Organometallic and Organometalloidal Compounds Containing Fluoroalkyl Groups

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THE SYNTHESIS in 1947 of trifluoroiodomethane and pentafluoroiodoethane may perhaps be considered as of special significance in the field of fluorocarbon chemistry, since it raised the possibility of obtaining organometallic and organometalloidal compounds containing fluoroalkyl groups. This field of investigation, which is as yet in its infancy, has already yielded a number of interesting results, and it is the purpose of this article to present the information so far gleaned and to draw attention to some outstanding differences between the well-known organometallic compounds and their fluorocarbon analogs.

Trifluoroiodomethane was first prepared by the interaction of carbon tetraiodide and iodine pentafluoride, and was found to be a stable gas (bp, −22.5°) (*1*). The homolog, pentafluoroiodoethane (bp, 13°) may be prepared similarly from tetraiodoethylene and iodine pentafluoride (*1*), or by the interaction of diiodotetrafluoroethane and iodine pentafluoride (*2*). Fortunately, however, a far more convenient method for preparing fluoroalkyl iodides was subsequently developed. This entails the thermal reaction between the silver salt of a fully fluorinated organic acid and iodine (*3*). Thus trifluoroiodomethane may be prepared very simply from silver trifluoroacetate and iodine:

$$CF_3COOAg + I_2 = CF_3I + CO_2 + AgI.$$

The higher members of the fluoroiodide series $CF_3[CF_2]_nI$ may be prepared by this route, or by the polymerization of tetrafluoroethylene with trifluoroiodomethane or pentafluoroiodoethane (*4*),

$$CF_3I + C_2F_4 \rightarrow CF_3(CF_2CF_2)_nI,$$
$$CF_3CF_2I + C_2F_4 \rightarrow CF_3CF_2(CF_2CF_2)_nI,$$

where $n = 1, 2, 3$, etc., and show properties very similar to the lower members of the series.

Trifluoroiodomethane has an absorption spectrum very similar to that of methyl iodide and shows a broad maximum at *ca.* 2700 A. The quantum yield for the photodecomposition is, however, low (< 0.01), unless an acceptor for either the trifluoromethyl radical or the iodine atom formed in the primary act be present. The fluoroalkyl radical produced photochemically is able to initiate the polymerization of unsaturated substances such as ethylene (*4*), tetrafluoroethylene (*5*), acetylene (*6, 7*), vinylic compounds (*8*), etc., in the vapor phase, and when in solution can abstract hydrogen or halogen atoms from neighboring solvent molecules (*9*). It appears that a similar homolytic fission of the trifluoroiodomethane molecule also occurs at a temperature of 200°, since, at this temperature, reactions are observed with parallel those initiated photochemically.

The first experiments designed to utilize the homolytic fission of trifluoroiodomethane in the synthesis of organometallic compounds were performed with mercury (*10*), which, when heated or irradiated with the fluoroalkyl iodide in the absence of a solvent, yielded the white crystalline compound trifluoromethyl mercuric iodide, CF_3HgI. This sublimed readily at atmospheric pressure and was soluble in organic solvents; unlike its methyl analog, however, it was also soluble in water. There was a slow decomposition in aqueous solution, but reactions involving the mercury-iodine bond could be effected as follows:

$$CF_3HgI \xrightarrow[H_2O]{Ag_2O} CF_3HgOH \left\{ \begin{array}{lll} HF & \longrightarrow & CF_3HgF \\ HCl & \longrightarrow & CF_3HgCl \\ HBr & \longrightarrow & CF_3HgBr \\ HNO_3 & \longrightarrow & CF_3HgNO_3 \end{array} \right.$$

The trifluoromethyl mercuric iodide can be converted into bistrifluoromethyl mercury, $Hg(CF_3)_2$, by reaction with either copper or cadmium amalgams, reagents that will also convert trifluoroiodomethane directly to the dimercurial (*11*). Several of the standard methods for obtaining dimethyl mercury from methyl mercuric iodide were found to be ineffective when applied to the fluorine-containing compound.

Bistrifluoromethyl mercury, unlike dimethyl mercury, which is a covalent liquid, is a white crystalline solid that is readily soluble in organic solvents and that sublimes at atmospheric pressure. It is also very soluble in water, in which solvent it is stable and shows a low conductivity which might be ascribed to complex ion formation—e.g., $Hg^{++}[Hg(CF_3)_4]^{--}$. It is believed that in the formation of these mercurials the metal acts as an acceptor for the CF_3 radical, and the same is almost certainly true of the reactions between mercury and other fluoroalkyl iodides, which has led to the synthesis of homologs of bistrifluoromethyl mercury (*9*).

