**4-Quinolyl methyl ether** was prepared from the 4-chloro compound[31] and resublimed: m. p. 39–39.5° (reported, 41°). The **hydrochloride** crystallized from absolute alcohol–ether in the form of white needles, m. p. 171° (reported,[32] 164–166°, dec.).

*Anal.* Calcd. for $C_{10}H_9NO \cdot HCl$: N, 7.16. Found: N, 7.06.

The **picrate** separated from alcoholic solution in the form of bright yellow needles, m. p. 199–199.2°, dec. (reported,[31] 203°). The **styphnate** crystallized as golden yellow needles from alcohol, m. p. 219–219.5°, dec.

*Anal.* Calcd. for $C_{10}H_9NO \cdot C_6H_3N_2O_8$: N, 13.87. Found: N, 13.84.

**8-Quinolyl methyl ether** was prepared by the method of Kaufmann and Rothlin.[33] The distilled product (b. p. 95–98° at 0.1 mm. pressure) was thrice crystallized from petroleum ether giving white prisms, m. p. 45–45.5° (reported,[33] 46–47°). The **picrate** was obtained from alcohol as fine yellow needles, m. p. 162.5–163° (reported,[34] 143°, dec.).

*Anal.* Calcd. for $C_{10}H_9NO \cdot C_6H_3N_3O_7$: N, 14.44. Found: N, 14.64.

It was observed that upon standing in the presence of air many of the hydroxy compounds, especially in basic solution, turned dark slowly. The naphthols were the worst offenders but several of the heterocyclic materials showed a similar effect in lesser degree. To determine the possible effect of such visible darkening upon the spectrum, an aging test was run upon $\alpha$-naphthol as an example of these compounds. The spectrum reported in Fig. 1 was determined on a fresh solution which showed no darkening. Another solution was prepared of approximately 0.5% $\alpha$-naphthol (highly purified) in 0.01 *N* sodium hydroxide. By the time the crystals had dissolved completely the liquid had assumed a light straw color. The spectrum was run immediately and after standing for various intervals in normal laboratory illumination. It was found that the color deepened very markedly, becoming almost black. By the end of sixty-nine hours the 333 m$\mu$ maximum had not changed appreciably in height, but by four hundred eighty-three hours it had dropped by some 30%. The absorption in the lower visible region had, of course, increased, but without showing any marked selectivity. No sign of the maxima of 1,4-naphthoquinone at 405 and 425 m$\mu$[3] were observed. All the spectra reported in this paper were run on fresh solutions, and it is thought that this darkening can have had but negligible effect on them.

**Acknowledgments.**—The authors' thanks are due to Miss N. K. Peck for preparative work, Mrs. C. M. Grant and Mrs. E. R. Falkner for operation of the spectrophotometer, and Miss P. Curran for the microanalyses.

## Summary

1. Ultraviolet absorption spectra have been determined for all the isomeric hydroxyquinolines and several hydroxyisoquinolines.

2. Spectrophotometric evidence is in general in agreement with chemical evidence in the assignment of phenolic structure to all hydroxyquinolines and -isoquinolines except where the substituent is in the $\alpha$- or $\gamma$-position relative to the ring nitrogen. These isomers are predominantly ketonic (or lactamic) in nature.

RENSSELAER, NEW YORK RECEIVED MAY 15, 1946

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[31] Backeberg, *J. Chem. Soc.*, 619 (1933).

[32] Reference $^m$ in Table II.

[33] Kaufmann and Rothlin, *Ber.*, **49**, 581 (1916).

[34] Fränkel and Grauer, *ibid.*, **46**, 2551 (1913).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

# The Action of Elementary Fluorine upon Organic Compounds. XII. Vapor Phase Addition to Certain Deactivated or Condensed Aromatic Rings[1,1a]

BY READE Y. TOMPSON,[2] PAUL TARRANT[3] AND LUCIUS A. BIGELOW

Several years ago it was reported from this Laboratory[4] that the vapor phase fluorination of benzene yielded $C_6F_{12}$, $C_6HF_{11}$ and $C_6F_{10}$, together with small amounts of $C_{12}F_{22}$, and several acyclic saturated fluorocarbons of lower molecular weight, but no trace of any aromatic substitution products. These results were explained upon the assumption that the attack of fluorine on the aromatic nucleus proceeds first by addition, then by substitution, and finally by degradation, in which all the reactions take place by atomic mechanisms, and may or may not be accompanied by polymerization.

