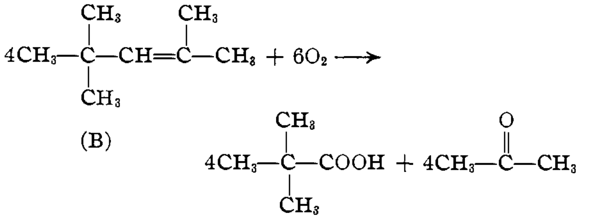
$$4CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3 + 6O_2 \longrightarrow 4CH_3-\underset{CH_3}{\overset{CH_3}{C}}-COOH + 4CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \quad (B)$$

The above assumption gives us a basis for calculating the yields of oxidation products. The low yield of the expected ketones as compared to the acids formed at the same time may be explained by the fact that the ketone is influenced by the potassium hydroxide for a much longer period of time than is the intermediate aldehyde. Under such conditions the primary reaction of the aldehydes is one of oxidation rather than condensation or polymerization. The ketones, however, remained in contact with the potassium hydroxide from the time of formation until the time of separation of the phases. There is evidence that secondary reactions took place giving rise to unpredicted compounds and substances present in quantities too small for absolute identification.

Summary

1. The action of molecular oxygen on diisobutylene in the presence of potassium hydroxide has been studied at 100° and 100 lb. per sq. in. pressure. The course of the reaction was followed by noting the drop in pressure in the bomb. Under the aforementioned conditions diisobutylene has an induction period of ninety to one hundred and twenty minutes. The reaction is essentially complete after eight hours.

2. A qualitative and quantitative study was made on the oxidation products.

3. The chief products obtained were acetone, 4,4-dimethyl pentanone-2, carbon dioxide, formic acid, and pivalic acid.

4. The presence of oxygen-containing compounds boiling higher than any of the predicted products was shown. These could not be obtained in sufficient quantity and purity for identification. Qualitative tests indicated that these substances contained the CH_3CO- and $-OH$ groups.

CHAPEL HILL, N. C. RECEIVED MAY 19, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. XI. The Vapor Phase Fluorination of Benzene

BY NOBUKAZU FUKUHARA AND LUCIUS A. BIGELOW

In Paper X of this series[1] we have described an efficient apparatus for the vapor phase fluorination of volatile organic liquids over a heated copper gauze catalyst and its successful use for the fluorination of acetone. This work led us rather directly to undertake the more difficult problem of fluorinating benzene. In the past, neither benzene itself, nor aromatic compounds in general, have been caused to react with elementary fluorine with satisfactory results. Now, however, we have found that the hydrocarbon can be fluorinated without any difficulty in the apparatus just referred to, yielding a clean, though complex, product.

Experimental Procedure

The fluorinations were carried out essentially as described before,[1] except that the reactor had an initial temperature of about 90° and was swept out with nitrogen for roughly half an hour after each period of operation, in order to collect all of the product volatile at this temperature. In most cases, the gas volume ratio of $F:C_6H_6:N$ used was 4:1:2. Under our present operating conditions, it was not practicable to raise the fluorination ratio of $F:C_6H_6$ above 6:1 in any case, and therefore the fluorine was actually well diluted by the excess of benzene. Nevertheless, a series of runs was made, in which the dilution ratio of F:N was increased progressively, in order to determine the effect of this change upon the reaction.

TABLE I

THE EMPIRICAL CUTS OBTAINED BY FRACTIONATING FLUORINATED BENZENE

Liquid vol. % of material boiling at	Gas volume ratio of $F:C_6H_6:N$ 4:1:0	4:1:2	4:1:4	4:1:8	4:1:16
−128 to −105 (mostly CF_4)	25	10	10	15	20
−105 to −58 (mostly C_2F_6)	Trace	Trace	5	5	5
−58 to −5 (largely C_3F_8)	5	Trace	5	10	5
−5 to 40	. .	10	10	5	10
40 to 79	. .	15	10	5	5
Above 79	. .	65	65	60	55
Total vol. of condensate per hr. in ml.	1.2	1.1	1.3	1.8	1.6

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(1) Fukuhara and Bigelow, THIS JOURNAL, 63, 788 (1941).