Elementary phosphorus, arsenic, antimony, sulfur, and selenium undergo analogous thermal reactions with trifluoroiodomethane. When, for example, the fluoroiodide is heated with white phosphorus at 250° C a mixture of the three compounds $P(CF_3)_3$, $P(CF_3)_2I$, and $P(CF_3)I_2$ is obtained in yields of about 60%, 30%, and 10%, respectively (*12*). The proportions may be varied by altering the reaction conditions, particularly the temperature and the relative amounts of the reactants.

The three trifluoromethyl-substituted phosphines are interconvertible. Thus, the iodo-compounds disproportionate on heating, and tristrifluoromethyl phosphine will react with iodine:

$$\begin{aligned}&2(CF_3)_2PI \rightleftharpoons P(CF_3)_3 + CF_3PI_2\\&2CF_3PI_2 \rightleftharpoons (CF_3)_2PI + PI_3\\&P(CF_3)_3 + I_2 \longrightarrow (CF_3)_2PI + CF_3PI_2 + CF_3I\end{aligned}$$

Tristrifluoromethyl phosphine reacts with chlorine and forms the pentavalent derivative $P(CF_3)_3Cl_2$ (bp, 95°). With bromine or chlorine at higher temperatures, the reaction is similar to that with iodine referred to above, and partial replacement of fluoroalkyl groups by halogen atoms occurs—e.g., $(CF_3)_3PCl_2 \rightarrow (CF_3)_2PCl$, CF_3PCl_2, PCl_3, CF_3Cl.

Tristrifluoromethyl phosphine is a colorless liquid (bp, 17.5°), which has a normal Trouton constant. Like trimethyl phosphine (bp, 38°), it burns in air, but, unlike this compound, does not give addition compounds with sulfur, carbon disulfide, or silver iodide (*12*). The influence of the strongly electronegative trifluoromethyl groups is clearly apparent. Triphenyl phosphine, which has a comparable molecular weight, is a solid (mp, 79°, bp $> 360°$), so that the influence of fluorine on volatility is again illustrated. Compounds such as $P(CCl_3)_3$ have not been prepared, and the known monochloro derivative $P(CH_2Cl)_3$ (bp, 100°/7 mm) is unstable on distillation at atmospheric pressure.

Iodobistrifluoromethylphosphine (bp, 73°) fumes in air but is noninflammable; the corresponding methyl phosphine has not been prepared. The diiodo compound, CF_3PI_2, is a yellow oil (bp, 69°/29 mm) which also has no hydrocarbon analog. All three trifluoromethyl-substituted phosphines are substantially insoluble in water, and the tris-substituted compound reacts with it only at temperatures $> 100°$ to give a slow hydrolysis with liberation of fluoroform. Both the mono- and the diiodo-compounds are hydrolyzed slowly by water at room temperature. The former loses one molecular proportion of fluoroform, and both reactions yield a crystalline dibasic acid formulated as $P(CF_3)(OH)_2 \cdot H_2O$, although the characterization is not yet complete. This acid, which has strong reducing properties, is readily oxidized by aqueous hydrogen peroxide to a second dibasic acid $P(CF_3)O(OH)_2$.

These acids are stable to dilute alkali, although the fluoroalkyl-substituted phosphines themselves are quantitatively decomposed with elimination of all the fluorine as fluoroform. These hydrolytic reactions constitute one of the most interesting features of this group of compounds. The chloro derivative $P(CH_2Cl)_3$ is reported to be stable to alkali, but little is known about other trialkyl or triaryl phosphines in this connection. Rupture of the P—C bond seems, however, to be rare. The ease of hydrolysis of the trifluoromethyl compounds is associated with the negativity of the CF_3 groups, and a parallel can be traced with phosphorus compounds that contain alkoxy or aryloxy groups attached to the phosphorus atom. Thus, tertiary phosphites are readily hydrolyzed by alkali to the more stable secondary phosphites which, on further hydrolysis, yield primary phosphites. Hot alkali or acid treatment is then necessary to give phosphorous acid—e.g.:

$$(EtO)_3P \xrightarrow{\text{NaOH}} (EtO)_2P(OH) \xrightarrow{\text{NaOH}}$$
$$(EtO)P(OH)_2 \xrightarrow[\text{or acid}]{\text{hot NaOH}} P(OH)_3.$$

Many tertiary phosphites can, indeed, be hydrolyzed by water alone, and in this respect the P—O bond is less stable than the P—C bond in the P—CF_3 derivatives. Of the aryl derivatives, $P(OC_6H_5)_3$ is also slowly decomposed by water to phenol and phosphorous acid, and, similarly, $(C_6H_5)_2P(OC_6H_5)$ with sodium hydroxide yields $(C_6H_5)_2P(OH)$ and phenol (as sodium salts).

