Perfluoroalkyl Grignard and Grignard-type Reagents. Part IV. Trifluoromethylmagnesium Iodide.*†

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Trifluoromethylmagnesium iodide is prepared from trifluoroiodomethane only with difficulty. Neutral-molecule Lewis bases are the best solvents, and temperatures of $-30°$ to $-10°$ should be used. Fluoroform and polytetrafluoroethylene are produced by decomposition of the Grignard compound and the mechanism of formation of these compounds is discussed. The conversion of $CF_3{\cdot}MgI$ into CHF_3, $CF_3{\cdot}CO_2H$, or $CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, and into the ketones $CF_3{\cdot}CO{\cdot}R$ (R = Me, Et, Pr^n, CH_2F, CHF_2, $CF_3{\cdot}CH_2$, CF_3, or C_3F_7) is described.

TRIFLUOROMETHYLMAGNESIUM IODIDE was the first perfluoroalkylmagnesium iodide to be prepared (Haszeldine, *Nature*, 1951, **167**, 139; **168**, 1028; Abs. Amer. Chem. Soc. Meetings, Sept. 1951, 6K; Sept. 1952, 13K), but it was soon found that the experimental results were difficult to reproduce and that a variety of factors were influencing the formation of the Grignard compound. Pentafluoroiodoethane also yielded a magnesium derivative, but the results were again difficult to reproduce precisely, although (as will be shown in a later paper) for a different reason. Heptafluoroiodopropane reacts with magnesium much more smoothly than does trifluoroiodomethane, and the results can readily be duplicated; for this reason heptafluoroiodopropane, which is typical of the iodo-compounds $CF_3{\cdot}[CF_2]_n{\cdot}I$ where $n > 1$, was used to determine the conditions necessary for the formation of a perfluoroalkyl Grignard compound in optimum yield (Part I, *J.*, 1952, 3423). The present communication reports the early results with trifluoromethylmagnesium iodide.

The conditions which affect the formation of trifluoromethylmagnesium iodide are, in decreasing order of importance, the initiation of the reaction, the temperature, the

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solvent, and the dilution of the fluoro-iodide in the solvent. Pure magnesium and completely anhydrous conditions are essential. The main difficulty in the preparation of the Grignard compound is to start the reaction with magnesium. Heptafluoroiodopropane reacts with magnesium approximately one thousand times as readily as does trifluoroiodomethane, particularly at the low temperatures which have to be used to prevent the extensive decomposition of the Grignard compound once formed. For this reason other methods, to be described later, for the preparation of a trifluoromethyl Grignard or Grignard-type reagent have been developed, notably exchange reactions of trifluoroiodomethane with aryl Grignard reagents or with alkyl-lithium compounds. The methods used to initiate reaction between trifluoroiodomethane and magnesium are described in the Experimental section, but it must be emphasised that there is often little or no formation of the Grignard compound under conditions apparently identical with those which, in a separate experiment, gave a relatively high yield. The amount of trifluoromethylmagnesium iodide (maximum yield 45%) available for a particular reaction should therefore be determined from an aliquot of the solution to be used.

The solvent plays an important part. Trifluoroiodomethane does not react with magnesium when benzene, *cyclo*hexane, or perfluoromethyl*cyclo*hexane is solvent. A basic solvent, in the Lewis sense, is required, and the reason for this is now clear. A solvent B, which contains an atom or atoms (*e.g.*, O, N) containing lone pairs of electrons, has been shown to form a molecular compound of the type (RI),B with a fully fluorinated iodo-alkane, RI (Haszeldine, *J.*, 1953, 2622); the iodo-compound is thus a neutral-molecule Lewis acid, and the complex is of the donor–acceptor type, the donated electron in the structure $\psi[B^{+}-(RI)^{-}]$ being derived from the lone pair of electrons in B. Thus, although in a non-polar solvent heterolytic fission of the carbon–iodine bond is difficult to achieve, in a basic solvent the carbon–iodine bond probably approaches more to that in an unsubstituted alkyl iodide such as methyl iodide in character, and reactions which involve ionic intermediates are facilitated. On this basis one can interpret the facts that the preparation of heptafluoropropylmagnesium iodide is possible in ethyl ether and triethylamine, but impossible in the non-basic solvents $N(C_3F_7)_3$ or $(C_4F_9)_2O$, and that the yield of the Grignard compound is increased if the more basic tetrahydropyran is used (Part I). Trifluoroiodomethane is similarly more reactive towards magnesium in tetrahydropyran than in ethyl ether. A basic solvent also doubtless stabilises the Grignard reagent by co-ordination and prevents coating effects on the magnesium.

