442. *The Preparation and Reactions of Carbonyl and Sulphuryl Fluorides and Chlorofluorides.*

By H. J. EMELÉUS and J. F. WOOD.

The preparation of carbonyl fluoride and chlorofluoride by the autoclave reaction of carbonyl chloride with antimony trifluoride is described. Sulphuryl fluoride and chlorofluoride may be similarly prepared from antimony trifluoride and sulphuryl chloride, but sulphuryl fluoride is more conveniently obtained from sulphur dioxide and argentic fluoride. Reactions of these substances are described, and it is shown that sulphuryl fluoride and chlorofluoride give no fluorinating reaction analogous to the chlorinating reaction of sulphuryl chloride catalysed by benzoyl peroxide.

CARBONYL fluoride was first prepared in a pure state by Ruff and Miltschitzky (*Z. anorg. Chem.*, 1934, **221**, 154) by the interaction of carbon monoxide and argentic fluoride. An alternative method of preparation by the reaction of carbonyl chloride with hydrogen fluoride under pressure, using antimony pentachloride as a catalyst, yields both the fluoride and the chlorofluoride, but the former is always contaminated by hydrogen chloride (Simons, Herman, and Pearlson, *J. Amer. Chem. Soc.*, 1946, **68**, 1672). Carbonyl fluoride and hydrogen chloride, b. p. $-83°$ and $-83{\cdot}7°$ respectively, cannot be separated by distillation. The preparative method described below is based on the autoclave reaction between carbonyl chloride and antimony trifluoride. It may be made to yield either carbonyl fluoride or the chlorofluoride as the main product, and has the advantage that the preparation of carbonyl fluoride free from hydrogen chloride is possible. The carbonyl fluoride is contaminated with 5—10% of carbon dioxide, which does not interfere with the study of the reactions with certain organic compounds.

Carbonyl fluoride is hydrolysed by water to carbon dioxide and hydrogen fluoride. It attacks glass but may be handled in silica or metal apparatus. No reactions with organic compounds have been described in the literature. It is now shown that the products with aniline, methylaniline, diethylamine, ethanol, and phenol are phenylcarbamyl fluoride, *phenylmethylcarbamyl fluoride*, *diethylcarbamyl fluoride*, ethyl fluoroformate, and *phenyl fluoroformate* respectively. Buckley, Piggott, and Welch (*J.*, 1945, 864) first prepared phenylcarbamyl fluoride by the addition of hydrogen fluoride to phenyl *iso*cyanate, and Ray (*Nature*, 1933, **132**, 173) prepared ethyl fluoroformate from ethyl chloroformate and thallous fluoride : the other compounds mentioned are new. The table below compares the boiling and melting points of the analogous fluoro- and chloro-derivatives. The fluoro-compounds are in general more stable to heat and less readily hydrolysed.

Deriv. from :	Fluoro-compound.	Chloro-compound.
NH_2Ph	M. p. 32°	M. p. 58°
NHMePh	B. p. 109/14 mm.	M. p. 88 [1]
$NHEt_2$	B. p. 154	B. p. 187—190 [2]
EtOH	B. p. 57	B. p. 94
PhOH	B. p. 153	B. p. 187 (decomp.) [3]

[1] Michler and Zimmermann, *Ber.*, 1879, **12**, 1165.
[2] Lumière and Perrin, *Bull. Soc. chim.*, 1904, **31**, 689.
[3] Hentschel, *J. pr. Chem.*, 1887, **36**, 305.

In its reactions with amines and ethanol, carbonyl chlorofluoride behaved as the acid chloride of the hypothetical fluoroformic acid. With diethylamine, methylaniline, and ethanol under suitable conditions only the carbamyl fluorides and fluoroformate were produced.