More recently some preliminary experiments made in this Laboratory by A. R. Gilbert[5] and dealing with the fluorination of a relatively unreactive aromatic ring made it seem particularly desirable at this time to obtain further information about the earlier stages of such reactions, presumably by studying the fluorination of either highly deactivated or condensed aromatic rings, eventually under the mildest practicable operating conditions. Accordingly, we are presenting here the results of a study of the vapor phase fluorination of 4-chloro-1,3-bis-(trifluoromethyl)-benzene (I), later referred to as the 4-chloro compound, benzotrifluoride, and 1-methylnaphthalene. While the findings, which are not as yet complete, do not constitute a total solution of the problem, they do represent a distinct advance in our knowledge of the mechanism by which elementary fluorine reacts with aromatic rings.

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[1] A part of this research program was sponsored by the Naval Research Laboratory.

[1a] This paper was prepared from portions of the Doctorate Theses submitted to the Graduate School of Duke University by R. Y. Tompson and Paul Tarrant in 1945 and 1944, respectively. This project was also supported in part by grants from the University Research Council.

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[4] Paper XI, Fukuhara and Bigelow, THIS JOURNAL, **63**, 2792 (1941).

[5] A. R. Gilbert, Master's Thesis, Duke University, 1943.

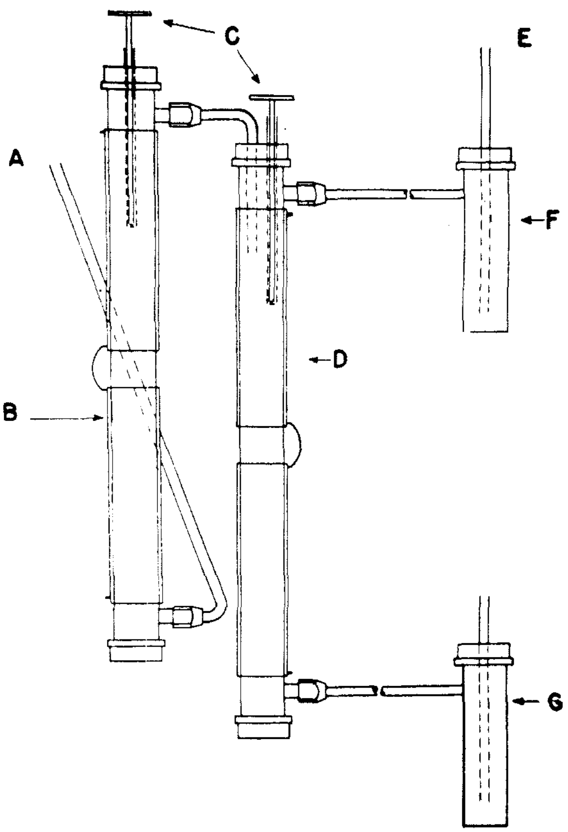

Fig. 1.—Fluorination apparatus.

## Experimental

### Apparatus

The simple all-metal apparatus used for the greater part of these fluorinations is illustrated in Fig. 1. It consisted essentially of a vertical reactor D and saturator B, made from 16″ lengths of 1″ brass pipe, closed at both ends by leaded brass caps, and electrically heated by means of 40′ coils of no. 28 Nichrome wire wound on the outside, which were suitably insulated and lagged. The upper caps on B and D were equipped with thermometer wells carrying metal Weston thermometers C, as shown; and the copper exit tube from B also passed through the upper cap on D, and extended downward for a distance of 3″. The reactor D was carefully packed with $^1/_4$″ strands of silver-plated copper wire made from 16 mesh copper screen, and the saturator was suitably filled with the liquid sample. In operation, a measured current of nitrogen entered at A, bubbled up through the heated sample, and then passed over into D, thus delivering the vapor of the reactant into the upper portion of the metal packing. At the same time the fluorine was led in at E, cooled by solid carbon dioxide in the metal trap F to condense hydrogen fluoride, and finally entered D at the top, whence it passed downward to mingle and react with the sample within the meshes of the packing. The products left the reactor at the bottom, and were condensed as far as possible in the metal trap G, also cooled by solid carbon dioxide.

In some of the experiments, much larger reactors were employed, about 3′ in length, one having an expanded head filled with silver-plated copper gauze, and the other constructed of concentric tubes with the annular space between them filled with a removable roll of plated screen; but these operated on the same principle as the smaller unit, and will not be described in detail here.

The fluorine was supplied by large generators similar in principle to, but differing in detail from, the model described by Cady,[6] which were designed by Drs. P. M. Gross, M. E. Hobbs and Paul Tarrant of this Laboratory, and will be discussed in detail elsewhere. One of these units, operating at a normal potential drop of 7–10 volts and using a current of 20 amp. delivered about 5.5 liters per hour of the gas.