Low reaction temperatures give a higher yield of trifluoromethylmagnesium iodide, since thermal decomposition of the Grignard compound is reduced. The improved yield is counteracted, from the point of view of convenience, by the decreased rate of reaction of the fluoro-iodide with the magnesium, and complete reaction of trifluoroiodomethane cannot be achieved. In cases where the second component can be added during the formation of trifluoromethylmagnesium iodide, however, a reaction temperature *ca.* 0° can be used, since the Grignard compound is removed by reaction as soon as it is formed, with only slight thermal decomposition.

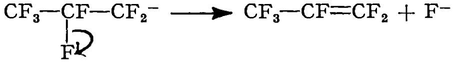
Hexafluoroethane is not a by-product from the formation of the Grignard compound (cf. the isolation of perfluorohexane when heptafluoroiodopropane reacts with magnesium; Part I). Two main by-products have been detected: fluoroform, and tetrafluoroethylene, which is obtained as a polymer. The formation of fluoroform is readily explained on the basis of a trifluoromethyl anion :

$$CF_3{\cdot}MgI \longrightarrow CF_3^{-} + \overset{+}{Mg}I ; \quad CF_3^{-} + \text{solvent} \longrightarrow CHF_3$$

That the polymer arises mainly from tetrafluoroethylene is shown by pyrolysis studies. Tetrafluoroethylene formation can be visualised as

$$2CF_3^{-} \longrightarrow C_2F_4 + 2F^{-}$$

i.e., elimination of fluoride ion from two fluorocarbanions. The formation of hexafluoropropene from heptafluoropropylmagnesium iodide is believed to involve



$$CF_3{-}\underset{F}{\underset{|}{C}}F{-}CF_2^{-} \longrightarrow CF_3{-}CF{=}CF_2 + F^{-}$$

Alternatively, trifluoromethylmagnesium iodide may undergo halogen exchange with trifluoroiodomethane to give difluorodi-iodomethane :

$$\text{CF}_3\cdot\text{MgI} + \text{CF}_3\text{I} \longrightarrow \text{CF}_3\cdot\text{MgF} + \text{CF}_2\text{I}_2$$

$$2\text{CF}_2\text{I}_2 \xrightarrow{\text{Mg}} \text{C}_2\text{F}_4$$

The formation of trifluoromethylmagnesium fluoride would account for the magnesium fluoride always produced during reactions of the Grignard compound. The polymerisation of tetrafluoroethylene cannot involve a simple ionic mechanism,

$$\text{CF}_3^- + \text{C}_2\text{F}_4 \longrightarrow \text{CF}_3\cdot\text{CF}_2\cdot\text{CF}_2^- \xrightarrow{\text{C}_2\text{F}_4} \text{etc.}$$

since compounds such as C_3HF_7, C_5HF_9, etc., would be expected in the reaction products. As suggested in Part I, however, anionic polymerisation by the Grignard compound is feasible :

$$\text{CF}_3^-\ \overset{+}{\text{Mg}}\text{I} \xrightarrow{\text{C}_2\text{F}_4} [\text{CF}_3\cdot\text{CF}_2\cdot\text{CF}_2]^-\ \overset{+}{\text{Mg}}\text{I} \xrightarrow{\text{C}_2\text{F}_4} \text{CF}_3\cdot[\text{CF}_2\cdot\text{CF}_2]_n^-\ \overset{+}{\text{Mg}}\text{I}$$

The decomposition of trifluoromethylmagnesium iodide into a trifluoromethyl radical would readily explain the isolation of fluoroform, but not the formation of polytetrafluoroethylene.

