632. *The Chemistry of Fluorene. Part I. Condensations with 9-Fluorenylsodium.*

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A convenient method for the preparation of 9-fluorenylsodium is described. Condensation of 9-fluorenylsodium with methyl iodide or sulphate, ethyl bromide or sulphate, allyl chloride, benzyl chloride, or ethylene dichloride gives the corresponding 9-substituted fluorene in good yield; with ethylene dibromide a low yield of difluorenylethane is obtained. 2 : 2′-Dichlorodiethyl ether gives 2-chloroethyl 2-9′-fluorenylethyl ether which on dehydrohalogenation yields fluorene-9-*spiro*-4′-tetrahydropyran. Ethylene chlorohydrin gives fluorene and 9-2′-hydroxyethylfluorene. No condensation occurred with vinyl chloride or bromide.

9-ALKYLFLUORENES are generally prepared by condensing an alkyl halide with (*a*) a 9-acylfluorene in the presence of sodium ethoxide (Brown and Bluestein, *J. Amer. Chem. Soc.*, 1943, **65**, 1084; Wislicenus and Mocker, *Ber.*, 1913, **46**, 2783), (*b*) 9-fluorenyl-lithium, or (*c*) 9-fluorenylmagnesium bromide (Miller and Bachman, *J. Amer. Chem. Soc.*, 1935, **57**, 766). The last method does not always yield the desired product; for example, benzyl bromide gives a mixture of dibenzyl and di-9-fluorenyl.

Failure hitherto to use 9-fluorenylsodium for such preparations is due to the absence of an easy method for its preparation reasonably pure in good yield. Patented methods involve high-temperature fusion of fluorene with sodium (Weissgerber, G.P. 209,432) or sodamide (Weissgerber, G.P. 203,312) but the product is of doubtful purity and in a form unsuited for the further reaction. Zeigler and Jakob (*Annalen*, 1934, **511**, 55) suggest that 9-fluorenylsodium is formed when fluorene is heated with finely divided sodamide in boiling ether but, according to Miller and Bachman (*loc. cit.*), no reaction is observed when these reagents are heated under reflux in xylene. According to Lebeau and Picon (*Compt. rend.*, 1921, **173**, 84) the reaction of fluorene, sodium, and ammonia under pressure yields disodiofluorene with reduction of part of the fluorene by the hydrogen liberated.

The only 9-monosubstituted fluorenes hitherto prepared by the use of 9-fluorenylsodium are fluorene-9-carboxylic acid and 9-diphenylmethylfluorene (Schlenk and Bergman, *Annalen*, 1928, **463**, 188). In these cases the sodio-derivative was formed by the action of triphenylmethylsodium, involving a tedious preparation and separation.

We have found that 9-fluorenylsodium can be prepared in good yield and in a sufficiently pure form from powdered sodamide and fluorene in boiling decahydronaphthalene, fluorenylsodium being deposited as a brownish-yellow powder. If excess of fluorene is used there is little chance of any disodium derivative being formed. The temperature and the nature of the solvent appear to be critical. In boiling light petroleum (b. p. 100—120°), less than 5% of the sodamide reacts in 18 hours. Methylnaphthalene and tetrahydronaphthalene yield a less satisfactory product.

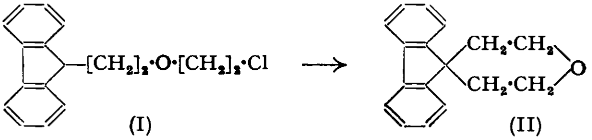
9-Fluorenylsodium, prepared in this manner, reacts readily with methyl iodide or sulphate, ethyl bromide or sulphate, allyl chloride, or benzyl chloride to produce the corresponding 9-substituted fluorene in good yield and with little or no by-product except unchanged fluorene. Our 9-benzylfluorene agrees in properties with that described by previous workers (*e.g.*, Wislicenus and Mocker, *Ber.*, 1913, **46**, 2772; Vansheidt, *Ber.*, 1931, **64**, 917). The compound described as 9-benzylfluorene by Weissgerber (*Ber.*, 1901, **34**, 1659) was later shown to be 9 : 9-dibenzylfluorene by Thiele and Henle (*Annalen*, 1906, **347**, 299).