A special apparatus was devised to remove hydrogen fluoride from the product without loss by volatilization or hydrolysis. For this purpose a brass pipe similar to D and maintained at the reactor temperature was used, but in this case it was placed horizontally and half filled with a layer of powdered sodium fluoride. On completion of a run, the metal condensing trap G was immediately attached to one end of this tube by its side-arm, and a glass trap cooled by solid carbon dioxide connected to the other end. Then, after a warming up period during which the vertical exit to G was kept closed, dry air was either pushed or aspirated through the apparatus, and ultimately allowed to bubble through the residue in G overnight. In this way the product was separated, in general, into a volatile and a nonvolatile portion, each of which was completely free from hydrogen fluoride, and could when desired be worked up separately. The sodium fluoride could be regenerated repeatedly by passing a current of dry air over it at 250° for six hours.

The products were originally fractionated by means of a 3′ column, packed with glass helices, and equipped with a standard type total reflux, partial take-off head adapted also for reduced pressures, together with an insulated electrically heated jacket. The boiler and head were attached by means of ground glass joints. For the more precise work a smaller column with a metal screen "staircase" packing similar to that described by Bower and Cooke,[7] or a standard Podbielniak Heli-Grid distilling tube was employed. Distillation temperatures were measured continuously by calibrated thermocouples together with a Micromax recorder, and refractive indices determined at intervals with an Abbe refractometer in the usual manner.

### Fluorinations

**4-Chloro-1,3-*bis*-(trifluoromethyl)-benzene (I).**—This compound was prepared in quantity by Drs. C. K. Bradsher, Paul Tarrant and co-workers of this Laboratory, by the successive ring and side-chain chlorination of *m*-xylene, followed by the replacement of the six side-chain chlorine atoms by fluorine using hydrogen fluoride under pressure. The details of this indirect fluorination will be described elsewhere. This product, which was released to us especially for this study, was a colorless liquid, b. p. 148–150°, with the correct composition, molecular weight and chemical stability; but the possibility that it could have contained isomeric substances in small amounts was not entirely excluded. The compound was fluorinated in the outfit described above. A current of nitrogen, at the rate of 5.5 liters per hour was led into the saturator heated at 104° and carried the sample at the rate of 7 liquid cc. per hour as vapor into the reactor which was maintained at 110°. The undiluted fluorine was introduced simultaneously at the same rate as the nitrogen, so that the molar ratio of $F_2$:sample:$N_2$ was 5:1:5, corresponding to a fluorination ratio of 5:1 and a dilution ratio of 1:1. The product, which was collected at the rate of 5 cc. per hour, was freed from hydrogen fluoride as described above. In this way 400 cc. of the 4-chloro compound (I) was fluorinated and yielded a total of 280 cc., or 70% by volume of crude product, which, after a preliminary distillation to remove high boiling presumably polymerized residue, left 255 cc. of colorless limpid liquid to be fractionated.

The next careful rectification was carried out using the Bower and Cooke column with the results shown in Table I.

From the above figures it will be seen that the fluorinated product was a complex mixture, from which certain significant portions with short boiling ranges could be separated. However, on the whole, the boiling point of the mixture

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[6] Cady, Rogers and Carlson, *Ind. Eng. Chem.*, **34**, 443 (1942).

[7] Bower and Cooke, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 290 (1943).

TABLE I

THE FRACTIONATION OF THE FLUORINATED PRODUCT

| B. r., °C. | Vol., cc. | Portions with short boiling ranges at, °C. |
|---|---|---|
| 25-104 | 18 | 48-50<br>75-77<br>99-100 |
| 104-108 | 13 | 106-107 |
| 108-121 | 50 | 112-113<br>119-121 |
| 121-129 | 20 | 127-129 |
| 129-140 | 23 | ..... |
| 140-146 | 65 | 142-143<br>146 |
| 146-151 | 52 | 147-149 |
| 151-156 | 13 | ..... |
| Boiler residue | 3 | |
| Total | 257[a] | |

[a] The boiler residue from the original distillation amounted to approximately 24 cc. which made a total recovery of 281 cc.

rose quite gradually over most of the range, and further careful fractionation was clearly indicated. At this point the respective fractions were somewhat augmented by like material from earlier operations (25 cc. in all), and all of them again distilled through the Bower and Cooke column, at the highest possible reflux ratio and a minimum practicable take-off rate not exceeding 2 cc. per hour. During the process, fore- and intermediate fractions were recombined with portions of like properties, and residues were added to the next higher boiling fractions. Also, when the boiling point rose above 104° the refractive index of the material became high enough (>1.300) to be measured in a refractometer, and this property was used in addition to the boiling point in the characterization of the several fractions. Furthermore, at certain times some hydrogen fluoride appeared in the distillates, and was always removed immediately by treatment with sodium fluoride. Finally five significant portions were obtained as follows: (1) b. p. 48-50° (1 cc.); (2) b. p. 75-77° (1 cc.); (3) b. p. 99-100° (8 cc.); (4) b. p. 112-118° (20 cc.); (5) b. p. 146-148° (35 cc.).

