even if $k_8 >> k_7$, the values of k_3 and k_{-5}/k_6 are not changed by as much as 1%. It is interesting to note that a twofold increase in the zero order rate results on decreasing the chloride ion concentration from 0.1 to 0.01 M at a constant concentration of benzhydryl chloride. Since the rate-controlling step in the zero order reaction is the rate of solvolysis of benzhydryl chloride, chloride ion can influence the rate only by participating in the equilibrium of Eqn. (4). The increase in rate is therefore a spectacular instance of the mass law effect on Eqn. (4) (with k_{-5}/k_6 equal to 8.0) which has been noted previously in other cases and interpreted as compelling evidence for the $\mathrm{S_N}1$ mechanism for alkyl halide hydrolysis.[33] Analysis of the effect in the present case is of course complicated by the presence of a double sequence of reactions: the simple solvolysis of benzhydryl chloride and the accompanying cycle of reactions in which diphenyldiazomethane participates. However, if Eqn. (4) were not an equilibrium step the zero order rate should show no dependence on chloride ion concentration; that the rate is actually affected can only be the result of the $\mathrm{S_N}1$ mechanism.

Summary

1. In ethyl alcohol solution diphenyldiazomethane reacts with ethyl alcohol in the presence of an acid catalyst to form ethyl benzhydryl ether. Kinetic studies by a spectrophotometric method have established that this reaction is subject to general acid catalysis. The effects on the rate of inert salt and of increasing concentrations of water in the ethyl alcohol solvent, both when the catalyst is solvated hydrogen ion and undissociated picric acid, have been determined.

2. In the presence of chloride ion, benzhydryl chloride is produced in a side reaction. With ethyloxonium ion in absolute alcohol the rate of disappearance of diphenyldiazomethane is accelerated by chloride ion; this effect vanishes in aqueous alcohol or if undissociated picric acid is the catalyst. The acceleration in rate is attributed to either a third order reaction involving diphenyldiazomethane, ethyloxonium ion, and chloride ion, or more probably a reaction between undissociated hydrochloric acid and diphenyldiazomethane.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. XV. Fluorine and Cobaltic Fluoride as Fluorinating Agents for Ketones[1]

BY FRED F. HOLUB[2] AND LUCIUS A. BIGELOW

This paper reports the results of a qualitative comparison of cobaltic fluoride with elementary fluorine as fluorinating agents for aliphatic ketones. Earlier work[3] here has shown that the direct fluorination of acetone over copper screen at about 100° and a molar reaction ratio of 6:1:18 yielded CF_3COCF_3 and CH_2FCOCH_3, together with CF_4, COF_2, CF_3COF and $(COF)_2$, about half the product being cleaved and a fifth of it self-condensed. This indicated that a good yield of the perfluoroketone should be obtained by using the milder cobaltic fluoride as the fluorinating agent.

Accordingly, acetone was fluorinated over cobaltic fluoride in a Fowler reactor (Fig. 2) at 60°, 0.2 mole per hour, and dilution (N_2) 1:10. Under such mild conditions only a trace of CF_4 was formed, but nevertheless the ketone was completely cleaved into COF_2, CHF_3, CH_3F, CH_2F_2, CH_3COF and CH_2FCOF. The appearance of CH_3F and CH_3COF in nearly equal amounts showed that part of the ketone had been cleaved before any hydrogen was substituted, and since no more highly fluorinated acyl fluorides than CH_2FCOF were formed, the molecule must have been split completely before half the hydrogen had been replaced, but no perfluoroketone was formed.

This quite unexpected result was shown to be general by fluorinating methyl ethyl ketone and diethyl ketone at 80 and 105°, respectively, under the same general conditions. Both were completely cleaved, the former yielding COF_2, CHF_3, impure CH_2F_2, CH_3CHF_2 + CHF_2CHF_2, CHF_2CH_2F, and CH_2FCOF; and the latter COF_2, CF_3CHF_2 + (?)CH_3CF_3, CH_3CHF_2 + CHF_2CHF_2, and CHF_2CH_2F, as could be predicted, but essentially nothing else. The unsymmetrical ketone was split mostly on the side of the carbonyl group next to the ethyl group and yielded much CHF_2CH_2F, while the symmetrical one as expected gave neither CH_2F_2 nor CH_2FCOF.

The general nature of the direct fluorination of acetone referred to above[3] was established by fluorinating methyl ethyl ketone over a copper shot packing in an improved reactor (Fig. 1)

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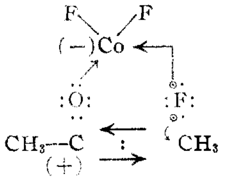
[1] This paper has been constructed from the Doctorate Thesis presented by Fred F. Holub to Duke University in March, 1949.