9-Ethylfluorene, obtained by our method after careful purification as a colourless oil, slowly deposits a crystalline hydroperoxide which on reduction gives an almost quantitative yield of 9-ethylfluoren-9-ol. The ready formation of this stable hydroperoxide may explain why 9-ethylfluoren has been variously described as an uncrystallisable oil and as a solid of m. p. 105—108° (Wislicenus and Densch, *Ber.*, 1902, **35**, 759; Wislicenus and Mocker, *loc. cit.*, p. 2781; Meerwein, *Annalen*, 1913, **396**, 244; Zelinsky and Gawerdowskaja, *Ber.*, 1928, **61**, 1052; Miller and Bachman, *loc. cit.*); the product isolated by Wislicenus and Densch was however later shown (Wislicenus and Mocker, *loc. cit.*, p. 2773) to be impure fluorene.

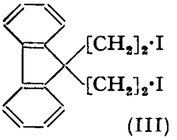
Ethylene dichloride reacts with 9-fluorenylsodium to give a moderate yield of the expected 9-2′-chloroethylfluorene, but ethylene dibromide even in considerable excess gives only difluorenylethane in poor yield.

When 9-fluorenylsodium is refluxed with ethylene chlorohydrin in light petroleum a considerable amount of fluorene is precipitated, but a small amount of 9-2′-hydroxyethylfluorene can be isolated from the reaction product.

With 2 : 2′-dichlorodiethyl ether an excellent yield of 2-chloroethyl 2-9′-fluorenylethyl ether was obtained, which on dehydrohalogenation by solid sodium hydroxide at 200° is converted into fluorene-9-*spiro*-4′-tetrahydropyran (II). The structure of the spiran was confirmed by its ultra-violet absorption spectrum which shows it to contain the fluorene nucleus (see table, p. 2851), and by reaction with phosphoric acid–potassium iodide to give a product having the iodine content required for 9 : 9-di-2′-iodoethylfluorene (III).



(I) (II)



(III)

When vinyl chloride or bromide is heated with 9-fluorenylsodium under pressure the products are fluorene, acetylene, and the sodium halide. Failure of these condensations is not surprising since the initial ionisation of the halogen atom is prevented by the neighbouring double bond. The low yields with ethylene dihalides may well be caused by dehydrohalogenation to vinyl halides with the formation of fluorene and sodium chloride.

EXPERIMENTAL.

Ultra-violet absorption spectra were determined in absolute ethanol, with a Hilger " Uvispek " spectrophotometer. We are indebted to Mr. W. G. Wilman for the measurements.

The fluorene (North Thames Gas Board) was recrystallised from light petroleum. The sodamide was purchased as a powder from Messrs. May and Baker Ltd. All m. p.s are uncorrected.

9-*Fluorenylsodium.*—Fluorene (183 g.), powdered sodamide (39 g.), and decahydronaphthalene (dried over sodium) (400 c.c.) were heated at the b. p. for 4 hours, with stirring, in an atmosphere of nitrogen. The hot solution was filtered and the brownish-yellow 9-fluorenylsodium (200 g.) washed with hot decahydronaphthalene and finally with hot light petroleum (b. p. 100—120°) (Found : Na, 12·3. Calc. for $C_{13}H_9Na$: Na, 12·2%).

9-*Methylfluorene.*—(*a*) 9-Fluorenylsodium (100 g.), methyl iodide (150 c.c.), and light petroleum (b. p. 40—60°) (200 c.c.) were refluxed for 12 hours. The product was filtered to remove the sodium iodide which was formed in quantitative amount, and the filtrate evaporated on a water-bath to recover the unchanged methyl iodide, finally under reduced pressure. The oily residue was fractionated *in vacuo*. The main fraction, b. p. 160—170°/24 mm. (85·1 g.), solidified on storage and crystallised from light petroleum (b. p. 40—60°) as prisms, m. p. 45—47° (Found : C, 92·7; H, 6·9%; *M*, 179. Calc. for $C_{14}H_{12}$: C, 93·3; H, 6·7%; *M*, 180).

(*b*) 9-Fluorenylsodium (65 g.), methyl sulphate (80 c.c.), and benzene (200 c.c.) were kept overnight at room temperature and then filtered from sodium methyl sulphate (quantitative amount), and the filtrate was refluxed on a water-bath for 2 hours with sodium hydroxide solution (40%; 120 c.c.). The benzene layer was washed with water, dilute hydrochloric acid, and finally sodium carbonate solution. Evaporation of the dried benzene solution left a red oil which solidified on cooling. 9-Methylfluorene, crystallised as above, had m. p. 45—46° (49 g.).