The iodine atom in iodobistrifluoromethylphosphine is reactive and can be replaced by other groups. Silver cyanide and chloride, for example, react very readily and give quantitative yields of the cyano and chloro derivatives, respectively,

$$(CF_3)_2PI \xrightarrow{\text{AgX}} (CF_3)_2PX.$$

With mercury the monoiodo compound gives a quantitative yield of the trifluoromethyl-substituted diphosphine, $(CF_3)_2P—P(CF_3)_2$ (bp, 84°), which has no known methyl analog. Its structure is verified by the reaction with iodine at 200°, from which trifluoroiodomethane corresponding to four trifluoromethyl groups has been isolated. A similar reaction has been observed with bromine. The monoiodo compound has also been shown to be reduced by hydrogen in the presence of Raney nickel to the substituted phosphine, $(CF_3)_2PH$ (bp, 1°), the chemistry of which is under investigation (*12*).

The reaction of arsenic with trifluoroiodomethane (*13*) is very similar to that of phosphorus. At 200°–240° the product from excess of solid arsenic contains *ca.* 60% $(CF_3)_3As$ (bp, 33.3°), 30% $(CF_3)_2AsI$ (bp, 92°), and 10% $(CF_3)AsI_2$(bp, 154°). These compounds can be interconverted by heating the iodo-compounds or by reaction with iodine, exactly as in the case of their phosphorus analogs. They do not ignite in air and are insoluble in, and stable with respect to, water at room temperature. The tristrifluoromethyl arsine shows no reaction with 3 *N* hydrochloric acid at room temperature but, at 200°, yields fluoroform and arsenious acid. As was found for the phosphorus compounds, the trifluoromethyl derivatives of arsenic are very susceptible to aqueous alkali, and use has again been made of this for analysis; cold 10% sodium hydroxide converts $(CF_3)_3As$, $(CF_3)_3AsI$, and $(CF_3)AsI_2$ quantitatively into fluoroform and sodium arsenite. The compound $As(OCH_2CH_2Cl)_3$, which bears some analogy to tristrifluoromethyl arsine by virtue of the negative oxygen atom attached to the arsenic, shows a similar hydrolysis with alkali and even with water: the products are $CH_2OH \cdot CH_2Cl$ and As_2O_3. Similarly, PhAs(OCH_2-

$CH_2Cl)_2$ yields PhAsO and CH_2OHCH_2Cl, and it will be noted that it is the more negative group that is lost. Trimethyl arsine is stable to hydrolysis by alkali, and when phenyl replaces the methyl groups, as in Ph_3As, the compound is also stable to hydrolysis by cold alkali; in this particular instance, hot alkali yields Ph_3AsO.

Like the iodine atom in iodobistrifluoromethylphosphine, that in $(CF_3)_2AsI$ is reactive and may be replaced by other groups by reaction with silver or mercury salts,

$$(\mathrm{CF_3})_2\mathrm{AsI} \xrightarrow[\text{or } \mathrm{Hg}X_2]{\mathrm{Ag}X} (\mathrm{CF_3})_2\mathrm{As}X,$$

where $X = $ F, Cl, Br, CN, CNO, SCN.

Attempts have been made to prepare an acid by the hydrolysis of $(CF_3)_2AsI$, but, as mentioned earlier, this compound does not hydrolyze with water at room temperature, and alkaline reagents yield only fluoroform. Aqueous silver oxide gives a compound that may be the silver salt, $(CF_3)_2AsOAg$, whereas moist mercuric oxide gives an immediate precipitate of mercuric iodide and white needle crystals, moderately soluble in water, of a compound believed to be $[(CF_3)_2AsO]_2Hg$. The monoiodide is oxidized by aqueous hydrogen peroxide to a dibasic acid, $(CF_3)_2AsO(OH)$, a white crystalline solid that is freely soluble in water and may also be recrystallized from chloroform. This acid is almost completely dissociated in aqueous solution, whereas the dissociation constant of the corresponding methyl acid is of the order of magnitude of 10^{-6} to 10^{-7}.

