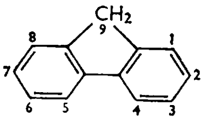
185. *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part XII.*[1] *Products of Chlorination of Fluorene in Acetic Acid.*

By G. H. BEAVEN, P. B. D. DE LA MARE, E. A. JOHNSON, and N. V. KLASSEN.

The products of reaction of fluorene with chlorine in acetic acid have been examined, particularly by vapour-phase chromatography and isotopic dilution. Despite earlier reports, 2-chlorofluorene constitutes no more than 69% of the product. 4-Chlorofluorene is formed to the extent of 9%, and most of the remainder consists of addition products.


(I)

FLUORENE (I) is planar.[2] Although the two aromatic rings are not exactly collinear, the π-electron system of one should readily be able to release electrons conjugatively to the other. As a consequence, it should be possible to regard it as a substituted biphenyl in which the reactivity to electrophiles is modified (*a*) by the CH_2Ar group, which should have no very large effect at positions 1 and 3,[3] but probably would somewhat deactivate the 2- and the 4-position, and (*b*) by the planarity. If it is assumed[4,5] that repulsions between the 2- and the 2'-hydrogen atom in biphenyl provide a barrier to rotation of a few kcal. per mole, the planarity of fluorene should considerably enhance its reactivity in the 2- and the 4-position.

The orientation and reactivity for nitration of fluorene have been examined by Dewar and Urch.[6] They record that the compound is considerably more reactive than biphenyl, and that the main products are 2- and 4-nitrofluorene (69% and 29%, respectively).

Fluorene is also more reactive than biphenyl in molecular chlorination in acetic acid.[4] Surprisingly, however, 2-chlorofluorene is the only product of monochlorination reported in a variety of solvents, and dichlorination is said to give 2,7-dichlorofluorene.[7] Re-examination of the problem has led to the conclusion that the 2-isomer is by no means the only product of monochlorination of fluorene in acetic acid.

EXPERIMENTAL

Materials.—Most of the present experiments were done with fluorene, m. p. 116°, which had been recrystallised from ethanol. Vapour-phase chromatography did not show the presence of a major impurity. In the product, however, there was detected a small amount (*ca.* 3%) of a dichloro-product, m. p. 135°, not derived from fluorene. This material was still

---

[1] Part XI, de la Mare, Klassen, and Koenigsberger, *J.*, 1961, 5285.
[2] Burns and Iball, *Nature*, 1954, **173**, 638; Brown and Bortner, *Acta Cryst.*, 1954, **7**, 139.
[3] Swindale, Swedlund, and Robertson, *J.*, 1950, 812.
[4] de la Mare, Hall, Harris, and Hassan, *Chem. and Ind.*, 1958, 1086.
[5] Howlett, *J.*, 1960, 1055.
[6] Dewar and Urch, *J.*, 1958, 3079.
[7] Buffle, *Helv. Chim. Acta*, 1932, **15**, 1483.

present in the product of chlorination of fluorene which had been purified by recrystallising the picrate, m. p. 80·5—81°. It was absent, however, from the product of chlorination of fluorene which had been prepared by reduction of fluorenone, itself prepared by cyclisation of diphenic acid. It seems, therefore, that some of our early results refer to specimens which contained up to about 3 mol. % of a reactive impurity, now identified [8] as 5,6-benzindane, which consumed about 6 mol. % of the chlorine. The later experiments, however, were made with purer samples of fluorene and confirmed the details of the earlier experiments.

2-Chlorofluorene was prepared from commercial 2-aminofluorene, m. p. 131°. As described by earlier investigators,[9] the diazonium salt was isolated and purified by precipitation with ether from ethanol solution; decomposition with cuprous chloride then gave 2-chlorofluorene, which, after several crystallisations, had m. p. 96·5°. We were unsuccessful in repeated attempts to isolate 2-chlorofluorene in adequate quantities from fluorene and chlorine after reaction in various proportions and in various solvents; in our experience (in contrast with that of Buffle [7]), this product was always of low m. p. and, though the impurities could be gradually removed by crystallisation or by fractional sublimation, the losses were so great as to make the method impracticable. In our hands the method described by Streitwieser [10] failed also.

4-Chlorofluorene. This was prepared from 6-chloro-*o*-toluidine ($NH_2 = 1$) by way of 2-chloro-6-methylbiphenyl and 4-chlorofluorenone.