[2] Allied Chemical and Dye Corporation Fellow, 1946–1947. Present address: du Pont Experimental Station, Wilmington, Delaware. This project was also sponsored in part by the Naval Research Laboratory and aided by the Duke University Research Council. Grateful acknowledgment is hereby made for this material assistance.

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

at a maximum temperature of 135° and a molar reaction ratio of 6:1:8. There were formed $CF_3COCF_2CF_3$, f. p. −126°, b. p. 0° (15%), C_4HOF_7 and $C_4H_2OF_6$ (mixtures of isomers), together with the fragmentation products CF_4, COF_2, C_2F_6 and CF_3COF, as well as high boiling products. The reaction pattern was much the same as before, although the fluorination was milder, since it produced only half as much CF_4 and cleavage products as were formed in the earlier case.

The anomalous behavior of the milder cobaltic fluoride in cleaving the ketones, may well be accounted for by an atomic mechanism involving a coördination complex at the cobaltic fluoride surface, which may be represented as



This postulates an ephemeral ring, in which a reactive fluorine atom on the cobalt might well attack the spatially adjacent α-carbon atom of the ketone, cleaving the latter in this case into $CH_3\underset{\cdot}{C}O$ and CH_3F. These fragments would easily give rise to the CH_3COF, CH_2FCOF, COF_2 and CH_2F_2 actually found. In this way the total cleavage of the ketones by cobaltic fluoride may be explained adequately; and inasmuch as elementary fluorine would not form such a complex, it should, and actually did, give rise to considerable amounts of the corresponding perfluoroketones.

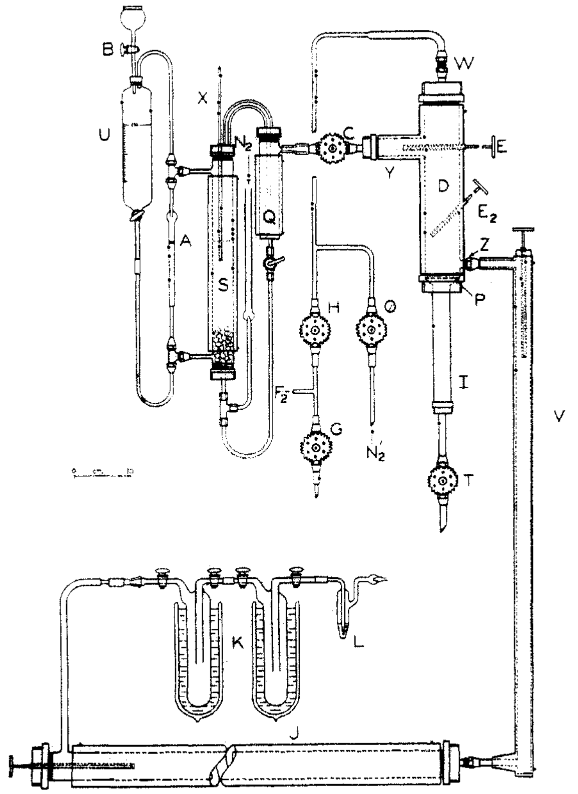


Fig. 1.—Apparatus for vapor-phase fluorination of volatile organic liquids.

The fluorinations of the various ketones, indirect and direct, were carried out under more than a dozen sets of conditions, as detailed for the most part in the experimental section. In general, while the temperature of the reaction zone had a marked influence upon the nature of the products formed, neither the rate of flow of the gases nor the dilution ratio had much effect, except as they influenced the temperature indirectly. In the direct fluorinations, the large mass of metal, the increased halide surface and the close packing of the reactor (Fig. 1), greatly reduced the rise in base temperature during the reactions with the result that of the lower boiling products (half or more of the total) from two-fifths to two-thirds was cleaved, while the rest consisted essentially of perfluoromethyl ethyl ketone, together with its mono and dihydro derivatives. In less well designed reactors, a much higher rise in base temperature produced complete cleavage by elementary fluorine.

Finally, the fluorination of pure fluoroethanes by cobaltic fluoride indicated that these compounds may be converted into one another in good yields, contrary to prevailing beliefs; and a single direct fluorination of cyclopentanone gave a small yield of the corresponding perfluoroketone, b. p. 24°.

In conclusion, it is clear that in the fluorination of aliphatic ketones the milder reagent, cobaltic fluoride, tended to cleave the molecules completely at an early stage and then to fluorinate the fragments so that no perfluoro compound could be formed; while the more vigorous reagent, elementary fluorine, tended to fluorinate the material first and then to split the resulting products so that a considerable yield of the perfluoroketone was formed, accompanied by its hydrogenated derivatives, cleavage products and polymeric material.