When trifluoromethylmagnesium iodide undergoes rapid thermal decomposition, fluoroform, polytetrafluoroethylene, and small amounts of tetrafluoroethylene monomer are produced.

Although difficult to prepare, trifluoromethylmagnesium iodide is a valuable reagent in synthetic fluorine chemistry, and its value will be increased once some way has been found to improve its preparation and to increase its thermal stability (*e.g.*, by formation of a co-ordination compound). Compounds which contain active hydrogen react immediately to yield fluoroform. The reaction with carbon dioxide gives a high yield of trifluoroacetic acid, thus providing an alternative to the oxidation route described earlier (*J.*, 1950, 3037; *Nature*, 1950, **166**, 192). The reaction with carbon dioxide proceeds smoothly at temperatures as low as $-60°$. Several unsuccessful attempts were made to cause methyl iodide to react with trifluoromethylmagnesium iodide, and it appears that the Grignard compound is anomalous in this respect.

Other reactions carried out with trifluoromethylmagnesium iodide are summarised by the following equations :

$$\text{CH}_3\cdot\text{CN} \longrightarrow \text{CF}_3\cdot\text{CO}\cdot\text{CH}_3\ (38\%);\ \text{CF}_3\cdot\text{CN} \longrightarrow \text{CF}_3\cdot\text{CO}\cdot\text{CF}_3\ (33\%)$$

$$\overline{\text{CH}_2\cdot\text{CH}_2\text{O}} \longrightarrow \text{CF}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}\ (57\%)\ [\longrightarrow \text{CF}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \longrightarrow \text{CF}_3\cdot\text{CH}_2\cdot\text{COCl}]$$

$$\text{CH}_3\cdot\text{COCl} \longrightarrow \text{CF}_3\cdot\text{CO}\cdot\text{CH}_3\ (59\%);\ \text{Et}\cdot\text{COCl} \longrightarrow \text{CF}_3\cdot\text{COEt}\ (47\%)$$

$$\text{Pr}\cdot\text{COCl} \longrightarrow \text{CF}_3\cdot\text{COPr}\ (51\%);\ \text{CF}_3\cdot\text{CH}_2\cdot\text{COCl} \longrightarrow \text{CF}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CF}_3\ (37\%)$$

$$\text{CH}_2\text{F}\cdot\text{COCl} \longrightarrow \text{CF}_3\cdot\text{CO}\cdot\text{CH}_2\text{F}\ (15\%);\ \text{CHF}_2\cdot\text{COCl} \longrightarrow \text{CF}_3\cdot\text{CO}\cdot\text{CHF}_2\ (59\%)$$

$$\text{CF}_3\cdot\text{COCl} \longrightarrow \text{CF}_3\cdot\text{CO}\cdot\text{CF}_3\ (49\%);\ \text{C}_3\text{H}_7\cdot\text{COCl} \longrightarrow \text{CF}_3\cdot\text{CO}\cdot\text{C}_3\text{H}_7\ (43\%)$$

The reactions of nitriles and of ethylene oxide proceed normally, and the reactions with acyl halides give satisfactory yields of the ketones. It is clear that as techniques for their manipulation are developed, the perfluoroalkyl Grignard compounds will be more used.

EXPERIMENTAL

Trifluoroiodomethane was prepared from carbon tetraiodide and iodine pentafluoride (*J.*, 1948, 2188) or, in the later studies, from silver trifluoroacetate and iodine (*J.*, 1951, 584); it was thoroughly dried and stored *in vacuo*. Sealed Pyrex 50—500-ml. tubes were used for the experiments, and where possible the reactants were transferred *in vacuo*. Stringent precautions were taken to use anhydrous reactants and to exclude moisture, oxygen, and carbon dioxide. Spectroscopically pure magnesium was used.

Conditions affecting Formation of Trifluoromethylmagnesium Iodide.—The effects observed in the early experiments were similar to those reported for heptafluoropropylmagnesium iodide (Part I). The yield of the Grignard reagent was determined (after removal of excess of magnesium, used in all experiments) (*a*) by hydrolysis with water, 5N-hydrochloric acid, or occasionally ammonium chloride, or (*b*) by carboxylation with carbon dioxide as solid or gas, or addition of the Grignard solution to a mixture of solid carbon dioxide and the solvent. Trifluoroacetic acid was isolated as its sodium salt and for estimation was converted into the amide, or more simply into the silver salt. Handling losses on the scale used were 10—20%, determined from blank experiments.