TABLE II

THE RESULTS OBTAINED BY FRACTIONATING FLUORINATED BENZENE

Fraction	Observed B. p., °C.	Observed Mol. wt.	Vol./100 hr. operation, cc.	Type	Product	Remarks
1	−128	88	10.0	Compound	CF_4	
2	− 78	138	1.5	Compound	C_2F_6	Quantity estimated
3	− 55	114	1.5	Azeotrope	...	Not as yet separated
4	− 36	188	3.0	Compound	C_3F_8	
5	−5 to −3	236	1.0	Compound	C_4F_{10}	Purified, b. p. −2, mol. wt. 238
6	22	246	4.0	Heterogeneous	...	B. p. −11 at 218 mm.; carries C_6H_6
7	48	246	13.0	Heterogeneous	...	B. p. 10–12 at 218 mm.; carries C_6H_6
8	61–63	220	6.0	Azeotrope	...	B. p. 15–17 at 170 mm.; carries C_6H_6
9	68	194	2.5	Azeotrope	...	B. p. 20° at 170 mm.; carries C_6H_6
10	74	...	3.0	Azeotrope	...	Carries much C_6H_6
11	79	...	...	Heterogeneous	...	C_6H_6 carries some product
12	80 up	...	...	Homogeneous	...	C_6H_6 + residue. Almost dry at 85°.

The fluorine flow was always closely 1.7 liters per hour, and the products were fractionated in Booth–Podbielniak stills. The results, expressed in liquid volume per cent. of the total condensate, and rounded off, as before, to the nearest 5%, are collected in Table I.

From these figures it will be seen that the crude condensate was collected at an average rate of 1.4 ml. per hour, including the unreacted benzene. We have estimated that this corresponded rather approximately to an average yield of 40 cc. of fluorinated product per one hundred hours of operation. The results also show that as the dilution ratio was increased, the proportion formed of the more highly fluorinated products increased, while that of the less fluorinated materials decreased. This unexpected observation may have been due to the fact that the partially fluorinated compounds were more reactive at higher dilutions than benzene itself; or to a better mixing of the gases at greater volume in this particular type of reactor, involving counter-current flow. Neither explanation, or even a combination of them, can be regarded as entirely conclusive.

Since a dilution ratio of F:N as 2:1 yielded a minimum of carbon tetrafluoride, and a maximum of the interesting portion, b. p. 40–79°, it was decided to concentrate upon this ratio (4:1:2). Accordingly, some five hundred hours of fluorination were carried out, mostly under these conditions, and the accumulated products carefully rectified. A summary of the results, in the form of a representative distillation, is presented in Table II.

These figures show that the distillation yielded several compounds, together with a number of heterogeneous and azeotropic constant boiling mixtures. All of these fractions were definitely reproducible. In addition, some silicon tetrafluoride and carbon dioxide came over from −90 to −80°, and the small amount of residue boiling above +80° did not have a molecular weight significantly greater than that of benzene. Roughly 4–5 g. of tar was deposited in the reactor per one hundred hours of operation. Several of the mixtures were then separated by various means, as described in the following paragraphs.

Mixture 6. B. p. 22°, Mol. Wt. 246.—This heterogeneous mixture, which contained only a little benzene, was distilled with an excess of *n*-pentane. The distillate was heterogeneous, and boiled at −5 to −3° at 330 mm., with a mol. wt. of 181, and the residue of excess pentane, containing most of the benzene, was discarded. The layers were separated and the upper pentane layer also discarded. The remainder was then fractionated, and following a small amount of the mixture (mol. wt. 181), pure C_5F_{10} came over, b. p. 0–1° at 330 mm.; 22° at atm. pres.; with a mol. wt. of 250 (calcd. 250). When a 2.5-cc. liquid sample of this product was vaporized, mixed with an excess of chlorine, and allowed to stand overnight, the pressure change was very small, and almost all of the sample was recovered unchanged, indicating that it was saturated.

Mixture 7. B. p. 48°, Mol. Wt. 246.—This heterogeneous mixture carried considerable benzene, and the layers were separated mechanically. The upper essentially hydrocarbon layer was discarded, and the other portion was distilled at 218 mm. until the contents of the column became solid. Considerably more of this solid could be obtained by redistilling the distillate from trap to trap at low pressures, which involved the partial melting of the sample, followed by the removal of the liquid portion, largely benzene, by the quick application of reduced pressure. The combined product melting above room temperature was again distilled from a small vacuum-jacketed column at atmospheric pressure. After a small forefraction boiling at 48°, pure C_6F_{12} came over, b. p. 50°, m. p. 48–49° (after passing over Drierite) with a mol. wt. of 300 (calcd. 300). It did not react with liquid chlorine.

