (m. p. and mixed m. p. 219—220°) and fluorene.

Reaction of 9-*Fluorenylsodium with Succinic Anhydride*.—9-Fluorenylsodium (from 60 g. of fluorene) and succinic anhydride (38·5 g.) in benzene (400 c.c.) were refluxed for 12 hr. The product was filtered from sodium succinate (35 g.) and other insoluble material (10·5 g.). The filtrate on evaporation of the benzene left partly solid residue (57·2 g.). The last two materials were chromatographed on silica gel, to give fluorene (34·3 g.), bisdiphenylene-ethylene (0·5 g.), di-9-fluorenyl (4·3 g.), 2 : 5-*di*-9′-*fluorenylidenetetrahydrofuran* (1·48 g.), red needles (from toluene), m. p. 314—315° (Found : C, 90·8; H, 5·1%; *M*, 400. $C_{30}H_{20}O$ requires C, 90·9; H, 5·05%; *M*, 396), and a white solid (5·6 g.).

Bromine (in carbon tetrachloride) at 0° added readily to the red compound (in carbon tetrachloride), and a white bromide was precipitated [m. p. *ca.* 360° (decomp.)]. Recrystallisation of this from benzene resulted, however, in decomposition, with evolution of hydrogen bromide and bromine to a bronze-green metallic *substance*, m. p. 314—316° (Found : C, 90·9; H, 4·65. $C_{30}H_{18}O$ requires C, 91·3; H, 4·57%).

The white solid crystallised from benzene as needles, m. p. 212—213°, and had an ultraviolet spectrum of the 9-ethylidenefluorene type (see Table). The infra-red spectrun shows bands due to the C:O group, probably as a lactone, the compound being γ-9-*fluorenylidene*-γ-*butyrolactone* (Found : C, 82·5; H, 4·9. $C_{17}H_{12}O_2$ requires C, 82·25; H, 4·8%). Hydrolysis by boiling for ½ hr. with alcoholic N-potassium hydroxide gave γ-9-*fluorenyl*-γ-*oxobutyric acid*, m. p. 154—155° (Found : C, 76·2; H, 5·4%; equiv., 268. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%; equiv., 266). The lactone forms a *picrate* (yellow needles, m. p. 177·5—180°) in acetic acid (Found : C, 57·75; H, 3·2; N, 8·6. $C_{23}H_{15}O_9N_3$ requires, C, 57·9; H, 3·2; N, 8·8%), and with 1 mol. of bromine gives a *dibromide*, m. p. 110—111° (decomp.) (prisms from light petroleum) (Found : C, 49·8; H, 2·9; Br, 38·9. $C_{17}H_{12}O_2Br_2$ requires C, 50·0; H, 2·9; Br, 39·2%), the ultra-violet spectrum of which is of the 9-bromofluorene type.

Reaction of 9-*Fluorenylsodium with Succinyl Chloride*.—9-Fluorenylsodium (from 50 g. of fluorene) and succinyl chloride (24·5 g.) in benzene (400 c.c.) were refluxed for 12 hr. The product was filtered from sodium chloride (19·0 g.), and the filtrate evaporated to a brown solid (52 g.). Chromatography on silica gel gave fluorene (32·0 g.), bisdiphenylene-ethylene (1·1 g.), di-9-fluorenyl (5·4 g.), and the above lactone (6·3 g.).

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
9-1′-Acetoxyethylidenefluorene	$\lambda_{max.}$, Å	2300	2475	2550	2675	2750	3000	3125
	log ε	4·60	4·46	4·56	4·19	4·20	4·07	4·07
9-1′-Propionoxypropylidenefluorene	$\lambda_{max.}$, Å	2300	2475	2550	2700	2800	3000	3125
	log ε	4·60	4·47	4·54	4·20	4·21	4·10	4·12
γ-9-Fluorenylidene-γ-butyrolactone	$\lambda_{max.}$, Å	2325	2475	2575	2750	2850	3025 *	3200
	log ε	4·56	4·27	4·31	4·19	4·14	3·92	3·93
Fluorene	$\lambda_{max.}$, Å	2260 *	2545 *	2610	2710 *	2885	3000	
	log ε	3·86	4·20	4·24	4·10	3·78	3·94	
Di-9-fluorenyl-9-carboxylic acid ...	$\lambda_{max.}$, Å	2375 *	2600 *	2675	—	2935	3050	
	log ε	4·31	4·39	4·44	—	3·95	4·00	

* Inflection.

Absorption Spectra.—Ultra-violet absorption spectra (see Table) 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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