Experimental

Apparatus.—The improved direct fluorination unit used is shown to scale in Figure 1. The brass reactor D, which was a modification of one described earlier by Gilbert,[4] was equipped with a wide sample inlet tube Y, fluorine inlet W, exit tube Z, sump I, Weston thermometers E, as shown, and was closely packed (including Y) with copper shot supported on copper screen at P, which was bevelled for good drainage. The brass saturator S was partially filled with glass beads and equipped with the level regulator A (including filling unit B-U), thermometer X, nitrogen inlet N_2, spray trap Q, and was connected to D through C. The necessary lines were of $^3/_8$" or $^1/_4$" copper tubing, metal joints were either silver-soldered or flare fitted, and the valves were $^3/_8$" Kerotest with annealed copper or Teflon packings. The delivery tube V led to a

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(4) Gilbert and Bigelow, THIS JOURNAL, **72**, 2411 (1950).

1.5" × 4' pipe J packed with $^1/_8$" sodium fluoride pellets, which was followed by the collecting traps K, while D, S, Q, V, and J were electrically heated.

In operation before each run the reactor at 200° was swept with fluorine, entering through H, with O and G closed, and Z disconnected, until it could be detected at this point. This was followed by nitrogen, with O and G open and H closed, after which Z was reconnected. Then the base temperatures in D, V and J were adjusted, the rest of the system swept with nitrogen, the traps K cooled with nitrogen flowing, the temperatures of S and Q regulated, and the sample level set at A while metered nitrogen entered at N_2, with C closed and B open until complete equilibrium conditions had been attained. Then, in order to start the reaction, B was closed, C and H opened, and G closed in rapid succession; and this sequence could be reversed quickly whenever necessary. Under such conditions fluorine could not enter the saturator or sample back up into the generator, in case the lines became obstructed and safety traps failed to operate. These same valve operations were used to terminate the reaction, after which the system was swept out with twenty times its volume of nitrogen, with the reactor at 200°, the traps disconnected, the sump drained, and the sodium fluoride tube regenerated in the usual manner.

The unit employed, using cobaltic fluoride, is illustrated to scale in Fig. 2. It was similar in principle although different in detail from the one previously described by Fowler and collaborators[5,6] and so a brief description only will be given. The electrically heated cylindrical copper reactor F was closed by accurately machined caps with copper gaskets, charged with 1.6 kg. of anhydrous cobalt fluoride, and equipped with a set of rotating copper paddles mounted on a coaxial monel shaft O, which was driven at 16 r. p. m. by a motor through gear-reducer P, leather vibration damper H, and graphite asbestos packing gland G lubricated with high boiling fluorocarbon oil. The charge, heated to 200°, was first subjected to a current of fluorine through E until an excess could be detected in the exit gases above I, after which the excess of fluorine was displaced by nitrogen, and the reactor temperature adjusted to the required value. Then the sample was admitted from the unit AB, along with metered nitrogen entering at N_2, into a heated vaporizer below C and finally through D into the reactor F. The products left through the heated, copper screen packed, dust settling tower I, heated sodium fluoride tube or tubes J, and were finally collected in the condensing traps L; after which the reactor temperature was raised to 250° and the unit flushed with nitrogen until all volatile material had been carried into the traps. Later the reactor charge was refluorinated if necessary, and the sodium fluoride pellets in J regenerated in the usual manner.

The Fluorination of Acetone by CoF_3.—The commercial sample was dried over calcium chloride and rectified, using a central cut, b. p. 56.5°. It was introduced into the apparatus (Fig. 2) at 0.2 mole (16 cc.) per hr., dilution ratio (sample to N_2) 1:10, and reaction zone temperature 60°, maintained by reducing the external heating to offset that produced by the reaction. After 3 hr. the apparatus was flushed with nitrogen, the total product freed from hydrogen fluoride by passage over sodium fluoride pellets (two tubes) and the crude product (58 cc.) carefully rectified in a Booth-Podbielniak fractionating unit. The results are shown in Table I.

Second Fraction.—This material (15 cc.) was passed through 8% NaOH saturated with NaCl which removed 5 cc. of COF_2, leaving a mixture, mol. wt. 55, presumably containing CH_3F and CHF_3. This was examined under the direction of Dr. Walter Gordy, of the Duke Physics Department, using the micro-wave technique. Two sharp peaks corresponding to significant proportions of two compounds were observed, the one a first rotational line, $J = 0 \rightarrow J = 1$ at 51060 megacycles per second (CH_3F), and the other a third rotational line, $J = 2 \rightarrow J = 3$ at 41406 megacycles per second (CHF_3). These values corresponded exactly with those obtained from pure CH_3F and CHF_3 respectively under the same conditions. From the average molecular weight, these two compounds must have been present in the molar ratio 2:3 and the original mixture must have contained COF_2, CH_3F and CHF_3 in the approximate molar ratio 5:4:6.