Mixtures 8, 9 and 10. B. p. 61–74°.—These mixtures were homogeneous and azeotropic. They were combined and in order to remove all the benzene, the mixture was distilled repeatedly at atmospheric pressure in the small still with C_6F_{12}, until this pure fluorocarbon came over at 50° and solidified at room temperature. The residue was fractionated further, and yielded pure C_6HF_{11}, b. p. 62° with a mol. wt. of 282 (calcd. 282), and a higher boiling residue not yet investigated. The C_6HF_{11} consisted of high- and low-melting isomers, the former more stable at low temperatures, and the latter at higher temperatures (0° and up). They existed in a mobile equilibrium and so could not be kept separately in a pure condition. The highest and lowest melting points obtained for the two isomers were 41–43° and −16 to −14°, respectively, indicating that their true melting points must lie over 60° apart. The equilibrium mixture, when treated with chlorine in the same manner as the C_5F_{10}, reacted very slowly, and gave no evidence of unsaturation.

Mixture 11. B. p. 79°.—This heterogeneous mixture consisted largely of benzene and the layers were separated mechanically. The lower layer was then fractionated in the small still at reduced pressure. A considerable low boiling fraction, apparently a mixture, came over first, followed by pure $C_{12}F_{22}$, b. p. 90° at 90 mm., m. p. (in bulk) 19–21°, with a mol. wt. of 563 (Victor Meyer) (calcd. 562).

All of the compounds thus far isolated from the fluorinated benzene are listed below in Table III, together with analytical data for the new or less well established substances. It will be seen that the constants in general agreed well with known values, and that the analyses were satisfactory. It is of interest that compounds containing all the way from one to six carbon atoms were formed by the fluorination of benzene.

TABLE III

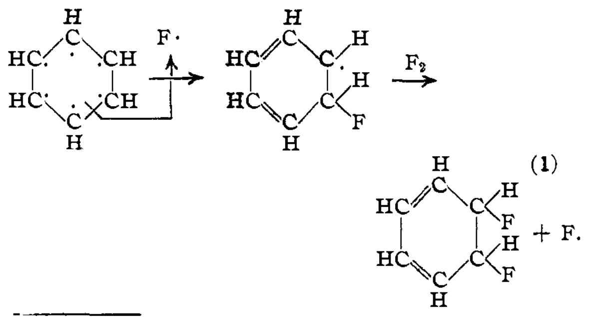
PURE COMPOUNDS ISOLATED FROM FLUORINATED BENZENE

Compd.	B. p., °C. Lit.	B. p., °C. Found	Molecular wt. Calcd.	Molecular wt. Found	Per cent. Fluorine Calcd.	Per cent. Fluorine Found	
CF_4	−128	−128	88	88	...	...	...
C_2F_6	− 78	− 78	138	138	...	...	...
C_3F_8	− 36	− 36	188	188	...	...	...
C_4F_{10}	−5 to +3[a]	− 2	238	238	79.8	80.0	...
C_5F_{10}	23[a]	22	250	250	76.0	76.1	76.3
C_6F_{12}	51[a]	50	300	300	76.0	76.1	75.8
C_6HF_{11}	...	62	282	282	74.1	74.2	74.1
$C_{12}F_{22}$	...	90[b]	562	563	74.4	74.1	...

[a] The compound reported in the literature[2] may not have the same structure as ours. [b] At 90 mm.

Discussion

The results summarized above in Table III furnish the first really definite information from which it is possible to get some picture of the attack of elementary fluorine upon the aromatic nucleus. No complete mechanism can be postulated as yet, but a number of important inferences are clearly indicated. In all probability, the reaction is of the free radical type already postulated[1] for vapor phase fluorinations; and since no aromatic fluorine compounds were isolated, the initial attack of the halogen is presumably by direct addition to the ring. The first stages of this change can be represented electronically in some such manner as follows



(1)

and so on until $C_6H_6F_6$ or like intermediate is produced. The saturated fluorocyclohexane can then react in two ways, (a) by the loss of hydrogen fluoride thermally, followed by the addition of more fluorine, and so on, or (b) by direct fluorination like a saturated hydrocarbon. Postulate (a) appears unlikely, because it would lead to aromatic fluorinated products, which were not isolated, and because the reaction mixture contains much hydrogen fluoride, which would tend to reverse such a change; while (b) is favored by the well-known fact that the $>CF_2$ group is a highly stable resonant structure. In any case C_6F_{12} is formed finally. These considerations raise an interesting question, namely, whether or not addition to the aromatic nucleus, known in the case of chlorine to be promoted by heat and light, is a free radical reaction; whereas substitution, favored by catalysts, is in general an ionic change. It has been shown recently that these two types of reaction often produce very different effects on the same compound. For example, Kharasch and Brown[3] have found that the chlorination of *n*-butyric acid by $SOCl_2$, in the presence of peroxides, is a free radical reaction, and leads to β- and γ-substitution exclusively; while the usual methods for the chlorination of saturated fatty acids, which presumably proceed by ionic mechanisms, lead only to α-substitution. They have also reported[4] that the chlorination of aromatic hydrocarbons by $SOCl_2$ produces only side-chain substitution, and no reaction on the aromatic ring. We hope to obtain further information bearing on this question later on.