(a) *Magnesium and initiation.* Although extensive reaction occurred once Grignard formation had been initiated, the yield of trifluoromethylmagnesium iodide ultimately available for reaction was very low unless pure magnesium was used (cf. Part I). For best results the magnesium was freshly cut from a magnesium rod, preferably covered by anhydrous ether and in the absence of air. With such magnesium the formation of trifluoromethylmagnesium iodide was seldom spontaneous, and various devices, not always effective, were used to bring about reactions : Iodine (10—20% of the amount required to form magnesium iodide) was heated (150°) with the magnesium in absence of solvent, and the resultant mixture was used immediately. Alternatively, the magnesium was pretreated with methyl or ethyl bromide or iodide in ether for several minutes until the formation of alkylmagnesium halide was proceeding smoothly; most of the Grignard solution was then drained off and the residual magnesium was sealed with fresh solvent and trifluoroiodomethane. If reaction failed to start at 0—15°, the mixture was heated to 40—50° to initiate the reaction and the temperature was gradually lowered to that required for the particular experiment. This must be done slowly otherwise Grignard formation stops. The formation of trifluoromethylmagnesium iodide is accompanied by a darkening of the solution and gradual deposition of a flocculent pale brown solid.

Note : It is strongly recommended that the conditions to be used for the preparation of trifluoromethylmagnesium iodide should be tested by use of heptafluoroiodopropane, from which Grignard formation is much more readily effected; if the conditions are such that a high yield (see Part I) of heptafluoropropylmagnesium iodide is not obtained, it is most unlikely that trifluoromethylmagnesium iodide will be prepared successfully when the same conditions are applied to trifluoroiodomethane.

(b) *Solvents.* (i) Trifluoroiodomethane (2·0 g.), magnesium (1·0—1·5 g.), and perfluoromethyl*cyclo*hexane (10—20 ml.) were heated in sealed tubes at temperatures from 50° to 250°. No significant reaction was detected below 150°, and at higher temperatures hexafluoroethane and magnesium iodide and fluoride were detected. Addition of water or of carbon dioxide, with or without an organic solvent, failed to produce fluoroform or trifluoroacetic acid. The formation of trifluoromethylmagnesium iodide could not be detected at temperatures up to 100° when benzene was used as solvent; at higher temperatures there was appreciable attack by trifluoromethyl radicals on benzene, but no formation of the Grignard compound.

(ii) The experiments summarised in Table 1 were carried out to determine the variation of yield with temperature and with solvent. Trifluoroiodomethane (5·0 g.), magnesium (2·5 g.), and solvent (150 ml.) were caused to react at the temperature indicated after initiation of reaction at 20°; the reaction time was 72 hr., and an atmosphere of carbon dioxide was used to remove the Grignard compound as soon as it was formed. The yields are based on the quantity of the fluoro-iodide taken and are the mean of at least two on this scale, the products being combined.

Trifluoroiodomethane could not be separated quantitatively from ethyl ether by trap-to-trap fractionation *in vacuo*, but distillation through a low-temperature column gave a satisfactory separation; conversion of the trifluoroiodomethane into fluoroform was sometimes used to estimate the amount of the fluoro-iodide recovered. The experiments reported are those in which Grignard formation was successfully initiated and the reaction continued when the mixture was cooled. In approx. 75% of the experiments either initiation of the reaction could not be effected, or, particularly at the lower temperatures, the reaction stopped when the tube was cooled; these experiments are not reported.