TABLE I

THE RECTIFICATION OF FLUORINATED ACETONE BY CoF_3 AT 60°

Compound	Boiling point (°C.) Observed	Known	Molecular wt. Found	Calcd.	Approx. liquid vol. per cent.[a]
CF_4	....	.....	85	88	Trace
$COF_2 + CHF_3 +$ CH_3F	−82 to −75	.....	66–43	..	25
CH_2F_2	−52 to −50	−51.6	52	52	35
CH_3COF	19	20.5	63	62	10
CH_2FCOF	23(276 mm.)	51.5–52	80	80	20
Transitions	....	.....	...	..	10

[a] The results in this and subsequent tables are expressed in liquid volume per cent. of the total condensate, rounded off to the nearest 5%.

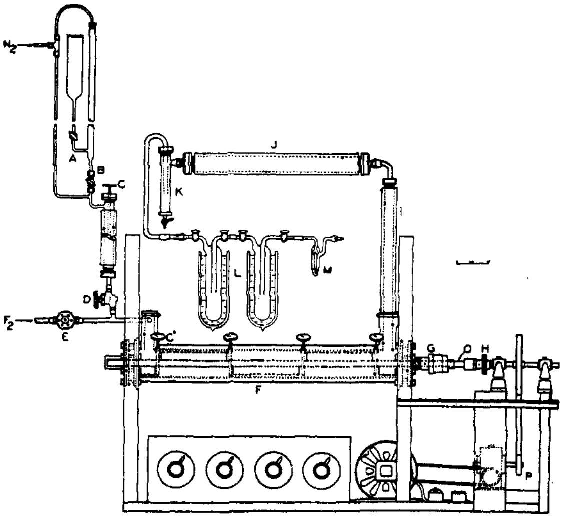

Fig. 2.—Cobalt trifluoride apparatus for vapor-phase fluorination.

Third Fraction.—Central cut b. p. −51.5°, mol. wt. 52, had a f. p. not previously reported, of −136°.

Fourth Fraction.—One cc. of this was treated with 2 cc. of $C_6H_5NH_2$ in ether and, after HCl extraction, removal of the ether, and recrystallization from water, pure C_6H_5-$NHCOCH_3$, m. p. 113-114°, was obtained.

Fifth Fraction.—See full characterization of corresponding material below.

The Fluorination of Methyl Ethyl Ketone by CoF_3.—The commercial sample was dried over calcium chloride and rectified, using a central cut, b. p. 79.5-79.8°, $n^{17}D$ 1.3811. This was fluorinated in the same unit (Fig. 2) under six sets of reaction conditions, and the products freed from hydrogen fluoride and carefully rectified as before. The results of the three most significant runs are collected in the following composite Table II. Run (3) under the mildest operating conditions was perhaps the most important, but even in this case the ketone was completely cleaved.

Fractions 1, 8 and 16.—These materials, b. p. −94 to −83°, mol. wt. 94-60, consisted essentially of liquid COF_2 (b. p. −83°, mol. wt. 66), contaminated with vary-

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[5] Fowler, Burford, Hamilton, Sweet, Weber, Kasper and Litant, *Ind. Eng. Chem.*, **39**, 292 (1947).

[6] Burford, Fowler, Hamilton, Anderson, Weber and Sweet, *ibid.*, **39**, 319 (1947).

TABLE II

THE RECTIFICATION OF FLUORINATED METHYL ETHYL KETONE BY CoF_3

Fraction	Boiling range, °C.	Mol. wt.	Approx. liquid vol. per cent.
(1) Rate 0.4 mole per hr.; diln. 1:6; temp. 120°; crude product 54 cc.			
1	−88 to −83	87–60	5
2	−83 to −80	66–70	25
3	−52 to −48	64–115	15
4	−26 to −20	96–98	15
5	+3	84	15
6	> +3	. . .	15
7	Transitions	. . .	10
(2) Rate 0.2 mole per hr.; diln. 1:5; temp. 80°; crude product 50 cc.			
8	−94 to −84	94–60	5
9	−84 to −80	63–69	15
10	−51	60–61	10
11	−25 to −24	74	10
12	4	84	10
13	0 to +7 (320 mm.)	66–68	10
14	0 (80 mm.)	81	20
15	Transitions	. . .	15
(3) Rate 0.2 mole per hr.; diln. 1:10; temp. 80°; crude product 55 cc.			
16	−88 to −83	82–69	5
17	−83 to −81	66–70	15
18	−51	60	10
19	−26 to −20	69–76	20
20	+1 to +2	84	20
21	0 to 24 (290 mm.)	68–84	10
22	5 (114 mm.)	80	20
23	Transitions	. . .	5

ing amounts of the subliming CO_2 (mol. wt. 44) and SiF_4 (mol. wt. 104).