Sulphuryl fluoride was first prepared by Moissan and Lebeau (*Compt. rend.*, 1901, **132**, 374) by the direct union of fluorine and sulphur dioxide on a hot platinum wire. Traube, Hoerenz, and Wunderlich (*Ber.*, 1919, **52**, 1272) prepared it by heating barium fluorosulphonate. It has been found, however, that the compound is more conveniently prepared by the reaction of sulphur dioxide with argentic fluoride. Some investigations were also made on the autoclave reaction between sulphuryl chloride and antimony trifluoride. With antimony pentachloride as a catalyst a 25% yield of sulphuryl fluoride was obtained, the other volatile product being sulphur dioxide, which is believed to be formed by reaction of sulphuryl chloride (*a*) with the walls of the autoclave or (*b*) with the antimony trifluoride, giving quinquevalent antimony halide. In an attempt to eliminate the second of these side reactions, antimony trifluoride was replaced by antimony trifluorochloride but the formation of sulphuryl fluoride was almost completely suppressed, sulphuryl chlorofluoride being obtained in fair yield (65%). The treatment of sulphuryl chlorofluoride with fresh antimony trifluorodichloride also gave only a low yield (5%) of the fluoride, together with much sulphur dioxide. Almost half of the chlorofluoride was recovered unchanged. Most of the sulphuryl fluoride used in this investigation was made from sulphur dioxide and argentic fluoride.

Sulphuryl chlorofluoride was first prepared in an impure state by Davies and Dick (*J.*, 1932, 2042) by chlorination of toluene-*o*-sulphonyl fluoride. This reaction has now been re-examined, and the product characterised. Booth and Herrmann (*J. Amer. Chem. Soc.*, 1936, **58**, 63) described the autoclave reaction between sulphuryl chloride and antimony trifluoride, with antimony pentachloride as a catalyst. The reaction was studied in an autoclave fitted with a water-cooled head, through which the volatile products were continuously taken off. At 300°/6·5 atm. no sulphuryl fluoride was obtained, the chlorofluoride being contaminated with sulphur dioxide. Gowland (B.P. 527,713) has shown that yields of the chlorofluoride up to 90% are obtained in this reaction if a little water is used as a catalyst, but no sulphuryl fluoride results. In repeating these experiments on the preparation of sulphuryl fluoride, a closed autoclave which was not fitted with a reflux head was employed. Much higher pressures (up to 100 atm.) were observed, which may well account for the production of the fluoride (see above) as well as the chlorofluoride in the present experiments.

The chief interest in studying the reaction of sulphuryl fluoride and chlorofluoride was in their possible use as halogenating agents. Kharasch and Brown (*J. Amer. Chem. Soc.*, 1939, **61**, 2142; *Ind. Eng. Chem.*, 1944, **36**, 785) have shown that sulphuryl chloride, catalysed by benzoyl peroxide, is able to chlorinate hydrocarbons at reasonably low temperatures. Typical reactions of this type are described below in which sulphuryl fluoride has been used in place of sulphuryl chloride, but it was found that no fluorination resulted. On the other hand, the reactions of sulphuryl fluoride and chlorofluoride with diethylamine were vigorous, leading to the formation of diethylsulphamyl fluoride with sulphuryl fluoride, and diethylsulphamyl chloride with sulphuryl chlorofluoride. The former has been prepared by the fluorination of diethylsulphamyl chloride with a concentrated aqueous solution of potassium fluoride (B.P. 457,119), and the latter by the reaction between diethylamine and sulphuryl chloride (Binkley and Degering, *J. Amer. Chem. Soc.*, 1939, **61**, 3250). This difference in the behaviour of sulphuryl chloride and fluoride may be attributed to the difference in the strength of the S–Cl and S–F bonds. The catalytic reaction of benzoyl peroxide in the case of sulphuryl chloride is attributed by Kharasch to the primary formation of a phenyl radical which reacts as follows:

$$C_6H_5^{\cdot} + SO_2Cl_2 \longrightarrow SO_2Cl^{\cdot} + C_6H_5Cl$$
$$SO_2Cl^{\cdot} \longrightarrow SO_2 + Cl^{\cdot}$$
$$Cl^{\cdot} + RH \longrightarrow R^{\cdot} + HCl$$

It appears from the experiments described here that sulphuryl fluoride is sufficiently stable to resist the first step in such a reaction.