TABLE 1. *Yield (%) of Grignard compound, and, in parentheses, recovery (%) of starting material, at various temperatures.*

	−60°	−40°	−30°	−15°	0°	20°	40°	60°
Et_2O	38(25)	35(18)	39(19)	41(18)	36(13)	33(8)	26(4)	20(~2)
Bu_2O	33(20)	37(—)	27(31)	39(16)	42(11)	30(10)	25(—)	18(6)
$[CH_2]_5O$	29(28)	28(—)	39(15)	45(11)	44(12)	40(7)	21(—)	20(—)

These results are not as reproducible as those obtained with heptafluoroiodopropane (Part I), but reveal the decrease in yield with increase in reaction temperature, and indicate that tetrahydropyran is more suitable than dialkyl ethers except for temperatures below −40°.

(c) *Dilution.* The marked increase in decomposition in concentrated solutions is shown by the results in Table 2. Magnesium (2·0 g.), trifluoroiodomethane (5·0 g.), and ethyl ether were kept at −10° for 48 hr. after initiation of reaction at 20°.

TABLE 2.

Solvent (ml.)	5	10	20	50	100	150	500
CF_3I recovered (%)	26 *	20 *	—	19	17	15	31
$CF_3 \cdot MgI$ formed (%)	0	12	29	37	41	43	21

* High yields of fluoroform obtained.

(d) *Temperature.* The effect of reaction temperature on yield is shown in Table 1. The rate of decomposition of trifluoromethylmagnesium iodide, prepared as in Table 1, but without a carbon dioxide atmosphere, is shown by the data of Table 3. Ethyl ether was used as solvent.

TABLE 3.

Temp.	−60°	−40°	−20°	0°	20°	40°
Time (hr.)	72	96	96	48	24	24
Decomp. (%)	6	21	33	35	75	80

(e) *Reaction with the second component.* It is often preferable to have the compound with which trifluoromethylmagnesium iodide is to react (*e.g.*, carbon dioxide) present in solution during formation of the Grignard reagent.

By-products. The volatile by-product arising during formation of trifluoromethylmagnesium iodide was fluoroform (Found : *M*, 70. Calc. for CHF_3 : *M*, 70), identified later by means of its infra-red spectrum, and readily separated from unchanged reactants by distillation *in vacuo*. Hexafluoroethane was not a reaction product. The amount of fluoroform as by-product varied from 10—15% at −30° to 25—30% at 40°. Magnesium iodide and fluoride and a tetrafluoroethylene polymer were also produced. The last material was isolated by treatment of the insoluble products obtained by filtration of the Grignard-reagent solution with acid, base, and alcohol; when heated in a high vacuum, the pale brown solid gave a white sublimate [Found : C, 24·0; H, 0. Calc. for $(C_2F_4)_n$: C, 24·0; H, 0%]. The residual solid (*ca.* 80%) was polymer of greater molecular weight [Found : C, 23·9; H, 0%]. An infra-red spectrum of the solid which sublimed was very similar to that of polytetrafluoroethylene. When the polymer which did not sublime was pyrolysed in a platinum crucible at 700° in a high vacuum, a 53% yield of tetrafluoroethylene was obtained, and only a small carbonaceous residue remained; hexafluoropropene was also produced (5—10%), but other fluorine-containing products could not be identified spectroscopically.

Reactions of Trifluoromethylmagnesium Iodide.—(a) *Thermal decomposition.* A solution of trifluoromethylmagnesium iodide, prepared in 41% yield at −15° in ethyl ether as described above, was freed from fluoroform, filtered, then heated rapidly to vigorous reflux. Fluoroform (81%) and tetrafluoroethylene (6%) were produced, and a small amount of flocculent solid was deposited.

(b) *With water.* It was assumed that the reaction with aqueous reagents was quantitative.

(c) *With compounds which contain active hydrogen.* The yields of fluoroform when an excess of ethanol, methanol, *n*-butylamine, acetic acid, or anhydrous hydrogen chloride was added to solutions of the Grignard compound were essentially the same as when water was added.