9-*Ethylfluorene.*—(*a*) 9-Fluorenylsodium (188 g.), ethyl bromide (200 c.c.), and light petroleum (b. p. 40—60°; 200 c.c.) were refluxed for 20 hours, and the product was filtered. The filtrate was evaporated and the oily residue distilled under reduced pressure. The fraction boiling at 180—200°/14 mm. (153 g.) was cooled in a refrigerator for 2 days and deposited 10 g. of fluorene which were removed by filtration. The filtrate, after distillation at 135° in superheated steam, was fractionated in a vacuum through a column of 20 theoretical plates. A colourless oil (112 g.) distilled at 156—158°/12·5 mm. and had n_D^{25} 1·6135 (Found : C, 92·55; H, 7·2%; *M*, 195. Calc. for $C_{15}H_{14}$: C, 92·8; H, 7·2%; *M*, 194). The structure of this compound was confirmed by its oxidation with lead oxide to 9-ethylidenefluorene, and to acetaldehyde and fluorenone with sodium dichromate in acetic acid.

(*b*) 9-Fluorenylsodium (65 g.), ethyl sulphate (80 c.c.), and benzene (200 c.c.) were kept overnight at room temperature. The product was filtered to remove the sodium ethyl sulphate, and the filtrate evaporated on a water-bath at reduced pressure. The residual oil, fractionated *in vacuo*, gave 9-ethylfluorene, b. p. 163—166°/15 mm. (61 g.) (Found : C, 92·6; H, 7·2%).

9-*Ethylfluorenyl* 9-*Hydroperoxide.*—On storage in daylight, with access to air, 9-ethylfluorene was gradually converted into solid 9-*ethylfluorenyl* 9-*hydroperoxide* (approx. 20% in 6 months). This was precipitated free from unchanged 9-ethylfluorene by addition of light petroleum (b. p. 40—60°); it crystallised from benzene as prisms, m. p. 106·5—107·5° (Found: C, 79·25; H, 6·3; peroxide-O, 7·3. $C_{15}H_{14}O_2$ requires C, 79·5; H, 6·2; peroxide-O, 7·1%). (Peroxide-oxygen was determined by titration of the iodine liberated from potassium iodide in methanol-acetic acid with 0·1N-sodium thiosulphate). On reduction with potassium iodide in methanol, iodine was liberated and 9-ethylfluorenol, m. p. 101°, was formed.

9-*Allylfluorene.*—9-Fluorenylsodium (60 g.) and allyl chloride (200 c.c.) were refluxed for 2 hours, then cooled, and the sodium chloride filtered off. The filtrate was evaporated on the water-bath to yield crude 9-allylfluorene as a dark oil (67 g.), which was fractionated through a packed column as above. A small quantity of fluorene and a main fraction (62·3 g.) of 9-allylfluorene, b. p. 154—158°/11 mm., n_D^{25} 1·6165, were obtained (Found : C, 93·1; H, 6·9%; *M*, 207. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%; *M*, 206). Oxidation with sodium dichromate in acetic acid yielded fluorenone.

9-*Benzylfluorene.*—9-Fluorenylsodium (100 g.), benzyl chloride (200 c.c.), and light petroleum (b. p. 60—80°; 200 c.c.) were refluxed for 20 hours and then cooled; water was added to dissolve the sodium chloride, and benzene added to dissolve the benzylfluorene which is not very soluble in light petroleum. The organic layer was dried and evaporated to dryness under reduced pressure. The residue, crystallised from benzene, gave prisms (75·3 g.), m. p. 135° (Found : C, 93·9; H, 6·3%; *M*, 248. Calc. for $C_{20}H_{16}$; C, 93·75; H, 6·25%; *M*, 256).

9-2′-*Hydroxyethylfluorene.*—9-Fluorenylsodium (188 g.), ethylene chlorohydrin (400 c.c.), and light petroleum (b. p. 60—80°; 400 c.c.) were refluxed for 20 hours, and the cooled solution diluted with an equal volume of water and filtered to separate precipitated fluorene. The filtrate was diluted with a large excess of water, and the solid crude 9-2′-*hydroxyethylfluorene* was filtered off (45 g.). The filtrate was separated into an aqueous and an organic layer; the latter on evaporation yielded a further quantity of fluorene (total 110 g.). 9-2′-Hydroxyethylfluorene, crystallised from light petroleum (b. p. 60—80°) and then from benzene, formed needles, m. p. 101° (43 g.) (Found : C, 85·3; H, 6·7%; *M*, 216. $C_{15}H_{14}O$ requires C, 85·5; H, 6·65%; *M*, 210). Von Braun and Anton (*Ber.*, 1929, **62**, 145), by the Ladenburg reduction of ethyl fluorenylacetate, obtained a compound as a " thick uncrystallisable oil " which they regarded as 9-2′-hydroxyethylfluorene.

s-*Di*-9-*fluorenylethane.*—9-Fluorenylsodium (56 g.) was heated under reflux with ethylene dibromide (200 c.c.) for 6 hours and, after filtration, the reaction mixture was freed from unchanged ethylene dibromide by evaporation *in vacuo*. When the oily residue was diluted with light petroleum (b. p.