Fractions 2, 9 and 17.—These mixtures, b. p. −84 to −80°, mol. wt. 63-70, consisted essentially of COF_2 and CHF_3, contaminated with subliming solids. Fraction 17 on rectification, yielded a portion, b. p. −82°, mol. wt. 66 (COF_2 b. p. −83°, mol. wt. 66); and also when this fraction was passed through NaOH and the neutral residue dried and rectified, it boiled at −82°, mol. wt. 70 (CHF_3 b. p. −82°, mol. wt. 70). Obviously the higher temperature favored the formation of these highly fluorinated fragments.

Fractions 3, 10 and 18.—These portions, b. p. −52 to −48°, mol. wt. 60-115, undoubtedly consisted mostly of CH_2F_2 (b. p. −51.6°, mol. wt. 52). Fraction 3, which was obviously favored by higher temperature, probably contained a considerable proportion of CF_3CHF_2 (b. p. −48°, mol. wt. 120), not present in fractions 10 and 18. These latter fractions, boiling at −51°, mol. wt. 60-61, could not be resolved by distillation, and presumably contained a different contaminant, which was not identified, but may have been CH_3CF_3 (b. p. −47°, mol. wt. 84) derived from CH_3CHF_2.

Fractions 4, 11 and 19.—These fractions, b. p. −26 to −20°, mol. wt. 69-98, were almost certainly mixtures of CH_3CHF_2, and CHF_2CHF_2. Fraction 4, favored by higher temperatures, was nearly pure CHF_2CHF_2 (b. p. −23°, mol. wt. 102); while fraction 19, highly favored by the mildest operating conditions, consisted largely of CH_3CHF_2 (b. p. −24.7°, mol. wt. 66), as did fraction 11. To prove this, an accumulated sample (5 cc., b. p. −25°, mol. wt. 69) reacted with an excess of chlorine for 20 hr., using a 200-watt light as the activator. The product was passed through a solution containing 8% NaOH and 6% $NaHSO_3$, dried, condensed and again rectified. A portion boiled at −8.5°, mol. wt. 102, corresponding to CH_3CF_2Cl (b. p. −9.6°, mol. wt. 100).

Fractions 5, 12 and 20.—These were essentially CHF_2CH_2F (b. p. +5°, mol. wt. 84), favored by mildest conditions.

Fractions 14 and 22.—These were favored by mild operating conditions. The first was slightly impure CH_2FCOF, while the second, b. p. +5° at 114 mm., mol. wt. 80, was pure CH_2FCOF, which has recently been described as boiling at 51.5-52°,[7] but not completely characterized It was found to be a colorless, fuming liquid presumably very toxic, m. p. −83°, b. p. 52° (micro).

Anal. Calcd. for $C_2H_2OF_2$: F, 47.5; mol. wt. 80. Found: F, 47.5, 47.7; mol. wt., 80.

All the analyses are by Mrs. A. R. Gilbert, to whom grateful acknowledgment is hereby expressed.

On treatment with an excess of gaseous ammonia the acid fluoride was readily converted into the corresponding amide CH_2FCONH_2, which separated from chloroform in white crystals, m. p. 107.5-108° (108°).[8]

The other three runs were operated on a qualitative basis, and represented vigorous operating conditions as follows: (4) rate 0.05 mole per hr., diln. 1:16, temp. 125-155°, crude product 50 cc.; (5) rate 0.2 mole per hr., diln. 1:3, temp. 155°, crude product 38 cc.; (6) rate 0.2 mole per hr., diln. 1:3, temp. 100°, product 24 cc. With respect to these, in (4) and (5), where the operating conditions were most vigorous, the material boiling near −52° was largely CF_3CHF_2, while that near −25° was entirely CHF_2CHF_2 and essentially none at +5° was isolated, since apparently neither CH_3CHF_2 nor CHF_2CH_2F had escaped further fluorination. On the other hand in (6), where the temperature was lower, the material boiling near −52° apparently contained much CH_2F_2, while that near −25° was contaminated with CH_3CHF_2, and much CHF_2CH_2F (b. p. +5°) was isolated.

The Fluorination of Diethyl Ketone by CoF_3.—This ketone was dried and redistilled in the usual manner, central cut, b. p. 102°. It was introduced into the reactor (Fig. 2) at 0.2 mole per hr., dilution ratio 1:10, and reaction zone temperature 105° representing mild operating conditions. The crude product, freed from hydrogen fluoride, amounted to 43 cc., and was rectified in the usual manner. The results are collected in Table III.

TABLE III

THE RECTIFICATION OF FLUORINATED DIETHYL KETONE BY CoF_3 AT 105°

Fraction	Boiling Range (°C.)	Vol. wt.	Approx. liquid vol. per cent.
1	−84 to −80	66	20
2	−47	102	15
3	−25 to −19	94–90	25
4	5	85	25
5	23 (600 mm.)	78	Trace
Transitions	....	....	10

Fraction 1.—This material was soluble in sodium hydroxide and was essentially pure COF_2 (b. p. −83°, mol. wt. 66), uncontaminated by CHF_3, as would be expected.

