163. *Alkylation of the Aromatic Nucleus. Part VI.* Fluorene.*

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When fluorene is alkylated by thermal decomposition of ethyl, isopropyl, or s-butyl benzenesulphonate in a moderate excess of fluorene, substitution occurs in the nucleus at all the possible positions. The proportions of the isomeric alkylfluorenes in each alkylation product have been determined and these values compared with those obtained by other methods of alkylation.

IN this work we examined the alkylation of fluorene by the thermal decomposition of ethyl, isopropyl, and s-butyl benzenesulphonate in fluorene, especially with regard to the distribution of the alkyl group in the nucleus, and we compared these results with those of other substitution reactions of fluorene. The results are summarised in the Table, together with alkylations by the alcohol or alkyl halide with aluminium chloride as catalyst. No precise figures can be given for experiments 7—10, for in these some dialkylfluorenes were also formed which could not be separated sufficiently cleanly.

Alkylation of fluorene.

Method	Temp.	Proportion of isomers in product (%)			
		1-	2-	3-	4-
1. $Ph{\cdot}SO_3Et$	250°	8	37	22	33
2. $Ph{\cdot}SO_3Pr^i$	150	10	40	31	19
3. $Ph{\cdot}SO_3Bu^s$	140	7	45	25	23
4. $EtBr-AlCl_3-CS_2$	46	14	31	50	5
5. $Pr^iOH-AlCl_3-CS_2$	20	15	30	55	0
6. $Bu^sOH-AlCl_3-CS_2$	20	10	36	54	0
7. $Bu^sOH-AlCl_3-PhNO_2$	20	2-Alkylfluorenes as main product; smaller amounts of 1-, 3-, and 4-isomers.			
8. $Bu^sBr-FeCl_3-CS_2$	46				
9. $Bu^sOH-BF_3-PhNO_2$	20				
10. $Pr^iOH-BF_3-PhNO_2$	20				

It is significant that in the thermal alkylation there is a considerable proportion of 3- and 4-isomers. These values, within the limit of errors of estimation (2—3%), are true values and represent the relative reactivities of these positions towards alkylation. The most complete figures for other substitutions are those of Dewar and Urch[1] for nitration in acetic anhydride who find 63%, 3%, and 34% of 2-, 3-, and 4-nitration, respectively, with no substitution in the 1-position. By contrast Anantakrishnan and Hughes[2] report 95% nitration in the 2-position. Only qualitative information is available

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* Part V, *J.*, 1959, 2520.

[1] Dewar and Urch, *J.*, 1958, 3081.

[2] Anantakrishnan and Hughes, *J.*, 1935, 1607.

for nuclear halogenation and sulphonation but in these it is agreed that substitution is predominantly in the 2-position.

It is evident that alkylation does not follow the usual pattern of substitution but appears to approximate to a random rather than a directed substitution. In this it resembles the alkylation of the alkylbenzenes.

EXPERIMENTAL

Alkylation of Fluorene.—(a) *By thermal decomposition of alkyl benzenesulphonates.* The ester was heated with a moderate excess of fluorene at a temperature sufficient to bring about decomposition of the ester. When the reaction was finished, the melt was cooled and taken up in ether, and the free benzenesulphonic acid removed by washing the solution with aqueous alkali. The dried ether solution was then distilled to separate the alkylfluorenes from the excess of fluorene and solvent.

From ethyl benzenesulphonate (42 g.) and fluorene (80 g.) at 250°, a mixture of ethylfluorenes (5 g.), b. p. 176—184°/13 mm., n_D^{20} 1·6089 (Found: C, 92·5; H, 7·4. Calc. for $C_{15}H_{14}$: C, 92·7; H, 7·3%), was obtained. Reaction is complete within 1 min.

Isopropyl benzenesulphonate (51 g.) and fluorene (80 g.) at 140° for 1·5 hours gave isopropylfluorenes (11 g.), b. p. 175—185°/10 mm., n_D^{19} 1·6110 (Found: C, 92·6; H, 7·6. Calc. for $C_{16}H_{16}$: C, 92·3; H, 7·7%).

s-Butyl benzenesulphonate (53 g.) and fluorene (83 g.) at 140° in 1 hr. gave s-butylfluorenes (19 g.), b. p. 192—210°/12 mm., n_D^{18} 1·6033 (Found: C, 92·1; H, 8·0. Calc. for $C_{17}H_{18}$: C, 91·8; H, 8·2%).