Fraction (1) was undoubtedly $C_6F_{12}$ (VIII), b. p. 50°,[4] mol. wt. calcd. 300, found 301; while (2) was clearly $C_6F_{11}(CF_3)$ (VII), b. p. 77.5° (see below), mol. wt. calcd. 350, found 352; and (3) was almost certainly 1,3-$C_6F_{10}(CF_3)_2$ (VI), mol. wt. calcd. 400, found 395.

Portion (4) was once more carefully fractionated, using the Bower and Cooke column, and the refractive index of the distillate measured repeatedly during the process. Finally, a 5-cc. sample was collected for analysis, b. p. 113-114°, and a constant refractive index of 1.3190 at 31°, which contained no chlorine and reacted vigorously with 10% alcoholic potassium hydroxide, to yield fluoride ion and an apparently polymerized product.

*Anal.* Calcd. for $C_6H_3F_7(CF_3)_2$: F, 71.4; mol. wt., 346; and for $C_6H_2F_6(CF_3)_2$: F, 69.9; mol. wt., 326. Found: F, 70.4, 70.5, 70.7; mol. wt., 333, 334, 335.

On this basis it was concluded that the sample was an apparently azeotropic mixture, containing 60% of the first compound, or the hexafluoride of the 4-chloro compound in which the chlorine had also been replaced by fluorine (V), and 40% of the second substance which had been formed from the other by the loss of hydrogen fluoride as actually observed during the corresponding distillation. It was not possible, however, to demonstrate the expected unsaturation experimentally.

Cut (5) was also refractionated very carefully, and two 2-cc. samples collected for analysis. The first of these, b. p. 143°, with a constant refractive index of 1.3607 at 32°, was the pure tetrafluoride of the 4-chloro compound (III), which on hydrolysis with 10% alcoholic potassium hydroxide furnished both chloride and fluoride ions.

*Anal.* Calcd. for $C_6H_3F_4Cl(CF_3)_2$: F, 58.5; Cl, 10.9; mol. wt., 325. Found: F, 58.4, 58.6; Cl, 11.1, 11.2; mol. wt., 322, 324.

The second sample, b. p. 147°, with a constant refractive index of 1.3922 at 32° also reacted vigorously with 10% alcoholic potassium hydroxide, to yield chloride ion. A larger sample (b. p. 146-150°) gave on hydrolysis chloride ion, a little fluoride ion, unchanged 4-chloro compound (I), and an apparently polymerized product.

*Anal.* Calcd. for $C_6H_3F_2Cl(CF_3)_2$: F, 53.0; Cl, 12.4; mol. wt., 287; and for $C_6H_3Cl(CF_3)_2$ (I): F, 45.9; Cl, 14.3; mol. wt., 249. Found: F, 51.1, 51.1, 51.2; Cl, 13.1, 13.2, 13.2; mol. wt., 277, 278.

On this basis it was concluded that this product was also an apparently azeotropic mixture containing about 75% of the first compound, or the difluoride of the 4-chloro compound (II), and 25% of the 4-chloro compound (I) itself, which, it should be noted here, is completely stable toward alcoholic alkaline hydrolysis at reflux temperature.

**Benzotrifluoride.**—The commercial product was fluorinated in the large reactor with the expanded head at the molar ratio of $F_2$:sample:$N_2$ as 8:1:6, corresponding to a fluorination ratio of 8:1 and a dilution ratio of 4:3. These values were determined by certain preliminary experiments with toluene, and were such that the temperature of the reaction zone remained relatively low at a reasonable rate of flow, while little or no unchanged sample remained. This required 8.3 liters per hour of nitrogen passing through the saturator at 48° and carrying about 7 liquid cc. per hour of sample as vapor into the reactor, where it mixed with 11 liters per hour of fluorine from the generators. During the runs the lower part of the reactor was kept at 150°, but the head, or reaction zone, maintained itself at 140° without applied heat at that point. Altogether about 200 cc. of product boiling from 25-200° was obtained at the rate of 4 cc. per hour, and was freed from hydrogen fluoride as already described. The material remaining in the metal trap was distilled rapidly through the helix-packed column in order to remove polymers, and the distillate, boiling from room temperature to about 115°, was combined with the volatile portion collected in the glass trap. About 40 cc. of high boiling, evidently polymeric, residue remained behind. The combined low boiling product was then carefully fractionated, and yielded three significant portions, boiling from 48-51° (15 cc.), 73-78° (62 cc.) and 85-87° (about 9 cc.), respectively.