EXPERIMENTAL.

Fluorinations under pressure were carried out in a rotating mild steel autoclave (1500 c.c. capacity) fitted with a thermometer pocket, fine-adjustment outlet valve, and Bourdon gauge. It was gas-heated. In charging it with substances boiling below room temperature the liquefied gas was sucked into the autoclave while the latter was cooled in an ice–salt mixture. Alternatively, the autoclave was cooled by allowing liquid air to evaporate in it, and the liquified gas was poured in. The copper autoclave used in the preparation of carbonyl chlorofluoride was of the type described by Booth and Herrmann (*loc. cit.*).

The low-temperature still (Fig. 1) had a vacuum-jacketed glass tube *A* (400 mm. × 15 mm.) packed with single-turn Fenske spirals, and was surrounded by an aluminium tube to act as thermal insulator.

The still-pot, *B*, was heated in an alcohol-bath on an electric hot-plate, and the rising vapours were condensed in the still head *C* which, for gases boiling above about − 70°, was filled with a solid carbon dioxide–alcohol mixture. For temperatures below − 70° the still head was filled with a suitable liquid maintained at its m. p. by the occasional addition of liquid nitrogen. The condensed liquid passed over the tip of the thermocouple (*D*) placed against the edge of the weir at *E*. The b. p. of liquids boiling below room temperature was indicated by the minimum temperature of the refluxing liquid. A little of the refluxing liquid was retained in the tube *F* leading to the tap *G*, lubricated with a silicone grease, which was opened momentarily when the column reached equilibrium to allow some of the reflux to flow into the cooled receiver *H*. Successive quantities of distillate were drawn off in this way as equilibrium was re-established in the column.

An apparatus for the measurement of boiling points below room temperature is shown in Fig. 2. The condenser *A* was suitably cooled below the b. p. of the compound, and the liquid in *B* (2—3 c.c.) was allowed to boil gently, some of the reflux being trapped in the well *C*, whilst the bulk returned to *B* by the spill-over hole. The temperature was recorded by the thermocouple with its tip immersed in the liquid in *C*.

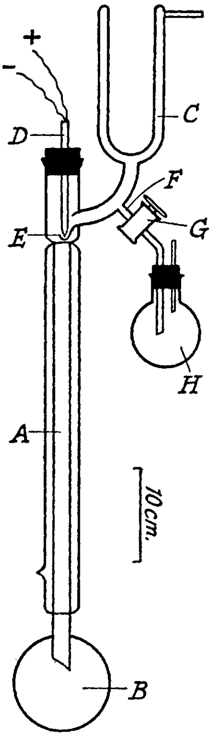

FIG. 1.

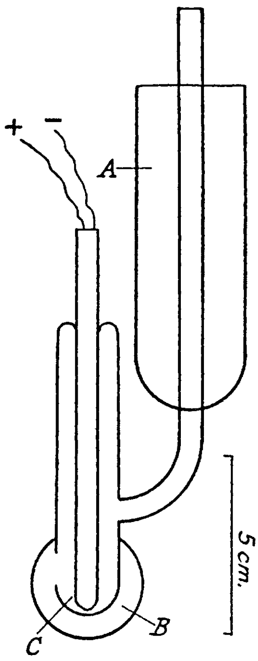

FIG. 2.