(*a*) 6-Chloro-*o*-toluidine (20 g.) and pentyl nitrate (27 g.) were refluxed together in benzene [11] (2 l.) for 8 hr., whereafter red fumes ceased to appear (they did not reappear on addition of acetic acid). The benzene was distilled off; the semisolid residue was stirred with light petroleum (b. p. 60—80°), collected, washed with light petroleum, and appeared to be *7-chloroindazole* (10·2 g., 47%), m. p. 136·5—137·5° after sublimation at 20 mm. and recrystallisation from benzene (Found: C, 55·0; H, 3·4; N, 17·9; Cl, 22·9. $C_7H_5ClN_2$ requires C, 55·1; H, 3·3; N, 18·4; Cl, 23·2%). The ultraviolet absorption spectrum in ethanol solution showed the characteristic pair of band systems [12] of almost equal intensity with principal maxima at 3025, 2905, and at 2610, 2530 Å. In 0·05M-hydrochloric acid the spectrum was not significantly changed, but in 0·5M-sodium hydroxide a single broader band appeared, with a maximum at 3030 Å. The compound is therefore practically non-basic but shows feebly acidic properties. It did not appear to form a stable picrate, but with acetic anhydride gave an *acetyl derivative*, m. p. 100—100·7° (from ethanol) (Found: C, 55·7; H, 3·7; N, 14·1; Cl, 18·2. $C_9H_7ClN_2O$ requires C, 55·6; H, 3·6; N, 14·4; Cl, 18·2%).

The light-petroleum washings were extracted once with M-alkali which removed the very small amount of 7-chloroindazole remaining; they were then concentrated, and distilled at 20 mm. The product (3·4 g.) was found by gas–liquid chromatography to be a mixture of the required 2-chloro-6-methylbiphenyl (*ca.* 70%) and biphenyl (*ca.* 30%). A sample of the former (yield 8%) isolated by this means had ultraviolet absorption almost identical with that of 2,6-dimethylbiphenyl.[13] No attempt was made to separate the bulk of the product; the mixture with biphenyl was used for the next stage.

(*b*) For the conversion of 2-chloro-6-methylbiphenyl into 4-chlorofluorene, the route used by Weisburger and Weisburger [14] for the preparation of fluorene-3-carboxylic acid was followed, without significant variations. From about 2 g. of chloromethylbiphenyl were obtained 650 mg. (28%) of *6-chlorobiphenyl-2-carboxylic acid*, m. p. 154·5—155·5° after vacuum-sublimation and crystallisation from benzene (Found: C, 67·1; H, 4·1; Cl, 15·1. $C_{13}H_9ClO_2$ requires C, 67·1; H, 3·9; Cl, 15·2%).

From 400 mg. of this acid were obtained by cyclisation 315 mg. (85%) of 4-chlorofluorenone, m. p. 148·5—149·5° (lit.,[15] 147—148°) after sublimation *in vacuo*.

From 215 mg. of 4-chlorofluorenone were obtained by reduction 102 mg. (51%) of *4-chlorofluorene*, m. p. 56—57° after sublimation *in vacuo* and recrystallisation from methanol (Found: C, 77·3; H, 4·7; Cl, 17·4. $C_{13}H_9Cl$ requires C, 77·8; H, 4·5; Cl, 17·7%).

---

[8] Johnson, following paper.

[9] Chanussot, *Anales Asoc. quím. argentina*, 1927, **15**, 216; *Bull. Soc. chim. France*, 1927, 1625, 1626; Courtot, *Ann. Chim.*, 1930, **14**, 5; cf. Courtot and Vignati, *Compt. rend.*, 1927, **184**, 607.

[10] Streitwieser, *J. Amer. Chem. Soc.*, 1944, **66**, 2127.

[11] Hwang, *Acta Chim. Sinica*, 1959, **33**, 171.

[12] Rousseau and Lindwall, *J. Amer. Chem. Soc.*, 1950, **72**, 3047.

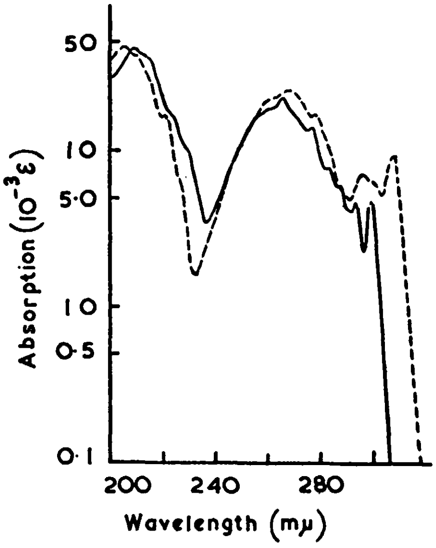
[13] Beaven and Johnson, *Spectrochim. Acta*, 1959, **14**, 78.