The first of these was partially frozen at 0° and the liquid portion withdrawn by means of a filter stick. The solid residue was mostly $C_6F_{12}$ (VIII), mol. wt. calcd. 300, found 305. The second and largest portion was refractionated through the Bower and Cooke column, and yielded a 25-cc. portion, m. p. −42°, b. p. 77-78°, which was divided into six cuts, the largest of which (15 cc.) boiled at 77.5°. This product was pure $C_6F_{11}(CF_3)$ (VII), mol. wt. calcd. 350, found, average for the six separate cuts, 350, maximum deviation, about 1%. The completely fluorinated toluene was refluxed with 80% sulfuric acid as suggested by Swarts,[8] and also by Simons and Ramler[9] in an attempt to hydrolyze the —$CF_3$ group; and also with granulated zinc, copper powder and metallic sodium, ultimately under pressure, in the hope of aromatizing the fluorocarbon, but none of these experiments was successful. In most cases, much of the sample was recovered unchanged, while the portion which was attacked was completely carbonized. The last fraction, after another distillation, b. p. 85-87°, was divided into five cuts. It gave analytical figures corresponding closely to those required by the formula $C_6HF_{10}(CF_3)$, and probably consisted of a mixture of both structural and geometric isomers.

*Anal.* Calcd. for $C_6HF_{10}(CF_3)$: F, 74.4; mol. wt., 332. Found: F, 74.3, 74.5; mol. wt. (av. of 4 cuts), 330.

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(8) Swarts, *Bull. acad. roy. Belg.*, [4] **2**, 414 (1900).

(9) Simons and Ramler, THIS JOURNAL, **65**, 389 (1943).

This product reacted readily with 10% alcoholic potassium hydroxide, yielding fluoride ion; but when the organic material was recovered and distilled, it boiled from 78–170°, and appeared to consist mostly of a mixture of polymers, from which no single substance could be isolated. Also, on refractionation of a higher boiling portion, b. p. 92–112° (25 cc.) obtained from the first distillation, there was isolated another small sample, b. p. 94–95° (about 2 cc.), which also had a composition corresponding to the formula $C_6HF_{10}(CF_3)$ and probably consisted of another of the many possible isomers, or perhaps a mixture of these.

*Anal.* Calcd. for $C_6HF_{10}(CF_3)$: F, 74.4; mol. wt., 332. Found: F, 74.8, 74.9; mol. wt., 333, 335.

**1-Methylnaphthalene.**—The commercial product was fluorinated in the large reactor at the molar ratio of $F_2$:$C_{11}H_{10}$.$N_2$ as 15:1:15; corresponding to the calculated complete fluorination ratio of 15:1 and a dilution ratio of 1:1. This called for 16.5 liters per hour of nitrogen passing through the saturator at 156°, and carrying 6.4 g. per hour of sample into the reactor, where it mixed with 16.5 liters of fluorine from the generators. During the runs the lower section of the reactor was kept at 200°, and the head or reaction zone at 180°, allowing in the adjustment for a heat of reaction equivalent to about 40° on the Weston thermometer. Under these conditions no excess of fluorine appeared in the exit gases unless the flow of the hydrocarbon was reduced by 20%. The crude product, which contained unchanged sample, was condensed at an average rate of 6 g. per hour, and a large quantity of the material was prepared. The production rate decreased with time, due to organic deposits on the metal packing, which had to be burned off periodically by a current of fluorine.

The crude sample was at first poured into water, washed with bicarbonate solution and dried, after which it was distilled in quantity from a Claisen flask by Mr. P. P. Phillips of this Laboratory into three main fractions, boiling from 70–200° (755 mm.); 65–145° (1 mm.); and 145–220° (1 mm.), respectively. Of these, the third, though clean, was so highly viscous that it could not be fractionated successfully, and was not further examined. The other two were combined, washed repeatedly with fuming sulfuric acid (15% $SO_3$) to remove unchanged hydrocarbon, again washed with water, neutralized and dried.

Then the combined product was recycled through the large reactor. Since it boiled over a wide range, a saturator could not be used, so the sample was introduced directly into the reactor maintained at 180–200° as above, at the rate of 15–20 g. per hour through a calibrated capillary under compressed air pressure as described by Fukuhara and Bigelow.[10] Under these conditions, which were adjusted for a maximum flow of fluorine per unit of sample without the simultaneous appearance of the halogen in the exit gases, there was little heat of reaction, not much hydrogen fluoride formed, and the product, cleaner than before, was recovered nearly quantitatively.