Preparation of Carbonyl Chlorofluoride.—Commercial antimony trifluoride (1 mol.), dried at 120° and ground to a fine powder, carbonyl chloride (4 mols. ≡ 33% excess), and antimony pentachloride (10 c.c.) were heated to 135° in the copper autoclave for one hour. The reflux head was cooled by running water at 15°. The pressure rose from an initial value of 40 lb./in.^{2} to approx. 475 lb./in.^{2}. The gases were led off from the cold autoclave, and the carbonyl chlorofluoride and unreacted carbonyl chloride condensed in glass traps cooled in solid carbon dioxide. A small quantity of carbonyl fluoride (b. p. −83°) escaped. The condensed gases were separated by distillation in the low-temperature liquid take-off still. Carbonyl chlorofluoride (2·1 mols.) was collected at approximately −45°. The unreacted carbonyl chloride amounted to 1·4 mols. The calculated yield of carbonyl fluoride was 0·3 mol. The carbonyl chlorofluoride was stored in glass globes attached to a vacuum system. It was refractionated three times, and the head and tail thirds rejected each time. The final middle fraction was taken back into the vacuum system and used for analysis and the measurement of vapour pressures and of the molecular weight by the Regnault method. After the molecular-weight determination, the weighed sample of gas was quantitatively transferred in the vacuum system to a vessel containing an excess of alcoholic potassium hydroxide. The chloride in the resulting solution of potassium carbonate, fluoride, and chloride was determined by titration using Pugh's method (*J.*, 1937, 1824), which is valid for the determination of chlorides in the presence of fluorides (Found : Cl, 43·0; *M*, 83·6, 83·2. Calc. for COClF : Cl, 43·0%; *M*, 82·5). The vapour-pressure measurements over the range −46·3° to −116·5° were made by the static method, using a silica U-tube manometer and a vapour-pressure finger. The carbonyl chlorofluoride was thus only in contact with silica and mercury throughout the series of measurements. The mercury pressure was measured with a cathetometer, and the temperatures with suitable vapour-pressure thermometers (ethylene, carbon dioxide, and ammonia).

The data are represented by the equation $\log P$ (mm.) $= 7{\cdot}9235 - 1151{\cdot}5/T$, where T is in °K., the calculated b. p. being −45·0° ± 0·2°.

Preparation of Carbonyl Fluoride.—Carbonyl chloride (3 mols.) and antimony trifluoride (3·75 mols. ≡ 50% excess) were heated in the rotating autoclave for 12 hours. In certain runs, and in certain preparations of carbonyl chlorofluoride, bromine or antimony pentachloride was added to test its effect as a catalyst, but these appeared to have little influence on the ease of reaction. In the particular run described, antimony pentachloride was not added. The autoclave was kept between 200° and 280°, and the pressure rose to 150 atm. The pressure in the cold autoclave was 40 atm. The gas was freed from carbonyl chloride and chlorofluoride by passage through copper traps cooled in solid carbon dioxide. The purity of the carbonyl fluoride was determined as follows : The gas was slowly passed down a silver tube into a tared flask containing a known excess of standard alkali, the quantity of gas absorbed being found by the increase in weight of the solution ; the solution was back titrated by standard hydrochloric acid in the cold to the phenolphthalein end-point, and was then heated to its boiling point to decompose the bicarbonate, and the titration continued until the pink colour of the phenolphthalein failed to reappear on further boiling. The first titration value depended on the quantity of carbon dioxide in the carbonyl fluoride, and the second value on the fluoride content of the solution, *i.e.*, on the carbonyl fluoride. As a check, one solution was analysed for fluorine by quantitative precipitation as calcium fluoride. Values obtained in various runs were COF_2 = 89·5, 92·5, 90·5; 95·2 (as CaF_2) ; CO_2 = 6·5, 5·5, 8·5%. The figures for carbon dioxide are uncertain owing to uncertainties in the first end-point and the percentages do not total 100%. However, it is apparent that carbonyl fluoride prepared by this method is 90—95% pure. The hydrolysed solution did not contain chloride and hence the carbonyl fluoride was free from hydrogen chloride.