(b) *By reaction with boron trifluoride and the alcohol.* Boron trifluoride was passed slowly into a stirred suspension of fluorene (20 g.) and the alcohol (0·1 mole) in nitrobenzene (150 c.c.) at room temperature until saturated. The mixture was kept overnight, then poured into an excess of dilute alkali, and the product taken up in ether and distilled.

Isopropyl alcohol gave isopropylfluorenes (2·5 g.), b. p. 190—198°/13 mm., n_D^{20} 1·6063 (Found: C, 92·0; H, 7·8%), and di-isopropylfluorenes (1·5 g.), b. p. 210—220°/13 mm., n_D^{20} 1·5923 (Found: C, 91·2; H, 8·9. Calc. for $C_{19}H_{22}$: C, 91·1; H, 8·9%).

s-Butyl alcohol gave s-butylfluorenes (2·8 g.), b. p. 203—212°/13 mm., n_D^{20} 1·5981 (Found: C, 91·7; H, 8·5%), and di-s-butylfluorenes, b. p. 222—230°/13 mm., n_D^{20} 1·5805.

(c) *By using aluminium chloride.* Attempts to prepare ethylfluorenes by reaction of ethyl alcohol or bromide with fluorene and aluminium chloride in cold carbon disulphide failed.

Ethyl bromide (6·5 g.) was added slowly to a stirred mixture of fluorene (10 g.) and aluminium chloride (8 g.) in carbon disulphide. Ethylfluorenes were obtained, having b. p. 158—168°/10 mm., n_D^{18} 1·6168 (Found: C, 92·5; H, 7·5%).

Isopropyl alcohol (3·7 g.), fluorene (10 g.), and aluminium chloride (16 g.) in carbon disulphide at 0° in 6 hr. gave isopropylfluorene (7·5 g.), b. p. 162—182°/9 mm., n_D^{20} 1·6008 (Found: C, 92·2; H, 8·1%).

s-Butyl alcohol (4·4 g.), fluorene (10 g.), and aluminium chloride (16 g.) in carbon disulphide gave s-butylfluorenes, b. p. 179—190°/9 mm., n_D^{20} 1·5946 (Found: C, 91·5; H, 8·3%). Using nitrobenzene instead of carbon disulphide and the same quantities of reactants s-butyl alcohol gave s-butylfluorenes (5·5 g.), b. p. 180—214°/11 mm., n_D^{18} 1·5950 (Found: C, 91·8; H, 8·5%).

(d) *With ferric chloride.* Fluorene (44 g.), s-butyl bromide (27 g.), and ferric chloride (37 g.) in boiling carbon disulphide (200 g.) in 3 hr. gave s-butylfluorenes (3 g.), b. p. 203—208°/22 mm., n_D^{20} 1·6050 (Found: C, 91·7; H, 8·2%).

Isomerisation of Alkylfluorenes.—2-Ethylfluorene, heated with aluminium chloride in boiling carbon disulphide, gave a product identical with that obtained on reaction of fluorene with ethyl bromide and aluminium chloride in carbon disulphide (Table, No. 4).

s-Butylfluorenes, from a reaction of s-butyl alcohol and aluminium chloride in nitrobenzene (Table, No. 7), when heated with aluminium chloride in carbon disulphide, gave a product having the same composition as the product from s-butyl alcohol and fluorene in carbon disulphide with aluminium chloride (Table, No. 6).

Attempts to isomerise the mixed s-butylfluorenes from s-butyl alcohol, fluorene, and aluminium chloride in carbon disulphide (Table, No. 6) by heating them with benzenesulphonic acid at 150° for 3 hr. were unsuccessful.

Analysis of the Products of Alkylation.—The composition of the product of each alkylation of fluorene was determined from the infrared spectrum by base-line technique.[3] All the alkylfluorenes have characteristic bands in the range 12—13 μ, and the following were used for the calculations: 1-alkylfluorenes, 12·55s; 2-ethyl- and 2-isopropyl-fluorene, 12·1vs; 2-s-butylfluorene, 12·1s; 3-ethyl- and 3-s-butyl-fluorenes 12·25vs; 4-alkylfluorenes 12·75s.

Preparations.—(a) 1-*Alkylfluorenes.* 1-Acetylfluorene, used as the starting point, was obtained in 61% yield by reaction of dimethylcadmium in benzene with fluorene-1-carbonyl chloride; it had m. p. 89—90° [after sublimation under reduced pressure and crystallisation from light petroleum (b. p. 80—100°)] (Found: C, 86·3; H, 5·8. Calc. for $C_{15}H_{12}O$: C, 86·5; H, 5·8%) and gave a 2,4-dinitrophenylhydrazone, m. p. 255—260° (decomp.).