About 200 cc. of the recycled product was fractionated through the helix packed column, and yielded two main portions, boiling from 45–195° (100 cc.); and 60–100° at 5 mm. (85 cc.) respectively, leaving a boiler residue (15 cc.) of clear material too viscous to be rectified. The first of these contained three constant boiling portions, b. p. 137° (10 cc.), 140° (5 cc.), and 160° (30 cc.), of which the last two were shown later to be mixtures. The other product, m. p. −40°, b. p. 137°, constant refractive index 1.3068 at 25° and density 1.8946 at 25° was almost certainly completely fluorinated 1-methylnaphthalene, $C_{11}F_{20}$.

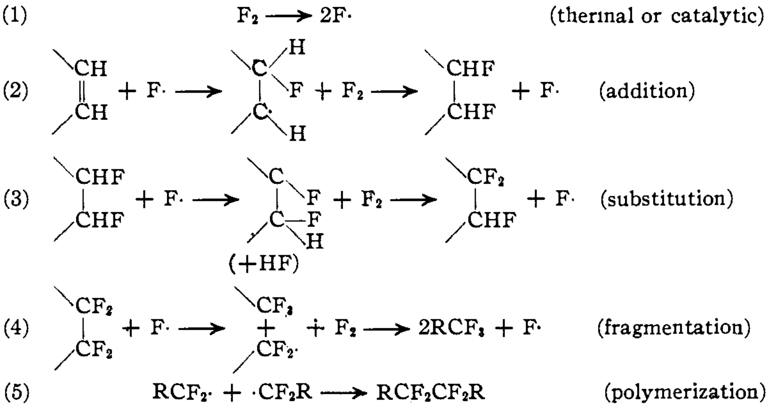
*Anal.* Calcd. for $C_{11}F_{20}$: F, 74.2; mol. wt., 512; *MR* 51.97. Found: F, 74.0, 74.4; mol. wt., 508, 514; *MR* 51.46.

The second main portion, distilling at reduced pressure, contained five constant boiling fractions, b. p. 75° (15 cc.), 82° (4 cc.), 85° (4 cc.), 88° (12 cc.) and 97° (10 cc.), all at 5 mm., together with 40 cc. of transition fractions. The molecular weights of these samples varied from 400–600, being in all cases close to multiples of 50, which is the molecular weight of the $-CF_2-$ unit, indicating that they all consisted of mixtures of polymerized fragments, which could be well represented by the formula $(CF_2)_x$. The stabilities of some of these portions toward reagents have been determined by A. R. Gilbert and Fred F. Holub of this Laboratory. It was found that they became stable toward refluxing 1% sodium hydroxide in twenty hours, with a loss of about 20% by hydrolysis; and that they were not affected appreciably by permanganate or bichromate solutions under strong oxidizing conditions.

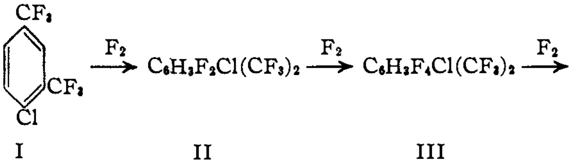
The analyses reported here were made by a modification of the well-known lead chlorofluoride method, after decomposition in a Parr bomb. The procedure is now under study in this Laboratory, and the results will be reported at a later date.

## Discussion of Theory and Results

As stated in the introduction, it seemed to be of considerable importance to study the intermediate stages, hitherto little known, of the progressive attack of elementary fluorine on the aromatic nucleus. The availability to us of well-purified 4-chloro-1,3-*bis*-(trifluoromethyl)-benzene, often referred to as the 4-chloro compound (I), fortunately provided an excellent example of an aromatic compound with a highly deactivated ring, which might well be expected to yield stable intermediates on fluorination. According to the postulates already referred to, the atomic chain reactions involved should take place by the mechanisms



Applying these to the progressive fluorination of I, the following changes, among others, might be expected to take place.



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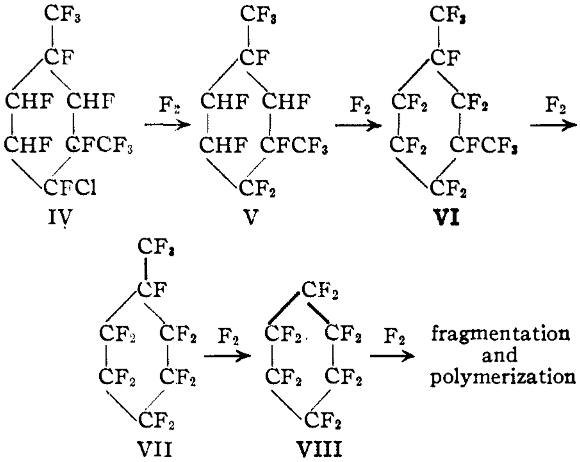
[10] Fukuhara and Bigelow, THIS JOURNAL, 63, 788 (1941).