100—120°) a white solid (14 g.) was precipitated. On recrystallising this from benzene, *s*-di-9-fluorenylethane was obtained as prisms, m. p. 226° (Found : C, 93·6; H, 6·1. Calc. for $C_{28}H_{22}$: C, 93·75; H, 6·1%).

9-2′-*Chloroethylfluorene*.—Ethylene dichloride (400 c.c.) and 9-fluorenylsodium (110 g.) were refluxed for 17 hours, the mixture, when cool, was filtered, and the excess of ethylene dichloride evaporated on the water-bath at 15 mm. Crude 9-2′-*chloroethylfluorene*, obtained as a brown oil (118 g.), was purified by vacuum-distillation, to give unchanged fluorene (53 g.) and a fraction, b. p. 135—146°/2 mm. (Found : Cl, 11%). Further purification was difficult but freezing and recrystallisation several times from light petroleum (b. p. 40—60°) gave a pure product as prisms, m. p. 41—41·5° (Found : C, 78·65; H, 5·7; Cl, 15·4. $C_{15}H_{13}Cl$ requires C, 78·6; H, 5·7; Cl, 15·5%).

2-*Chloroethyl* 2-9′-*Fluorenylethyl Ether*.—9-Fluorenylsodium (110 g.) and 2 : 2′-dichlorodiethyl ether (400 c.c.) were refluxed for 6 hours, and the sodium chloride produced was filtered off from the hot solution. Excess of dichlorodiethyl ether was removed from the filtrate by vacuum-distillation and the residue, a viscous oil (142 g.), purified by vacuum-fractionation. The 2-*chloroethyl* 2-9′-*fluorenylethyl ether* was finally obtained as a pale yellow oil, b. p. 197—199°/7·5 mm. (83 g.) (Found : Cl, 12·9%; *M*, 270. $C_{17}H_{17}OCl$ requires Cl, 13·0%; *M*, 272·5).

Fluorene-9-spiro-4′-*tetrahydropyran*.—2-Chloroethyl 2-9′-fluorenylethyl ether (5 g.) was heated with solid potassium hydroxide (1·5 g.) for 4 minutes at 270°. The solid product was washed with water and crystallised from propanol; it formed flat needles, m. p. 201° (4·1 g.), of *fluorene*-9-spiro-4′-*tetrahydropyran* (Found: C, 86·3; H, 6·8%; *M*, 232. $C_{17}H_{16}O$ requires C, 86·3; H, 6·8%; *M*, 236). Absorption spectra of this and the following compound, and of fluorene, are recorded in the table.

Fluorene	λ, Å	2260 *	2610	2885	3000
	log ε	3·86	4·24	3·78	3·94
Fluorene-9-*spiro*-4′-tetrahydropyran	λ, Å	2280	2670	2900	3010
	log ε	3·78	4·24	3·77	3·94
9 : 9-Di-2′-iodoethylfluorene	λ, Å	2300	2680	2910	3030
	log ε	3·91	4·23	3·74	3·88

* Inflection.

9 : 9-*Di*-2′-*iodoethylfluorene*.—Fluorene-9-*spiro*-4′-tetrahydropyran (1·3 g.) was added to potassium iodide (17·6 g.), 89% phosphoric acid (7·2 ml.), and phosphoric oxide (3·5 g.). The mixture was heated for 3 hours in an oil-bath, with stirring, under reflux, the temperature being raised from 80° to 130°, and kept at 95—100° for approx. 1½ hours. The cooled mixture was diluted with water and extracted with ether. The ethereal layer was decolourised with sodium thiosulphate solution, washed with sodium chloride solution and water, and dried ($MgSO_4$). On evaporation of the ethereal solution, an oil remained which was dissolved in benzene and chromatographed through alumina (8″ × ½″) which was eluted with benzene. Unchanged spiran was retained more strongly than was the iodo-compound, giving a fairly sharp separation. Final traces of the spiran were washed from the column with chloroform. 1·56 g. of iodo-compound (m. p. 174—178°) were obtained and 0·51 g. of unchanged starting material. The 9 : 9-*di*-2′-*iodoethylfluorene*, on recrystallisation from light petroleum (b. p. 80—100°), had m. p. 181·5—182° (prisms) (Found : C, 42·7; H, 3·4; I, 53·3%; *M*, 479. $C_{17}H_{16}I_2$ requires C, 43·0; H, 3·4; I, 53·6%; *M*, 474).

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