Fluorene-1-carboxylic acid was prepared by heating 9-oxofluorene-1-carboxylic acid (28 g.) with 99% hydrazine hydrate (15 c.c.) and sodium hydroxide (18 g.) in diethylene glycol (220 c.c.) at 140° for 3 hr. and then at 205° for 2 hr. The product (16 g.), sublimed at 15 mm. and crystallised from acetone, had m. p. 244—245° (Fieser and Seligmann give m. p. 243—246°) (Found: C, 80·1; H, 4·7. Calc. for $C_{14}H_{10}O_2$: C, 80·0; H, 4·8%).

Preparation of the acid chloride has been reported by Fieser and Seligman[4] but they do not describe their product. The following method, due to Fieser and Peters,[5] permitted the isolation of the acid chloride. To the acid (15 g.), suspended in dry ether (150 c.c.), was added thionyl chloride (50 c.c.) and 5 drops of pyridine. After 8 hours' refluxing, the suspended matter was collected and the filtrate evaporated under reduced pressure. The residual acid chloride separated from light petroleum (b. p. 80—100°) as yellow crystals, m. p. 105—108° (13·4 g.). A sample purified by sublimation under reduced pressure was white and melted at 108—110°. The m. p. fell on storage over silica gel in a vacuum-desiccator for some days and the product became sticky. No satisfactory analysis could be obtained (Found: C, 70·7; H, 4·2; Cl, 13·3. Calc. for $C_{14}H_9ClO$: C, 73·5; H, 4·0; Cl, 15·5%).

1-*Ethylfluorene.* 1-Acetylfluorene (2·5 g.), sodium hydroxide (2·5 g.), and hydrazine hydrate (1·5 c.c.) in diethylene glycol (75 c.c.) were heated at 140° for 1 hr., and then, after removal of water and volatile matter at 205° for 3 hr. Ethylfluorene (2·0 g.), precipitated by pouring the residue into an excess of dilute acid, had m. p. 48—49° after sublimation and crystallisation from methanol (Found: C, 92·8; H, 7·2. Calc. for $C_{15}H_{14}$: C, 92·7; H, 7·3%).

1-*Isopropylfluorene.* A solution of 1-acetylfluorene (2·5 g.) in ether was added to methylmagnesium iodide [from methyl iodide (4·5 g.) and magnesium (0·75 g.)] in ether. After 1 hour's heating the product was isolated and heated with acetic anhydride for 2 hr., to give 1-*isopropenylfluorene* as a yellow oil (Found: C, 93·1; H, 6·7. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%). This was hydrogenated in ethanol over palladised charcoal at 3 atm., to give 1-isopropylfluorene, b. p. 105—108°/0·1 mm., m. p. 46—47° (from aqueous methanol) (Found: C, 92·3; H, 7·6. Calc. for $C_{16}H_{16}$: C, 92·3; H, 7·7%).

1-s-Butylfluorene, b. p. 114—116°/0·25 mm., n_D^{17} 1·6049 (Found: C, 91·6; H, 8·5. Calc. for $C_{17}H_{18}$: C, 91·8; H, 8·2%), was obtained by similar hydrogenation in ethanol of 1-1 *methylpropenylfluorene*, b. p. 110—125°/0·05 mm. (Found: C, 91·3; H, 7·3. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%).

(b) 2-*Alkylfluorenes.* 2-Ethyl-, 2-isopropyl, and 2-s-butylfluorene[6] were prepared from 2-acetylfluorene by the methods described above for 1-alkylfluorenes, with the following properties:

2-Ethylfluorene, plates, m. p. 99—100°, from light petroleum (b. p. 60—80°) and then ethanol (Found: C, 92·7; H, 7·4. Calc. for $C_{15}H_{14}$: C, 92·7; H, 7·3%) [Campbell and Wang[7] give m. p. 81—82°; Sawicki[8] gives m. p. 99·5—100°] [picrate, orange (from ethanol), m. p. 68—70°].

2-*Isopropylfluorene*, m. p. 81—82° (Found: C, 92·2; H, 7·5%; *M*, 197. $C_{16}H_{16}$ requires C, 92·3; H, 7·7%; *M*, 208] (picrate, orange, m. p. 104—109°).