[14] Weisburger and Weisburger, *J. Org. Chem.*, 1958, **23**, 1193.

[15] Campaigne and Reid, *J. Org. Chem.*, 1947, **12**, 807.

The ultraviolet spectra of 2- and 4-chlorofluorene are shown in the Figure. They are sufficiently different to be used for analysis of mixtures. Infrared spectra of these and related compounds are recorded in Table 1.

Other materials. 9-Chlorofluorene was prepared from fluorenone by reduction to fluoren-9-ol with lithium aluminium hydride,[16] followed by chlorination with phosphorus pentachloride in benzene.[17] When chromatographed on alumina and recrystallised from ethanol, it had m. p. 91·5° (lit.,[17] 92°).



Ultraviolet spectra of (– – –) 2- and (——) 4- chlorofluorene in light petroleum (b. p. 100—120°).

TABLE 1.

Infrared absorption bands * (cm.$^{-1}$; range 645—1300 cm.$^{-1}$) of some derivatives of fluorene.

Un-subst.	2-Chloro-	4-Chloro-	9-Chloro-	2,7-Dichloro-
			645m	
			668w	668w
		683m	678m	676w
694w		692w		689w
722sh		726w		725w
739sh	728vs		734s	
	749w		749m	
	762vs	769s	799w	
	821s	823w		811s
			833w	833w
				855m
862vw	857w			
		856m		
	866m		861m	
	875s	893s	872w	
957w	952m	946m	935w	930m
		960m		951w
	1006m	999m	1002w	1006w
		1011w		
		1020m	1024w	
	1073s	1064m		1054m
	1098m	1098w		1117w
	1151m	1133s		
	1168m			1163m
	1181m	1166s		
1190w	1193m	1190m	1199m	
	1230m	1221w		1224w
	1271m	1250w		1274w
	1293m	1294m		1290w

* For Nujol mull, except for 4-chlorofluorene which was measured as a melt between rock-salt plates and had additional bands at 1309w, 1389s, 1422s, 1437s, 1477m, and 1563 cm.$^{-1}$.

2,7-Dichlorofluorene was prepared by chlorination of fluorene in acetic acid. The product was precipitated by adding water to the reaction mixture and, recrystallised from n-hexane, had m. p. 126° (lit.,[9] 128°).

2-Chlorofluorenone, prepared by heating 2-chlorofluorene with potassium dichromate and acetic acid under reflux for 4 hr., had m. p. 125°.

[16] Hochstein, *J. Amer. Chem. Soc.*, 1949, **71**, 305.
[17] Werner and Grob, *Ber.*, 1904, **37**, 2887.

Radioactive chlorine was obtained by allowing chlorine to exchange with Li^{36}Cl in acetic acid; the solution of chlorine was distilled *in vacuo*.

Products of Chlorination.—(a) *2-Chlorofluorene; analysis by isotopic dilution.* Fluorene (0·07M) was allowed to react with ^{36}Cl-labelled chlorine (0·008M) in acetic acid (90 ml.) at 25°. After all the chlorine had disappeared, 2-chlorofluorene (5·4 g.) was added to the mixture, which was then oxidised with potassium dichromate in boiling acetic acid and poured into water; the solid was filtered off, dissolved in ether, and passed through an alumina column. After removal of ether, the eluted material was repeatedly crystallised from ethanol. The final product, m. p. 125°, had a radioactivity which on comparison with that of the original chlorine (converted into lithium chloride for measurement of radioactivity) corresponded with the formation of 68% of 2-chlorofluorene. A second experiment, in which a larger excess of fluorene was used, gave a value of 70%. (Allowance has been made for the fact that the specimen of fluorene used for these experiments was later found to contain *ca.* 3% of the reactive impurity described above.)

(b) *4-Chlorofluorene; analysis by vapour-phase chromatography.* The products from the chlorination of fluorene under various conditions were investigated by vapour-phase chromatography, Apiezon M and ethylene glycol adipate polyester at 200° being used as stationary phases. The principal peaks had retention volumes corresponding to fluorene, 2-chlorofluorene, and 2,7-dichlorofluorene, and their identities were confirmed by the ultraviolet spectra of recovered samples.

A number of minor components (total amount less than 1%) were observed. Their retention volumes relative to the major peaks differed for the two stationary phases, and screening by ultraviolet spectroscopy indicated that they were mostly fluorenones; they were not investigated further. The compound, m. p. 135°, discussed above, was also found in a number of the specimens. Besides 2-chlorofluorene, another monochlorofluorene was identified. By repeated chromatography on the packed columns we eventually separated a specimen sufficiently pure for determination of the infrared and ultraviolet spectra, which were identical with those of synthetic 4-chlorofluorene. The following are the retention volumes relative to fluorene on (i) Apiezon M and (ii) the polyester: 2-chlorofluorene 2·55, 2·52; 4-chlorofluorene 2·52, 2·32; 2,7-dichlorofluorene 6·50, 6·15; compound, m. p. 135°, 5·90, 3·22.