(d) *With carbon dioxide.* In a typical experiment, spectroscopically pure magnesium shavings (3 g.; prepared under *n*-butyl ether) were freed from organic solvent by pumping *in vacuo* in a 500-ml. Pyrex tube and then heated with dry iodine as described earlier. After cooling, *n*-butyl ether (150 ml.) was condensed into the tube *in vacuo*, followed by methyl iodide (0·5 g.) and trifluoroiodomethane (10·0 g.). Dry carbon dioxide was condensed into the tube, which was then sealed *in vacuo* and allowed to warm to room temperature; the pressure of carbon dioxide was *ca.* 5 atm. The tube was shaken vigorously at 20° for 30 min. before reaction could be detected by formation of a light brown flocculent precipitate and darkening of the solution. The reaction at 20° was allowed to proceed for 10 min. to ensure that trifluoroiodomethane was reacting as well as methyl iodide, and the tube was then cooled (20 min.) to −10° at which temperature it was kept for 12 hr. The tube was then cooled by liquid oxygen, opened, recharged with carbon dioxide, and kept at 20° for 30 min., then at −10° for 30 hr. The tube was warmed stepwise to 40° during 12 hr., then frozen in liquid oxygen and opened. The products with b. p. <0° were fractionated *in vacuo* and shown to be carbon dioxide, trifluoroiodomethane (12%), and fluoroform (12%); carbon dioxide was absorbed by aqueous alkali to enable the fluoroform to be separated. The contents of the reaction vessel were filtered in absence of air to remove the excess of magnesium, magnesium fluoride, polymer, etc., and to the filtrate were added water (20 ml.), then 5N-hydrochloric acid (100 ml.). Fluoroform (6%) was evolved, showing that the trifluoromethylmagnesium iodide had not all reacted. The ethereal layer was extracted with aqueous sodium hydroxide, and the aqueous layer was filtered and extracted with ethyl ether, and the ethereal extract concentrated in presence of 5N-sodium hydroxide. The combined aqueous alkaline extracts were neutralised (bromothymol-blue) and evaporated to dryness *in vacuo*. Extraction with hot ethanol gave sodium trifluoroacetate, converted into the acid (39% based on trifluoroiodomethane taken; *ca.* 80% based on $CF_3{\cdot}MgI$), b. p. 70—72°, and thence into the silver salt (37%), identified by comparison with a genuine specimen prepared earlier. The resinous material obtained at the filtration stage was treated with acid as described above, to give a polytetrafluoroethylene-type polymer (12%). Distillation of the butyl ether after extraction with aqueous sodium hydroxide gave a residue which contained covalent fluorine, but attempts to isolate definite products were unsuccessful.

In the following experiments trifluoromethylmagnesium iodide was prepared in ethyl- or butyl-ethereal solution at a temperature between 0° and $-30°$. The yield of the Grignard compound was derived from the data recorded earlier, or, when the completeness of the Grignard reaction was in doubt, by measuring the fluoroform evolved on hydrolysis of an aliquot. The filtered solution of the Grignard reagent was used for the reaction described. Fluoroform was removed in all instances before reaction with the second component. The solvent was chosen to make separation of reaction products easy. Unchanged trifluoroiodomethane, which could not be separated completely from ethyl ether, was present during some reactions, but did not interfere.

(e) *With methyl iodide.* Reaction of trifluoromethylmagnesium iodide (3·0 g.) with an excess of methyl iodide was investigated in experiments at $-30°$, $-10°$, 0°, 20°, and 40°, but 1 : 1 : 1-trifluoroethane was not detected as a product; fluoroform was produced by thermal decomposition of the Grignard compound.

(f) *With acetonitrile.* To trifluoromethylmagnesium iodide (4·5 g.) was added a solution of acetonitrile (2·5 g.) in butyl ether (10 ml.) in three portions. Between each addition the reaction tube was sealed, shaken, and warmed from $-25°$ to $+10°$ (1 hr.); the next portion was then added. Finally the reaction tube was vigorously shaken and heated to 50° (3 hr.). When it was cool, an excess of 10N-sulphuric acid was added cautiously. The volatile products were distilled *in vacuo*, to give 1 : 1 : 1-trifluoroacetone (15%) (Found: *M*, 112. Calc. for $C_3H_3OF_3$: *M*, 112), b. p. 21°. The ethereal extracts were dried (P_2O_5) and distilled, to give a further amount of trifluoroacetone (17%). The aqueous solution yielded the 2 : 4-dinitrophenylhydrazone of trifluoroacetone (6%).