The compound C_6F_{12}, obtained in the greatest yield, is almost certainly dodecafluorocyclohexane, since it did not react with chlorine and was apparently saturated. The appearance of C_6HF_{11}, in all likelihood undecafluorocyclohexane, as the last stage in the formation of C_6F_{12} might have been expected, but the existence of two forms of this apparently saturated compound, in mobile equilibrium, would scarcely have been predicted. They may be isomorphous, or possibly boat and chair forms. Both of the latter would tend to be somewhat stabilized by hydrogen bond formation. The compound $C_{12}F_{22}$ or diundecafluorocyclohexyl was undoubtedly formed by the fluorination of undecafluorocyclohexane, according to the equations

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(2) J. H. Simons, THIS JOURNAL, **61**, 2962 (1939).

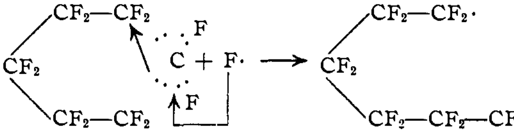
(3) Kharasch and Brown, *ibid.*, **62**, 925 (1940).

(4) Kharasch and Brown, *ibid.*, **61**, 2142 (1939).

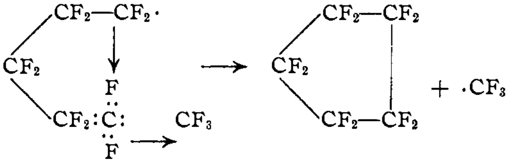
$$C_6HF_{11} + F\cdot \longrightarrow HF + C_6F_{11}\cdot \qquad (2)$$

$$2C_6F_{11}\cdot \longrightarrow C_6F_{11}:C_6F_{11}, \text{ or } C_{12}F_{22} \qquad (3)$$

The further attack of the fluorine upon dodecafluorocyclohexane may be considered to take place in a manner similar to that postulated for hexafluoroacetone (1), as follows


(4)

Since the benzene and not the fluorine is in great excess, this fragment may well react with itself


(5)

$$2CF_3\cdot \longrightarrow C_2F_6 \qquad (6)$$

closing the stable five-membered ring and eliminating the $CF_3\cdot$ radical, which can easily polymerize to form C_2F_6. This mechanism is quite in accord with the fact that neither of the saturated fluorocarbons C_5F_{12} or C_6F_{14} could be isolated from the reaction mixture. The latter compound especially would be almost certain to result if either a fluorine atom or molecule should react with the fragment $C_6F_{13}\cdot$ shown in (4) and (5).

The fluorocarbons of lower molecular weight than C_5F_{10}, namely, CF_4, C_2F_6, C_3F_8 and C_4F_{10} may be accounted for either by the further degradation of the larger molecules, or by the combination of smaller free radicals which are undoubtedly present. It should be recalled here that we have found[5] that the vapor phase fluorination of methane yielded much C_2F_6 and C_3F_8 as well as all of the fluoromethanes. Also, it is quite possible, for example, that the dodecafluorocyclohexane ring may be attacked simultaneously at more than one point, yielding free radicals of lower molecular weight directly. We have as yet no evidence to decide whether the C_4F_{10} is *n*- or *i*-decafluorobutane.

From the foregoing description it appears that the action of elementary fluorine on the aromatic nucleus is very complex, but all of the products, none of which were aromatic, may be accounted for on the basis of a free radical mechanism involving addition to the ring. However, the results so far can be regarded only as a first attack upon this most interesting problem.

The writers are happy to acknowledge here their indebtedness to Mr. Henry Freiser of this Laboratory for substantial assistance, and to the Research Council of Duke University for a grant.

Summary

The vapor phase fluorination of benzene has been carried out, using the improved apparatus recently described.

The products so far isolated were CF_4, C_2F_6, C_3F_8, C_4F_{10}, C_5F_{10}, C_6F_{12}, C_6HF_{11} and $C_{12}F_{22}$. It is believed that the last four of these are decafluorocyclopentane, dodecafluorocyclohexane, undecafluorocyclohexane and diundecafluorocyclohexyl, respectively. Apparently no aromatic compounds were formed.

The reaction mechanism, which is considered to be non-ionic, has been discussed.

DURHAM, N. C. RECEIVED AUGUST 2, 1941

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[5] Hadley and Bigelow, THIS JOURNAL, **62**, 3302 (1940).