Fraction 2.—This portion was believed to consist of CF_3CHF_2 (b. p. −48.5°, mol. wt. 120) and CH_3CF_3 (b. p. −46.7°, mol. wt. 84). It is unlikely that CH_2F_2 would have been formed in this case.

Fraction 3.—This material was undoubtedly the usual mixture of CHF_2CHF_2 (b. p. −23°, mol. wt. 102) and CH_3CHF_2 (b. p. −24.7°, mol. wt. 66).

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[7] Gryszkiewicz-Trachimowski, Sporzynski and Wnuk, *Rec. trav. chim.*, **66**, 422 (1947).

[8] Swartz, *Bull. classe sci., Acad. roy. Belg.*, **11**, 30 (1909).

Fraction 4.—This was pure CHF_2CH_2F, as would be expected.

Fraction 5.—This very small portion may have contained some CH_3CH_2COF (b. p. 43.5°, mol. wt. 76), but this was not proved.

The Fluorination of Certain Fluoroethanes by CoF_3.—These experiments were conducted in general as described before to show how efficiently these fluoroethanes could be converted into one another by cobaltic fluoride, under varying conditions. The low boiling samples were slowly vaporized into the reactor from a graduated ampoule suspended over a refrigerant, instead of being metered in from a buret. The products were processed, collected, and subsequently rectified as before, and the essential results are summarized in Table IV, in which the percentages given represent pure compounds, and the transition fractions are not indicated.

TABLE IV

THE FLUORINATION OF CHF_2CH_2F AND CHF_2CHF_2 BY COBALTIC FLUORIDE

Fluoroethanes	Rate,[a] cc. hr.	N_2 diln. ratio	Temp., °C.	Approx. liquid vol. per cent. of CHF_2-CH_2F	CHF_2-CHF_2	CF_3-CHF_2	C_2F_6
CHF_2CH_2F	20	1:3	40	95	Trace	..	...
CHF_2CH_2F	20	1:3	100	65	25	..	...
CHF_2CH_2F	10	1:1.5	155–170	..	45	35	...
CHF_2CHF_2	8	1:1	170	..	40	50	10[b]

[a] Approximately. [b] Mol. wt. 130, calcd. 138.

Stratification of Boiling Points.—A real difficulty encountered in the separation of the low-boiling products formed during the indirect fluorinations was the extraordinary stratification in the boiling points of these compounds in the vicinity of −80, −50, and −25°. However, it was possible to interpret the changes in the molecular weights of the respective fractions as the vigor of the fluorinations increased, in a very satisfactory manner. For example, in the various fluorinations of methyl ethyl ketone by cobaltic fluoride, the material boiling near −25° varied progressively in molecular weight from 69 to 103. This meant that CH_3CHF_2, molecular weight 66, was being gradually removed by further fluorination to form the higher boiling CHF_2CH_2F, or perhaps the lower boiling CH_3CF_3, and being gradually replaced by CHF_2CHF_2, molecular weight 102, itself being formed by the further fluorination of the higher boiling CHF_2CH_2F. When the temperature was high enough so that the portion boiling near −25° had become pure CHF_2CHF_2, the reaction mixture appeared to contain neither CH_3CHF_2 nor CHF_2-CH_2F. The other fractions difficult to separate could be dealt with equally well.

The Direct Fluorination of Methyl Ethyl Ketone at 120°.—The ketone was fluorinated in the unit illustrated in Fig. 1, and described in detail above. A total of 2.8 l. per hr. nitrogen was passed through the saturator at 60°, and carried 0.05 mole sample into the reactor, maintained at base temperature 80°, where it met and reacted with 0.3 mole fluorine carried in on 17.1 l. per hr. nitrogen, corresponding to a molar reaction ratio (F_2:sample:N_2) of 6:1:16. The base temperature at the reaction zone rose to 120°, where it remained essentially constant. The exit gases were passed over sodium fluoride pellets at 100°; and condensed by liquid air in the usual manner. The crude product (100 cc. in 20 hr. operation), was transferred as far as possible into the low temperature fractionating unit, and carefully rectified. The results are shown in Table V.

TABLE V

THE RECTIFICATION OF FLUORINATED METHYL ETHYL KETONE BY ELEMENTARY FLUORINE AT 120°

Compound	Boiling point (°C.) Observed	Known	Molecular wt. Found	Calcd.	Approx. liquid vol. per cent.
CF_4	−127	−128	87	88	5
COF_2	−82	− 83	67–72	66	5
Transition	−82 to −0.5	...	......	...	10
$CF_3COCF_2CF_3$	−0.5 to 0.0	...	205–251	216	10
C_4HOF_7	0.0 to 21 and up to 5 (237 mm.)	...	199–197	198	10
Transition	6 to 24 (237 mm.)	...	175–163	...	10
Residue	....	...	......	...	50

The COF_2 Fraction.—When this impure sample (7 cc.) was passed through 8% NaOH, 5 cc., essentially COF_2, was absorbed, leaving a neutral residue, mol. wt. 111–124, which probably contained C_2F_6.