(g) *Trifluoroacetonitrile.* The nitrile was prepared by dehydration of trifluoroacetamide with phosphoric anhydride. To trifluoroacetonitrile (4·3 g.) frozen in three Carius tubes was added a solution of trifluoromethylmagnesium iodide (9·7 g.) in butyl ether (100 ml.). The tubes were sealed, and kept at $-20°$ for 3 days with intermittent shaking. The temperature was then slowly raised to 30° (2 days), before addition of sulphuric acid as in (f) above. Hexafluoroacetone was not present in the volatile products, but was isolated from the combined ethereal and aqueous layers as follows: The ethereal layer was separated, combined with the ethereal extracts (5) of the residual aqueous layer, and distilled from a small amount of phosphoric anhydride, to give hexafluoroacetone hydrate containing water, b. p. 50—60°/35 mm., and a small amount of hexafluoroacetone. These substances, together with the small amount of butyl ether which had distilled over, were combined and treated with an excess of phosphoric anhydride in a sealed tube at 80° (3 hr.). Distillation *in vacuo* gave hexafluoroacetone (33% based on $CF_3{\cdot}MgI$), b. p. $-28°$ (Found: *M*, 166. Calc. for C_3OF_6: *M*, 166), identified by means of its semicarbazone, m. p. 154° (decomp.). Fukuhara and Bigelow (*J. Amer. Chem. Soc.*, 1941, **63**, 788) report m. p. 153° (decomp.).

(h) *Ethylene oxide.* Ethylene oxide (2·5 g.) was condensed into a tube containing trifluoromethylmagnesium iodide (6·8 g.) in ethyl ether (130 ml.), and after being sealed the tube was kept at 0° for 12 hr., then warmed to 40° during 30 hr. A polymeric material could be seen on the walls of the tube. Sulphuric acid (5N) was added to the tube, and the ethereal layer was separated. Ethereal extracts (twice) of the aqueous layer were combined with the original ethereal layer and, after being dried (P_2O_5), were distilled, to give 3 : 3 : 3-trifluoropropan-1-ol (57%), b. p. 100—101° (Found: C, 31·2; H, 4·6. Calc. for $C_3H_5OF_3$: C, 31·6; H, 4·4%). For further identification the alcohol was oxidised by chromic anhydride–sulphuric acid (cf.

Part II), to give βββ-trifluoropropionic acid, b. p. 145° (Found: equiv., 127. Calc. for $C_3H_3O_2F_3$: equiv., 128).

Reaction of Trifluoromethylmagnesium Iodide with Acyl Chlorides.—The following general procedure was adopted to obtain maximum yields of ketones. The acid chloride (prepared by interaction of the corresponding acid and phosphorus pentachloride in the usual way) was condensed from a vacuum-system into the reaction vessel which was cooled in liquid oxygen. A solution of trifluoromethylmagnesium iodide (4—5 g.) was then added, and whilst still frozen the tube was sealed off. A two-molar excess of acyl halide was used. The mixture was heated stepwise from −30° to 40° during 7 days, and the volatile products were transferred to a vacuum-system. The ketones of higher b. p. were isolated from the ethereal solution by distillation. Yields are based on trifluoromethylmagnesium iodide. No attempt was made to investigate the other reaction products.

(a) *Acetyl chloride.* 1 : 1 : 1-Trifluoroacetone was isolated by distillation *in vacuo* (59%), b. p. 21° (Found: *M*, 111. Calc. for $C_3H_3OF_3$: *M*, 112), identical with the compound obtained above.