Separation of 4- from 2-chlorofluorene was ultimately found to be complete on a capillary polyester column (argon detector); measurements with this were made by courtesy of Dr. J. E. Lovelock, and it was found that the ratio of isomers determined by peak-areas was in good agreement with estimates made on the basis of the ultraviolet spectra. It seems likely, therefore, that no other isomeric monochlorofluorenes were present in significant amounts. Ultimately, for analysis, a complete mixed monochlorofluorene fraction (usually about 0·3—1·0 mg.) was collected from the effluent chromatograph gas-stream in an air-condenser. The material thus isolated was dissolved in light petroleum and diluted to give suitable absorbances at the wavelengths 3075, 2990, 2890, and 2320 Å, at which the molar absorptivities of the 2-isomer are, respectively, 9100, 6300, 5250, and 1600; and of the 4-isomer 75, 4750, 5250, and 7500. It is clear that the most satisfactory pair for analytical purposes would be the first and last of these wavelengths, but until measurements on the synthetic 4-chlorofluorene had shown that base-line corrections were small throughout the range (provided that an adequate fraction was collected) it was thought safest to work within the short wavelength ranges represented by the first pair of wavelengths listed, with the third as a check on the total quantity.

TABLE 2.

Products of reaction of chlorine with fluorene in acetic acid at 25°.

Expt.	Fluorene (M)	Cl_2 (M)	4-Chlorofluorene / 2-Chlorofluorene	Dichlorofluorene / 2-Chlorofluorene	Fluorene / 2-Chlorofluorene
(*a*)	0·29	0·10	0·130	0·019	2·94
(*b*)	0·58	0·10	0·130	0·011	7·91

Values for the ratio of 2-chlorofluorene to 4-chlorofluorene, determined in this way on products from reaction under various conditions, are given in Table 2. In this are included also estimates, from the gas-chromatographic results, of the amount of dichlorofluorenes produced under the same conditions, and of the proportion of fluorene recovered unchanged.

(c) *Possible formation of* 9-*chlorofluorene*. Fluorene (0·0600M) and ^{36}Cl-labelled chlorine (0·00515M) were allowed to react in acetic acid (40 ml.) at 25° in the dark. To the product was added non-labelled 9-chlorofluorene (2·12 g.). The organic material was recovered, and from it was obtained by a number of crystallisations a sample of 9-chlorofluorene, the radioactivity of which was very small and corresponded with the formation of not more than 0·0033 mole of 9-chlorofluorene from each mole of reacting chlorine.

(d) *Formation of adducts*. (i) Production of hydrogen chloride. In these experiments (cf. ref. 1) great care was taken to ensure that neither chlorine nor hydrogen chloride was lost by volatility. The following are the results; some higher values were discarded after it was discovered that some of the products are very easily decomposed if the mixture is not worked up cautiously:

ArH (M)	0·057	0·075	0·075	0·150
Cl_2 (M)	0·006	0·015	0·026	0·026
HCl/Cl_2 consumed	0·885	0·863	0·864	0·865

(ii) Thermal decomposition of the products of chlorination. The above results suggested that some addition accompanied the substitution, so the organic product from chlorination was sealed in a glass tube under a vacuum and heated to 220°. Fluorene and 2-chlorofluorene when so treated remained unchanged; the product became brown, and analysis of the product showed that 10 mol. % of the chlorine in the original sample had been converted into chloride ions. Replication gave the same result.

(iii) Alkaline decomposition of adducts. After fluorene (0·096M) had been allowed to react to completion with chlorine (0·0247M, 49·4 millimoles) in acetic acid, the organic product was isolated and its freedom from acid confirmed. Aliquot parts were then treated with an excess of standard alcoholic alkali. One was back-titrated with standard acid; the acid (hydrochloric plus acetic) liberated with alkali was thereby estimated to amount to 0·0052 millimole (21·2%, based on the chlorine consumed). Another was used for determination of chloride; the hydrochloride liberated with alkali was thereby estimated to amount to 0·0046 millimole (18·7%).

The total organic product and the organic material recovered after decomposition with alkali were analysed chromatographically for the presence of dichlorofluorenes. The ratio of di- to mono-chlorofluorene was found to be *ca.* 0·04 in both samples; the ultraviolet spectra of the recovered samples of dichlorofluorene showed that 2,7-dichlorofluorene did not form a major part of the dichlorofluorene fraction.