Compounds II and III have been represented empirically, since no definite evidence was available to distinguish between the possible structural isomers which could result from 1,2 and 1,4 addition; and no account has been taken of stereochemical configurations in any case.

Actually, when I was fluorinated in the vapor phase under mild conditions, over a silver-plated copper wire packing as catalyst, all of the compounds I to VIII except IV were shown to have been formed, and even the latter may well have been present in the complex product. Substances VI, b.p. 99–100°, VII, m.p. −42°, b.p. 77.5° and VIII, b.p. 50° were known compounds which were separated and adequately identified; while the tetrafluoride III, b.p. 143°, was isolated and fully characterized so far as its empirical composition was concerned. It reacted vigorously with boiling alcoholic alkali to furnish both chloride and fluoride ions as would be expected in the case of an addition compound of this type. The difluoride II was separated in an apparently azeotropic mixture, b.p. 147°, with a constant refractive index, containing about 25% of unchanged I which boils only 1° higher. The mixture was believed to have this composition, and to contain II since (1) it gave the correct analysis and had the proper molecular weight; (2) it reacted vigorously with boiling alcoholic alkali to furnish chloride ion, while I was completely inert to this reagent; and (3) a larger sample, b.p. 146–150°, reacted readily with the same reagent to yield chloride ion, some fluoride ion, unchanged I, and a polymerized organic product of unknown composition. This evidence, while not entirely final, is considered to be at least reasonably conclusive. With regard to the structures of II and III, all that can be said now is that presumably a fluorine atom has added to position 4 in both cases, since the corresponding chlorine atom was activated. Finally, the heptafluoride V, that is, the hexafluoride in which the chlorine atom was also substituted by fluorine, was separated in an apparently azeotropic mixture, b.p. 113–114°, with a constant refractive index, containing about 40% of a corresponding cyclohexene derivative formed from it by the loss of hydrogen fluoride. This mixture was believed to have this composition and to contain V since (1) it also gave the requisite analysis and had the proper molecular weight; (2) it reacted vigorously with alcoholic alkali to furnish fluoride ion only; and (3) the loss of hydrogen fluoride was actually observed during the rectification. However, since the assumed unsaturation could not be demonstrated experimentally, this evidence, although good, cannot be regarded as quite so conclusive as that presented in favor of II.

The isolation of III represents the first case, it is believed, in which a fluorine addition product to an aromatic ring has been obtained with strictly constant physical properties, precise analysis and correct molecular weight.

It was hoped that benzotrifluoride, a much more available, somewhat similar substance with a deactivated ring, might also yield stable addition products with fluorine, but so far as we have been able to determine, such does not appear to be the case. Actually, when this compound was fluorinated in a large reactor under mild operating conditions, only the completely fluorinated products VII and VIII, as might be expected, and two isomers or isomeric mixtures having compositions corresponding to the formula $C_6HF_{10}(CF_3)$, b.p. 85–87° and 94–95°, respectively, were formed, together with polymerized material. All of our efforts to aromatize VII with metals, or to hydrolyze the —$CF_3$ group, were unsuccessful. The isomeric mixture, b.p. 85–87°, reacted readily with boiling alcoholic alkali to furnish fluoride ion, but only polymerized organic products resulted from the reaction.

The fluorination of 1-methylnaphthalene, a compound with a condensed ring system, was undertaken at this time since it should yield not only the completely fluorinated molecule, $C_{11}F_{20}$, but also fragmentation and polymerization products which might prove to have significant properties. When the compound was fluorinated in a large reactor over the usual catalyst at a rather high temperature, once recycled, rigorously purified and then repeatedly fractionated, only a very small proportion of $C_{11}F_{20}$, m.p. −40°, b.p. 137°, was obtained. The remainder of the product was a nearly colorless liquid, boiling all the way from 70° at 755 mm. to 220°, at 1 mm., and yielding fractions with progressively increasing viscosities as the boiling point rose. The highest boiling portions were too viscous to be fractionated, and set to transparent glasses on cooling. The lower-boiling fractions were repeatedly rectified, and yielded a considerable number of samples having constant boiling points, but all of these were clearly complex mixtures of highly fluorinated polymerized fragments. The molecular weights of a number of these varied from 400–600, being in all cases close to even multiples of 50, which is the molecular weight of the —$CF_2$— unit. These mixtures could not be resolved by any means now at our disposal.