(b) *Propionyl chloride.* Butyl ether has to be used to enable the ketone to be isolated easily. The product, 1 : 1 : 1-*trifluorobutan*-2-*one* (47%), b. p. 46° (Found: C, 38·3; H, 4·7%; *M*, 126. $C_4H_5OF_3$ requires C, 38·1; H, 4·0%; *M*, 126), is an isomer of the 4 : 4 : 4-trifluorobutan-2-one, b. p. 95—96°, obtained by the hydration of 1 : 1 : 1-trifluorobut-2-yne (Haszeldine and Leedham, *J.*, 1954, 1261). Its 2 : 4-*dinitrophenylhydrazone* (Found: C, 39·0; H, 3·2; N, 18·3. $C_{10}H_9O_4N_4F_3$ requires C, 39·2; H, 3·0; N, 18·3%), m. p. 93°, has ultra-violet absorption maxima in EtOH at 336, 254, and 220 mμ (ε 20,000, 12,000, 13,500), and minima at 288 and 238 mμ (ε 4500, 11,400). The isomeric ketones are readily distinguished by means of their b. p.s, the m. p.s and ultra-violet spectra of their 2 : 4-dinitrophenylhydrazones, and their infra-red spectra; CF_3·COEt shows C:O absorption at 5·62 μ (cf. CF_3·COMe, 5·61 μ) and CF_3·CH_2·COMe at 5·72 μ. The ultra-violet spectrum of 1 : 1 : 1-trifluorobutan-2-one vapour ($\lambda_{max.}$ 286·5, ε 8·9; $\lambda_{min.}$ 236·5, ε 2·2) is very similar to that of 4 : 4 : 4-trifluorobutan-2-one ($\lambda_{max.}$ 286, ε 7·5; $\lambda_{min.}$ 242, ε 2·9). Barkley and Levine (Abs. Amer. Chem. Soc. Meeting, 1952, 5M) prepared 1 : 1 : 1-trifluorobutan-2-one by an alternative route.

(c) *Butyryl chloride.* This gave 1 : 1 : 1-*trifluoropentan*-2-*one* (51%) b. p. 68° (Found: C, 42·6; H, 4·8%; *M*, 140. $C_5H_7OF_3$ requires C, 42·8; H, 5·0%; *M*, 140), characterised as its 2 : 4-*dinitrophenylhydrazone*, m. p. 74° (Found: N, 17·7. $C_{11}H_{11}O_4N_4F_3$ requires N, 17·5%). Barkley and Levine (*loc. cit.*) have prepared this ketone by an alternative route (b. p. 65°/735 mm.; personal communication).

(d) 3 : 3 : 3-*Trifluoropropionyl chloride.* This reaction, carried out with the acyl halide (2·3 g.) and trifluoromethylmagnesium iodide (2·5 g.), with conditions as described above, gave 1 : 1 : 1 : 4 : 4 : 4-hexafluorobutanone (37%), b. p. 54—55° (Found: *M*, 179. Calc. for $C_4H_2OF_6$: *M*, 180), identified by means of its infra-red spectrum.

(e) *Monofluoroacetyl chloride.* This reaction was carried out in a fume-chamber. A four-molar excess of the acyl chloride was used, since an initial experiment showed that it or the resultant ketone was readily decomposed to magnesium fluoride and chloride by the Grignard compound. 1 : 1 : 1 : 3-Tetrafluoroacetone, isolated in 15% yield, had b. p. 45—46° (Found: C, 27·3; H, 1·6%; *M*, 128. Calc. for $C_3H_2OF_4$: C, 27·7; H, 1·5%; *M*, 130). McBee, Pierce, Kilbourne, and Wilson (*J. Amer. Chem. Soc.*, 1953, **75**, 3152) prepared this ketone from the corresponding acetylacetone.

(f) *Difluoroacetyl chloride.* The acyl halide did not lose fluoride when treated with the Grignard compound, and the usual reactant ratio was used to give pentafluoroacetone (59%), b. p. 4° (isoteniscope) (Found: C, 24·2; H, 0·7%; *M*, 148. Calc. for C_3HOF_5: C, 24·3; H, 0·7%; *M*, 148). McBee *et al.* (*loc. cit.*) report b. p. 2—3°.

(g) *Trifluoroacetyl chloride.* The conditions were as before, except that the temperature was raised from −15° to 50° during 8 days. Butyl ether is the most suitable solvent. The hexafluoroacetone (49%) was identified as described above, and as its 2 : 4-dinitrophenylhydrazone.

(h) Heptafluorobutyryl chloride was similarly treated, to give perfluoropentan-2-one (43%), b. p. 30° (Found: *M*, 266. Calc. for C_5OF_{10}: *M*, 266), identical with the compound isolated in Part II (*loc. cit.*).

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