The $CF_3COCF_2CF_3$ Fraction.—This portion contained only a trace of material having a molecular weight less than 210. The pure perfluoroketone (5% of total condensate) boiled at 0.0°, and froze at −126°, mol. wt. 215 (calcd. 216).

The C_4HOF_7 Fraction.—On redistillation this portion yielded a small amount (2.5% of total) of the pure heptafluoro methyl ethyl ketone, C_4HOF_7 (mixture of isomers), which was a straw yellow liquid, b. p. 21°.

Anal. Calcd. for C_4HOF_7: F, 67.2; mol. wt., 198. Found: F, 67.1, 67.1, 66.9; mol. wt., 198.

The Direct Fluorination of Methyl Ethyl Ketone at 135°.—The ketone was fluorinated as before. A total of 2.8 l. per hr. of nitrogen was passed through the saturator at 60°, and carried 0.05 mole of sample into the reactor maintained at a base temperature of 80°, where it met and reacted with 0.3 mole of fluorine carried in on 7.2 l. per hr. of nitrogen, corresponding to a molar reaction ratio of 6:1:8. The base temperature at the reaction zone rose to 135° and remained constant. The products (130 cc. in 25 hr. of operation), were collected and processed as before. At first about 35 cc. of material, boiling up to −75°, was separated from the main product, passed through 10% NaOH saturated with NaCl to remove COF_2 and other reactive gases, after which it was rectified separately and yielded CF_4, C_2F_6 and some transition material. Then the main product was rectified in the usual manner and the combined results, which were significant, are shown in Table VI.

TABLE VI

THE RECTIFICATION OF FLUORINATED METHYL ETHYL KETONE BY ELEMENTARY FLUORINE AT 135°

Compound	Boiling point Observed	(°C.) Known	Molecular wt. Found	Calcd.	Approx. liquid vol. per cent.
CF_4	−126	−128	88–89	88	10
COF_2	....	...	.....	...	10
C_2F_6	−78	− 78	137	138	5
Transition	−75 to 0.0	...	.....	...	15
$CF_3COCF_2CF_3$	0.0	...	215–216	216	15
C_4HOF_7	15 to 21	...	200–198	198	5
$C_4H_2OF_6$	3 to 17 (140 mm.)	...	183–179	180	Trace
Transition	17 to 29 (140 mm.)	...	168–153	...	Trace
Residue	....	...	.....	...	35

The First Transition.—On redistillation this fairly large portion yielded a fraction, b. p. −60 to −55°, mol. wt. 101–117, believed to contain CF_3COF (b. p. −59°, mol. wt. 116). To prove this, the material was treated with an excess of liquid ammonia, the ammonia removed, the residue neutralized, extracted with ether, and the solvent again removed, leaving a white solid, which on crystallization from chloroform yielded pure CF_3CONH_2, m. p. 74–75° (74.8°).[9]

The $CF_3COCF_2CF_3$ Fraction.—This product was pure perfluoromethyl ethyl ketone, which was a colorless, water soluble liquid, f. p. −126°, b. p. 0.0°.

Anal. Calcd. for C_4OF_8: F, 70.4; mol. wt., 216. Found: F, 70.3, 70.5; mol. wt., 215–216.

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[9] Swartz, *Bull. classe sci., Acad. roy. Belg.*, **8**, 343 (1922).

The perfluoroketone readily yielded a semicarbazone from a concentrated aqueous solution, which, on recrystallization from a benzene alcohol mixture and drying at 78° under reduced pressure, melted at 137-138° (dec.).

Anal. Calcd. for $C_5H_3N_3OF_8$: F, 55.6. Found: F, 55.6.

The C_4HOF_7 Fraction.—On redistillation this fraction yielded a small amount (1.5% of the total) of pure C_4HOF_7, b. p. 21°, mol. wt., 198 (see analysis above).

The $C_4H_2OF_6$ Fraction.—This portion on redistillation gave a considerable central cut (1.5% of the total), which was pure hexafluoromethyl ethyl ketone, $C_4H_2OF_6$ (mixture of isomers), b. p. 15° at 140 mm.

Anal. Calcd. for $C_4H_2OF_6$: F, 63.3; mol. wt., 180. Found: F, 63.5, 63.4; mol. wt., 179, 180.

The Second Transition.—This material contained a small amount of unstable product (1% of the total), b. p. 26° at 140 mm., mol. wt., 164, 162, which may have contained isomeric pentafluoromethyl ethyl ketones (calcd. mol. wt. 162).