Reactions of Carbonyl Fluoride.—(1) *With aniline : preparation of phenylcarbamyl fluoride.* Carbonyl fluoride, from the autoclave, was purified by passage through two copper traps cooled in solid carbon dioxide. The gas was bubbled through ether (100 c.c.) into which was slowly dropped a solution of aniline (5 g.) in ether (50 c.c.). Considerable quantities of diphenylurea were formed and tended to clog the tip of the dropping funnel. When all the aniline had been added, the urea and aniline hydrofluoride were filtered off and the ether evaporated off in a vacuum. The solid residue of phenylcarbamyl fluoride was crystallised from ether–pentane (Found : N, 10·0. Calc. for C_7H_6ONF : N, 10·1%). The solid gave no depression of m. p. (32°) when mixed with a sample of phenylcarbamyl fluoride prepared by the addition of hydrogen fluoride to phenyl *iso*cyanate. On hydrolysis with water, a solution of hydrofluoric acid was obtained together with a white crystalline solid, diphenylurea (m. p. 238°).

(2) *With methylaniline : preparation of phenylmethylcarbamyl fluoride.* An excess of carbonyl fluoride was passed into a solution of methylaniline (5 g.) in benzene (50 c.c.). The liberated hydrogen fluoride was absorbed on sodium fluoride. The solids formed were filtered off, the benzene evaporated, and the liquid residue distilled in a vacuum (b. p. 103—109°/14 mm.). On redistillation, the main fraction (b. p. 109°/14 mm.) was analysed (Found : C, 62·8; H, 5·2; N, 9·0. C_8H_8ONF requires C, 62·9; H, 5·2; N, 9·2%). *Phenylmethylcarbamyl fluoride* is a colourless liquid when pure, but on exposure to moist air it turns green then purple. It is stable to glass and is hydrolysed only on prolonged boiling with water to hydrofluoric acid and *NN'*-diphenyl-*NN'*-dimethylurea. It has a peculiar odour, and exposure to the vapours causes temporary contraction of the pupils of the eyes.

(3) *With diethylamine : preparation of diethylcarbamyl fluoride.* A similar reaction between carbonyl fluoride and diethylamine gave *diethylcarbamyl fluoride* (b. p. 154°) (Found : C, 51·1; H, 8·9; N, 11·3. $C_5H_{10}ONF$ requires C, 50·4; H, 8·4; N, 11·8%). The compound is slowly decomposed by water to give hydrogen fluoride and tetraethylurea.

(4) *With ethanol : preparation of ethyl fluoroformate.* Carbonyl fluoride was bubbled through a mixture of ethanol (5 g.), toluene (30 c.c.), and pyridine (10 g.). The white pyridine compounds were filtered off, and the ethyl fluoroformate distilled out of the solution (b. p. 57°). The molecular weight was determined by Regnault's method (Found : *M*, 91·6. Calc. for $C_3H_5O_2F$: *M*, 92). By reaction with an aqueous solution of sodium *p*-hydroxybenzoate, the white crystalline compound *p*-carboxyphenyl ethyl carbonate was obtained. There was no depression of m. p. when the compound was mixed with the product of a similar reaction between ethyl chloroformate and sodium *p*-hydroxybenzoate (Found: C, 56·8; H, 4·7. Calc. for $C_{10}H_{10}O_5$: C, 57·1; H, 4·76%).