It seems that in this reaction, the completely fluorinated molecule may have been formed at first, and then literally smashed by impacting high energy fluorine atoms. In this connection it is of interest that when certain fluorinations were conducted in an experimental glass reactor they were clearly seen to be accompanied, except under the mildest conditions, by intermittent or even continuous bluish flashing or glowing, indicating that a certain amount of combustion was nearly always taking place. Subsequently, the numerous fragments presumably polymerized to form the highly complex mixture actually observed. It is clear from the structure of $C_{11}F_{20}$, or, for that matter of any other similar fluorocarbon, that such a process would result in the formation of a product having an average composition very close to that represented by the formula $(CF_2)_x$. It is equally possible, of course, that the fragmentation and polymerization could have taken place, either wholly or in part, prior to the complete substitution of the hydrogen by the fluorine.

These results, taken together, provide concrete support for the assumption that the primary attack of elementary fluorine on the aromatic nucleus is one of addition, followed in most cases by varying degrees of substitution, fragmentation and polymerization.

## Summary

The compound 4-chloro-1,3-*bis*-(trifluoromethyl)-benzene, $C_6H_3Cl(CF_3)_2$, has been fluorinated in the vapor phase over a metal wire catalyst under mild conditions, yielding the tetrafluoride addition product having the exact composition required by the formula $C_6H_3F_4Cl(CF_3)_2$, but presumably consisting of a mixture of isomers, together with the completely fluorinated molecules $C_6F_{10}(CF_3)_2$, $C_6F_{11}(CF_3)$ and $C_6F_{12}$. Good evidence also has been presented to show that the related difluoride $C_6H_3F_2Cl(CF_3)_2$, and fluorohexafluoride $C_6H_3F_7(CF_3)_2$ were formed at the same time.

Benzotrifluoride, under similar conditions, yielded the expected completely fluorinated molecules $C_6F_{11}(CF_3)$ and $C_6F_{12}$; together with two distinct isomeric mixtures having the exact composition corresponding to the formula $C_6HF_{10}(CF_3)$, but apparently no stable addition products.

1-Methylnaphthalene, when fluorinated at somewhat higher temperatures and recycled, yielded only a small amount of the completely fluorinated molecule $C_{11}F_{20}$. Most of the product consisted of a clear, stable, highly complex liquid mixture of fragmentation and polymerization products. This mixture could not be separated by distillation, but numerous portions had average high molecular weights which corresponded closely to the formula $(CF_2)_x$.

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# Magnesium Dichromate and its Hydrates

BY WINSLOW H. HARTFORD

The state of the literature regarding magnesium dichromate is confused. It is reported by Reinitzer[1] that magnesium dichromate is soluble in alcohol, but no details are given of the preparation or composition of the salt. This is the reference on which Mellor[2] reports the existence of the compound, while Friend[3] states that it has not been prepared. An American patent[4] discloses the preparation of a paste of magnesium dichromate crystals by evaporation of a solution of magnesium chloride and sodium dichromate, separation of sodium chloride, and allowing the resulting solution to cool. No analysis of the product or properties of the material, other than great solubility, are given.

Further investigation of this problem yielded the following previously undescribed compounds.

## Experimental

**$MgCr_2O_7 \cdot 5H_2O$.**—In a typical experiment, 500 g. of magnesium oxide (U. S. P.) was added slowly with agitation to a solution of 2500 g. of technical chromium trioxide in 5 liters of water. The *p*H, as measured by a glass electrode meter, was then adjusted by the addition of magnesium oxide or chromium trioxide as needed to 2.8–3.0. The solution has a dark color due to small quantities of $Cr^{+++}$; this may be removed by electrolytic oxidation at 4–6 v. using lead electrodes. It is then filtered, concentrated to a volume of 2.5 liters (sp. gr. 1.74 at b. p.) and allowed to crystallize with agitation and slow cooling. The solution is very viscous and has a strong tendency to supersaturate; therefore it is desirable to seed when the mixture has cooled to about 60°. This may be conveniently done by wetting a glass rod with the solution, drying out partially over a low flame and adding the crust to the solution, or by chilling a small sample until crystals separate and pouring the slurry back into the main container. A crop of bright red-orange crystals was obtained on cooling to room temperature; the product was centrifuged and dried by passing a stream of dry air over the material in a rotating dryer at 50°. The yield is approximately 2 kg.

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[1] B. Reinitzer, *Z. angew. Chem.*, **26**, 456 (1913).

[2] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., New York, 1931. Vol. XI, 341.

[3] J. N. Friend, editor, "A Text-Book of Inorganic Chemistry," VII, part 3, J. F. Lippincott Co., Philadelphia, 1926, p. 56.

[4] G. Kranzlein and A. Voss, "Process for the Preparation of Magnesium Chromates," U. S. Patent 1,632,299; June 14, 1927.