2-*Isopropenylfluorene*, m. p. 156—157°, from light petroleum (b. p. 80—100°) (Found: C, 93·1; H, 6·7. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%).

2-s-Butylfluorene, m. p. 46—47° (lit.,[9] m. p. 47—48°) (Found: C, 91·7; H, 8·3. Calc. for $C_{17}H_{18}$: C, 91·8; H, 8·2%).

[3] Heigl, Bell, and White, *Ind. Eng. Chem., Analyt. Edn.*, 1947, **19**, 293.

[4] Fieser and Seligman, *J. Amer. Chem. Soc.*, 1935, **57**, 2175.

[5] Fieser and Peters, *J. Amer. Chem. Soc.*, 1932, **54**, 4376.

[6] Bachmann and Sheehan, *J. Amer. Chem. Soc.*, 1940, **62**, 2688.

[7] Campbell and Wang, *J.*, 1949, 1514.

[8] Sawicki, *J. Amer. Chem. Soc.*, 1954, **76**, 2269.

[9] Hickinbottom and Rule, *J.*, 1959, 2509.

(c) 3-*Alkylfluorenes.* Similar reactions gave 3-*ethylfluorene,* flakes, m. p. 43—44°, from methanol (Found: C, 92·6; H, 7·1. $C_{15}H_{14}$ requires C, 92·7; H, 7·3%), and 3-*s-butylfluorene,* b. p. 111—112°/0·14 mm., n_D^{20} 1·5993 (Found: C, 92·0; H, 8·1. $C_{17}H_{18}$ requires C, 91·8; H 8·2%). Attempts to prepare 3-isopropylfluorene by hydrogenation of 3-isopropenylfluorene gave a product, m. p. 220—224° (decomp.), presumably a dimer (Found: C, 91·3; H, 6·8%; *M*, 373. Calc. for $C_{16}H_{16}$: C, 92·3; H, 7·7%; *M*, 208).

3-Acetylfluorene required for these preparations was obtained as needles, m. p. 86—87° (Found: C, 86·4; H, 5·7. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%) [2,4-dinitrophenylhydrazone, scarlet, m. p. 247° (decomp.)], by reaction of fluorene-3-carbonyl chloride with dimethylcadmium in benzene. The chloride prepared from the acid by the method described above for fluorene-1-carboxylic acid melts at 123—125° after sublimation under reduced pressure and gives the *amide,* m. p. 250—252° (Found: C, 80·2; H, 5·2; N, 6·9. $C_{14}H_{11}NO$ requires C, 80·4; H, 5·3; N, 6·7%).

Fluorene-3-carboxylic acid, m. p. 232—235°, after sublimation (Found: C, 79·8; H, 4·7. Calc. for $C_{14}H_{10}O_2$: C, 80·0; H, 4·8%), is conveniently prepared from 9-oxofluorene-3-carboxylic acid by a Wolff–Kishner reduction. Morrison [10] gives m. p. 229·5—231·5°; Campbell and Stafford [11] give m. p. 231°.

(d) 4-*Alkylfluorenes.* 4-*Ethylfluorene,* needles (from ethanol), m. p. 41—42° (Found: C, 92·5; H, 7·2. $C_{15}H_{14}$ requires C, 92·7; H, 7·3%) (no picrate), 4-*isopropylfluorene,* b. p. 101—105°/0·1 mm., n_D^{20} 1·6134 (Found: C, 92·3; H, 718. $C_{16}H_{16}$ requires C, 92·3; H, 7·7%), and 4-*s-butylfluorene,* b. p. 98—106°/0·05 mm., n_D^{17} 1·6081 (Found: C, 92·2; H, 8·1. $C_{17}H_{18}$ requires C, 91·8; H, 8·2%), were similarly prepared.

4-*Acetylfluorene* was prepared from fluorene-4-carbonyl chloride by reaction with dimethylcadmium in benzene; it had m. p. 62—63° (Found: C, 86·5; H, 5·8. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%) and gave an orange 2,4-dinitrophenylhydrazone, m. p. 230—232°.

Fluorene-4-carboxylic acid, m. p. 193—194° (Found: C, 79·6; H, 4·9. Calc. for $C_{14}H_{10}O_2$, C, 80·0; H, 4·8%), is conveniently obtained by the Wolff–Kishner reduction of fluorenone-4-carboxylic acid. (Graebe [12] gives m. p. 175°; Suzuki [13] m. p. 189—191°).

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