(5) *With phenol : preparation of phenyl fluoroformate.* No reaction occurred when carbonyl fluoride was passed into a solution of phenol in ether. A similar reaction with phenol (3 g.) in benzene (50 c.c.) and pyridine (10 c.c.) gave a quantitative yield of diphenyl carbonate. Carbonyl fluoride (10 c.c. of liquid at −95°), phenol (10 g.), and benzene (25 c.c.) were heated in a small tube autoclave for one hour at 100°. The solution was filtered through sodium fluoride to remove hydrogen fluoride, and the benzene evaporated off. The *phenyl fluoroformate* distilled off between 145° and 155°. On redistillation, 7·5 g. of liquid (b. p. 153°) were obtained (Found : C, 60·2; H, 4·0. $C_7H_5O_2F$ requires C, 60·0; H, 3·6%). Phenyl fluoroformate is a colourless lachrymatory liquid. It slowly attacks glass, presumably because of traces of water, by which it is hydrolysed to diphenyl carbonate and hydrogen fluoride. It is quite stable at the b. p., unlike phenyl chloroformate which decomposes into diphenyl carbonate and carbonyl chloride.

Reactions of Carbonyl Chlorofluoride.—(1) *With ethanol.* Ethanol (3 g.) was dropped on liquid carbonyl chlorofluoride (10 g.) cooled in solid carbon dioxide. The excess of gaseous reagent was evaporated off, and the residue fractionated. Considerable etching of the flask occurred, but two distinct fractions were obtained. They were ethyl fluoroformate (3 g.), boiling in the range 52—58°, and diethyl carbonate (1·5 g.) (b. p. 125°). No ethyl chloroformate (b. p. 94°) was obtained.

(2) *With methylaniline.* A solution of methylaniline (8 g.) in ether (75 c.c.) was added dropwise to a solution of carbonyl chlorofluoride (10 g.) in ether (25 c.c.) cooled in solid carbon dioxide. A white precipitate was formed but most of this redissolved when the excess gas was boiled off. The ether was evaporated, and the liquid phenylmethylcarbamyl fluoride distilled off in a vacuum (b. p. 110°/15 mm.). A small quantity of tarry material remained in the flask. 10 G. of phenylmethylcarbamyl fluoride were obtained, representing a yield of 88% on the reaction $NHMePh + COClF = NMePh{\cdot}COF + HCl$.

(3) *With diethylamine.* An ethereal solution of diethylamine (30 g.) was similarly caused to react with carbonyl chlorofluoride (11 g.). The reaction was extremely vigorous even at −78°. The white precipitate of diethylamine hydrochloride was filtered off, and the diethylcarbamyl fluoride separated by distillation. The latter was obtained in 45% yield based on the reaction $2NHEt_2 + COClF = NEt_2{\cdot}COF + NHEt_2,HCl$.

The Preparation of Sulphuryl Chlorofluoride.—(a) *Chlorination of toluene-*o*-sulphonyl fluoride.* Toluene-*o*-sulphonyl fluoride (50 g.), prepared as described by Davies and Dick (*loc. cit.*), was chlorinated at a temperature between 145° and 160° for an aggregate time of 45 hours. The exit gases (approx. 250 g.) were collected in glass traps cooled in solid carbon dioxide. The bulk of this was chlorine, but on fractionation in the low-temperature still a small quantity (1 g.) of sulphuryl chlorofluoride was obtained. It was freed from chlorine by repeated distillation and condensation from traps cooled to −20°, and analysed for chlorine as described by Booth and Herrmann (*loc. cit.*) (Found : Cl, 30·1, 30·0. Calc. for SO_2ClF : Cl, 29·9%). The molecular weight was determined by Regnault's method and the b. p. measured in the separate apparatus already described (Found : *M*, 119·0; b. p. + 7·6°. SO_2ClF has *M*, 118·5, b. p. + 7·6°). The liquid and solid products from the chlorination were not examined further.

(b) *Fluorination of sulphuryl chloride.* (i) Sulphuryl chloride (7·4 mols.) and antimony trifluoride (2·9 mols.) together with antimony pentachloride (50 g.) as catalyst were heated in the rotating autoclave for 3 hours at 220—260°. The pressure rose to 100 atm. The gases were led off from the cold autoclave and collected in glass traps cooled in solid carbon dioxide. The mixture of sulphuryl fluoride (b. p. – 55°), sulphur dioxide (b. p. –10°), and sulphuryl chlorofluoride (b. p. 7·6°) was separated by fractionation in the low-temperature still. Yields were: SO_2F_2 0·1 mol., SO_2 3·8 mols., SO_2ClF 3·4 mols. (46%).