The Direct Fluorination of Cyclopentanone.—This ketone was fluorinated as before at 0.05 mole (4.2 g.) per hr., saturator temperature 84°, reaction ratio 6:1:16, base temperature 127°, and equilibrium reaction temperature 178°. After processing in the usual way, the crude product in 5 hrs. of operation amounted to 28 cc., which was subsequently rectified. From this preliminary run, only one pure product could be isolated, which was perfluorocyclopentanone (1 cc.), a colorless liquid boiling at 24°.

Anal. Calcd. for C_5OF_8: F, 66.6; mol. wt., 228. Found: F, 66.5, 66.8; mol. wt., 226, 228.

This perfluoroketone formed a semicarbazone which separated from water, and on recrystallization from a benzene-alcohol mixture, came down as white crystals of the monohydrate, m. p. 185-186° (dec.).

Anal. Calcd. for $C_6H_3N_3OF_8 \cdot H_2O$: F, 50.1. Found: F, 50.2, 50.3.

Summary

Acetone, methyl ethyl ketone and diethyl ketone have been fluorinated by cobaltic fluoride in a modified Fowler apparatus. The ketones were completely cleaved under the mildest conditions used, and it has been shown that acetone was split, in part at least, before any substitution had occurred.

In contrast, methylethyl ketone has been fluorinated by elementary fluorine, in a recently modified unit which is described in detail. Under these conditions the perfluoroketone $CF_3COCF_2CF_3$ was formed in significant yield, together with smaller amounts of the corresponding heptafluoro- and hexafluoroketones (isomeric mixtures), as well as a number of cleavage products, including CF_4, C_2F_6 and CF_3COF.

The observed total cleavage by the milder reagent, and only partial fragmentation by the more vigorous reagent, has been attributed to the formation of transitional complex compounds between the ketones and the cobaltic fluoride, which would be expected to promote cleavage. Presumably such complexes would not be formed when elementary fluorine was used.

Certain related work has also been described, including the formation of perfluorocyclopentanone by the direct method, and the conversion of some fluoroethanes into one another in good yields by cobaltic fluoride.

DURHAM, N. C. RECEIVED SEPTEMBER 2, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Some Substituted Naphthylsilanes

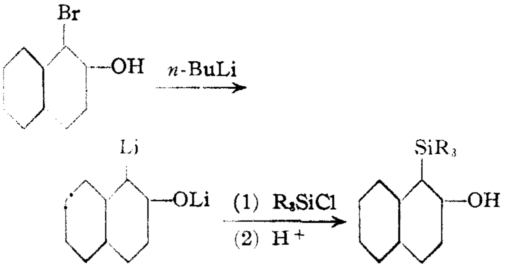
BY S. V. SUNTHANKAR AND HENRY GILMAN

Although a large number of alkyl- and aryl-silanes have been prepared, very few naphthylsilanes have been reported. The only compounds recorded in the literature are triethoxynaphthylsilanes and trichloro-1-naphthylsilane prepared, respectively, by the action of ethyl silicate and silicon tetrachloride upon the corresponding Grignard reagents.[1] Several di- and tri-naphthylsilanes have recently been prepared[2] in connection with a study of steric effects in silicon compounds.

We now wish to report the preparation and properties of several new naphthylsilanes which were needed for the synthesis of silicon-containing azo dyes.

A convenient method for the preparation of organosilicon compounds is by the action of chlorosilanes upon organolithium compounds.[3] Trialkylsilyl- and triarylsilyl-naphthols were compounds of choice for our work. Therefore, trimethyl- and triphenylchlorosilanes were used to react with the lithium compounds of naphthols and their methyl ethers. The lithium compounds of methoxynaphthalenes were prepared both by

(I)



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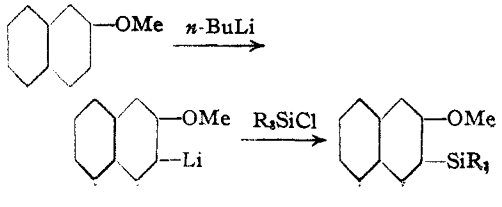

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[1] Khotinsky and Seregenkoff, *Ber.*, **41**, 2952 (1908); Melzer, *ibid.*, **41**, 3394 (1908); Andrianov, *J. Gen. Chem.* (*U. S. S. R.*), **16**, 487 (1946) [*C. A.*, **41**, 701 (1947)].

[2] Unpublished studies of Cecil G. Brannen.

[3] (a) Fleming, U. S. Patent 2,386,452 (1945) [*C. A.*, **40**, 603 (1946)]; (b) Gilman and Clark, THIS JOURNAL, **68**, 1675 (1946); (c) *ibid.*, **69**, 1499 (1947); (d) Tyler, Sommer and Whitmore, *ibid.*, **70**, 2876 (1948).