(iv) *Isolation of the acetoxy-containing adduct*. The hydrogen chloride produced in the reaction accounts for only 86·5% of the chlorine consumed; the discrepancy (13·5%) must represent the formation of adducts analogous to those formed in the chlorination of biphenyl.[18] Accordingly, an attempt was made to effect a separation chromatographically.

On silica gel, with light petroleum as eluant for the organic material, a by-product, monochlorofluorenes, and fluorene were first eluted, in that order. A relatively strongly adsorbed fraction was then eluted with mixtures of benzene and light petroleum. This was isolated as an oil, which seemed to be a mixture of acetoxy-chlorides, since it contained oxygen and had strong peaks in the infrared absorption spectrum in the region (1750 cm.$^{-1}$) expected for acetoxy-containing materials; it decomposed slowly, with loss of hydrogen chloride.

DISCUSSION

2-Chlorofluorene.—Contrary to Buffle's report,[7] 2-chlorofluorene is not the only monochlorofluorene produced in the reaction. Determination of the amount of this material from the ratio of fluorene to 2-chlorofluorene in the product of the reaction is complicated by the necessity of making allowance for the amount of chlorine used in forming adducts. After this allowance, the results given in Table 2 indicate that, in experiments (*a*) and (*b*), 68 and 62 mole %, respectively, of the chlorine reacted to form 2-chlorofluorene. The latter value should be the less certain, since the excess of fluorene was very large and correspondingly there was greater difficulty in recovering the minor component quantitatively. The isotopic dilution analysis is strictly to be regarded as giving a maximum value (69 ± 1%) since it is feasible that adducts which could give 2-chlorofluorenone on oxidation are minor components of the reaction mixture. We shall, however, adopt the value of 69% for the following discussion.

4-*Chlorofluorene*.—As would be expected by analogy with nitration,[6] and by theoretical considerations based on the view that fluorene can be treated as a planar 2-alkylbiphenyl, a further component of the reaction mixture is 4-chlorofluorene, and this is the only other monochlorofluorene that we have detected. Both the 2- and the 4-position are conjugated with the aryl group, and both are very substantially activated relatively to positions in benzene, or even to the corresponding positions in biphenyl. The 4 : 2 ratio is 0·13; this is lower than that (0·3) recorded[18] for the $\frac{1}{2}$*ortho* : *para* ratio for the similar chlorination of biphenyl. A change in this direction is observed also for nitration.[6] Further aspects of the structural factors determining reactivity of alkyl-substituted and bridged biphenyls will be discussed in a subsequent paper.

Acetoxy-chloride Adducts.—The amount of acetoxy-chloride adduct formed in the reaction is small; from the difference between total acid and halide liberated from the crude organic product by alkali, only *ca.* 2·5% of chlorine is consumed in formation of such an adduct. It proved, however, to be relatively easily removed from the reaction mixture by chromatography on silica gel and was clearly a complicated mixture, which may in part have decomposed or rearranged on the column.

Polychloride Adducts.—Of the chlorine consumed, 13·5% was consumed without liberation of hydrogen chloride. Very little of this (about 3%) can be ascribed to the formation of a tetrachlorotetrahydrofluorene, analogous to the tetrachlorotetrahydrobiphenyl described elsewhere;[18] such a material should with alkali give a dichlorofluorene with substituents only in one ring, and such materials comprised less than half of the very small dichlorofluorene fraction isolated from the vapour-phase chromatograms after treatment of the product with alkali.

It seems likely, therefore, that polychlorides, or acetoxy-polychlorides, were produced in the reaction, but the details have not been established, though we hope to follow this aspect further.

The following, therefore, represents our best estimate of the way in which chlorine is consumed in reaction with an excess of fluorene.

Product	Moles % of chlorine consumed
2-Chlorofluorene	$\ngtr 69$
4-Chlorofluorene	9
2,7-Dichlorofluorene	2
Acetoxy-chloride adduct (calc. as acetoxytrichlorotetrahydrofluorene)	5
Tetrachloride adduct	3
Other adducts formed without production of HCl	8
Total	96%

We are indebted to Mr. S. French for valuable technical assistance.

William Ramsay & Ralph Forster Laboratories,
University College London, Gower Street, London, W.C.1.
Bedford College, Regent's Park, London, N.W.1.
Medical Research Council Laboratories,
Holly Hill, London, N.W.3.

[*Received, July* 20*th*, 1961.]

---

[18] Beaven, de la Mare, Hassan, Johnson, and Klassen, *J.*, 1961, 2749.