(ii) A mixture of chlorine (2·9 mols.) and antimony trifluoride (2·9 mols.) was heated in the rotating autoclave to form SbF_3Cl_2. The autoclave was evacuated, and the sulphuryl chloride (7·4 mols.) syphoned on to the fluorinating agent. The mixture was heated as before, and the products separated. Yields were: SO_2F_2 0·15 mol., SO_2 1·8 mols., SO_2ClF 5·3 mols. (72%). A combined sample from these two preparations was analysed as before (Found: Cl, 29·5, 29·8. Calc. for SO_2ClF: Cl, 29·9%).

Preparation of Sulphuryl Fluoride.—(a) *Fluorination of sulphur dioxide.* Fluorine was passed over coarsely powdered silver fluoride (180 g.) in a copper tube heated to about 180°. The current in the fluorine generator was 25 amps. After 4 hours, when no further gas appeared to be absorbed, the argentic fluoride was cooled to room temperature in a slow stream of fluorine. Sulphur dioxide was passed over the argentic fluoride and a mixture of excess sulphur dioxide and sulphuryl fluoride was collected in glass traps cooled in solid carbon dioxide. The reaction was strongly exothermic and the sulphur dioxide was passed until the copper tube and contents regained room temperature. The sulphuryl fluoride was separated by fractionation in the low-temperature still. The fraction boiling between –56° and –53° was refractionated. The bulk (33 g.) boiled at –55°. The identity of the compound was confirmed by analysis. A pure sample was weighed in the Regnault bulb and quantitatively transferred to a vessel containing an excess of alcoholic potassium hydroxide. The gas was hydrolysed to potassium fluoride and fluorosulphonate. The solution was transferred to a platinum dish and evaporated to dryness on a steam-bath to hydrolyse the fluorosulphonate to fluoride and sulphate. An excess of concentrated hydrochloric acid was added, and the solution again evaporated to dryness to remove the fluoride as hydrogen fluoride. The resulting solution, free from fluoride, was analysed for sulphate by precipitation with barium chloride in the usual way (Found: S, 31·3; *M*, 101. Calc. for SO_2F_2: S, 31·4%; *M*, 102).

(b) *Fluorination of sulphuryl chloride.* (i) Sulphuryl chloride (4 mols.), antimony pentachloride (50 g.), and an excess of antimony trifluoride (3·5 mols.) sufficient to replace both halogen atoms were heated in the rotating autoclave for 7 hours at about 260°. The pressure rose to 100 atm. The gaseous products were fractioned in the usual way and found to consist of sulphuryl fluoride (1·0 mol. ≡ 25%) and a large quantity of sulphur dioxide (2·3 mols. ≡ 57%). No sulphuryl chlorofluoride was obtained.

(ii) Sulphuryl chloride (7·4 mols) and antimony trifluorodichloride (3·5 mols) were heated as before in the rotating autoclave. The gases were fractionated in the usual way. The yields obtained were: sulphur dioxide (1·4 mols.), sulphuryl fluoride (5 g.), and sulphuryl chlorofluoride (4·8 mols. ≡ 65%).

(c) *Fluorination of sulphuryl chlorofluoride.* (i) Sulphuryl chlorofluoride (2·1 mols.), antimony trifluoride (2·1 mols.), and antimony pentachloride (25 g.) were heated in the rotating autoclave for 5 hours at 250°. On fractionation of the products, unchanged sulphuryl chlorofluoride (0·90 mol.), sulphur dioxide (0·94 mol.), and sulphuryl fluoride (0·16 mol. ≡ 8%) were obtained.

(*ii*) Sulphuryl chlorofluoride (2 mols.) and antimony trifluorodichloride (1 mol.) were heated as above in the rotating autoclave. A mixture of unchanged sulphuryl chlorofluoride (0·85 mol.), sulphur dioxide (0·34 mol.), and sulphuryl fluoride (0·10 mol. ≡ 5%) was obtained.

Reactions of Sulphuryl Chlorofluoride and Fluoride.—(1) *With hydrocarbons.* No reaction occurred when sulphuryl fluoride was bubbled through boiling hexane or toluene containing 1% of benzoyl peroxide, or when sulphuryl fluoride and chlorofluoride were heated with hexane (containing 1% of benzoyl peroxide) under pressure at 130—150°. When sulphuryl chlorofluoride (90 g.), benzene (65 g.), and aluminium chloride (1 g.) were heated under pressure at 130° most of the benzene (63 g.) was recovered unchanged. A small quantity of chlorobenzene (Found: Cl, 31·3. Calc. for C_6H_5Cl: Cl, 31·5%) was obtained but there was no trace of fluorobenzene.

(2) *With* 1 : 2-*dichloroethylene.* No reaction occurred when sulphuryl chlorofluoride was heated under pressure with dichloroethylene containing 1% of benzoyl peroxide.

(3) *With phenol.* No fluorination took place when sulphuryl fluoride was bubbled through a boiling solution of phenol (10 g.) in chloroform (50 ml.) containing a little iodine (1 g.). Similarly no halogenation occurred when sulphuryl chlorofluoride (20 ml.) was heated under pressure with a solution of phenol (10 g.) and benzoyl peroxide (1 g.) in chloroform (15 ml.).

(4) *With diethylamine.* (a) A solution of diethylamine (40 ml.) in ether (50 ml.) was dropped into a solution of sulphuryl fluoride (23 g.) in ether (50 ml.) cooled in dry ice. A vigorous reaction took place with formation of a white precipitate of diethylamine hydrofluoride. The mixture was warmed to room temperature, and the solid filtered off. The ether was evaporated from the filtrate, and the residue distilled in a vacuum (b. p. 72°/14 mm.). A colourless liquid was obtained which was stable to water but gave a solution containing fluoride on prolonged boiling with concentrated sodium hydroxide solution The elements nitrogen and sulphur were shown to be present by fusion with sodium followed by the usual tests. Analysis by standard microanalytical methods showed that the liquid was diethylsulphamyl fluoride (Found: C, 31·2; H, 6·5; N, 8·8. Calc. for $C_4H_{10}O_2NSF$: C, 30·9; H, 6·45; N, 9·0%). The compound was obtained in an overall yield of 35% based on the diethylamine.

(b) A solution of diethylamine (35 g.) in ether (25 ml.) was similarly treated with sulphuryl chlorofluoride (25 ml.) in ether (25 ml.). The white precipitate (approx. 25 g.) obtained was diethylamine hydrochloride. The ether was evaporated, and the liquid residue distilled in a vacuum. The distillate (15 g.) boiled over the range 70—110°/18 mm. A quantity of black tar remained in the distillation flask. On redistillation, a few drops of liquid (b. p. 70—85°/15 mm) were obtained and were shown by sodium fusion to contain nitrogen, sulphur, and fluorine, but the quantity was insufficient to permit positive identification as diethylsulphamyl fluoride (b. p. 72°/14 mm.). The major fraction boiling in the range 90—100°/15 mm. was refractionated, and the portion, b. p. 97°/13 mm., shown to be free from fluoride. This colourless liquid was readily hydrolysed by water to give a solution containing chloride. It also contained nitrogen and sulphur and analysis confirmed it as diethylsulphamyl chloride (Found: C, 28·0; H, 5·85; N, 7·9; Cl, 21·2. Calc. for $C_4H_{10}O_2NSCl$: C, 28·0; H, 5·8; N, 8·1; Cl, 20·7%).

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