The bistrifluoromethyl halogeno arsines readily attack mercury, and, if this reaction is allowed to proceed to completion, then a simple dimerization to perfluoro cacodyl—i.e., tetrakis trifluoromethyl diarsine—occurs. For example:

$$2(\mathrm{CF_3})_2\mathrm{AsI} + \mathrm{Hg} = (\mathrm{CF_3})_2\mathrm{As{-}As}(\mathrm{CF_3})_2 + \mathrm{HgI_2}.$$

The boiling point of the perfluoro cacodyl (106°–107°) is *ca.* 64° lower than that of the methyl cacodyl. A similar reaction with mercuric oxide yields perfluoro cacodyl oxide (bp, 95°–97°):

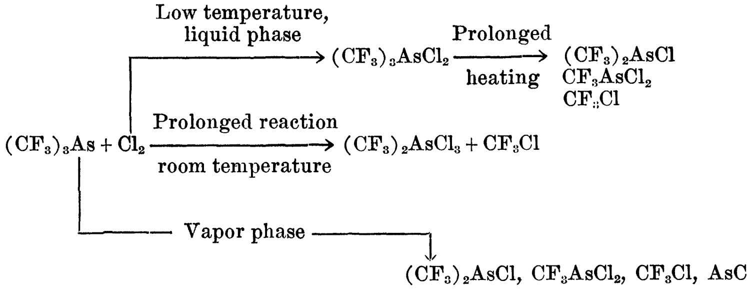
$$2(\mathrm{CF_3})_2\mathrm{AsI} + \mathrm{HgO} = (\mathrm{CF_3})_2\mathrm{As{-}O{-}As}(\mathrm{CF_3})_2 + \mathrm{HgI_2}.$$

The hydrolysis of the perfluoro cacodyl by aqueous alkali is interesting in that approximately 75% of the fluorine appears as fluoroform and the remainder as fluoride and carbonate ions. The same is true of the phosphorus analog $P_2(CF_3)_4$. The hydrolysis of the perfluoro cacodyl oxide, on the other hand, is normal in the sense that all the fluorine is evolved as fluoroform. Although the complete mechanism of the hydrolysis of tetrakistrifluoromethyldiarsine has not yet been fully established, it is likely that hydrolysis involves attack of the As—As bond, as shown below:

$$\begin{tikzcd}[column sep=small]
(\mathrm{CF_3})_2\mathrm{As{-}As}(\mathrm{CF_3})_2 \arrow[r] & (\mathrm{CF_3})_2\mathrm{AsH} + \arrow[d] & (\mathrm{CF_3})_2\mathrm{AsOH} \arrow[dr] & \\
& \mathrm{CF_3H} + \mathrm{F^-} + \mathrm{CO_3^{--}} & & 2\mathrm{CF_3H}
\end{tikzcd}$$

Both of the substituted arsines, $(CF_3)_2AsH$ (bp, 19°) and $(CF_3)AsH_2$ (bp, −14°), have been prepared in good yield by reduction of the corresponding iodides with lithium aluminium hydride and, in their reaction with alkali, provide evidence in support of the above mechanism, since fluoride and carbonate, as well as fluoroform, are liberated (*13*).

The interaction of tristrifluoromethyl arsine with the halogens has been investigated, and it has been found that with chlorine there is a slightly exothermic reaction at room temperature to give $(CF_3)_3AsCl_2$ (bp, 98.5°), only a trace of CF_3Cl being formed. The dichloro-compound may be distilled rapidly at atmospheric pressure without decomposition, but, on heating in a sealed vessel at 125° for several hours, chlorination occurs to give CF_3Cl, CF_3AsCl_2, and $(CF_3)_2AsCl$. Prolonged reaction of chlorine and tristrifluoromethyl arsine at room temperature gives $(CF_3)_2AsCl_3$ (bp, 94°), together with CF_3Cl. It will be noted that replacement of a CF_3 group by chlorine in the pentavalent arsenic compound changes the boiling point only slightly.



Arsenic tribromide formation can be observed when tristrifluoromethylarsine and bromide are mixed even at temperatures below 0°, and a stable pentavalent compound $(CF_3)_3AsBr_2$ cannot be isolated. The products of reaction at room temperature are $(CF_3)_2AsBr$ (bp, 60°), CF_3AsBr_2 (bp, 119°), CF_3Br, and $AsBr_3$. Tristrifluoromethylarsine reacts very slowly with iodine at room temperature, if at all, and appreciable reaction occurs only at 100° to give $(CF_3)_2AsI$, CF_3AsI_2, CF_3I, and AsI_3.

Irradiation with ultraviolet light of a mixture of tristrifluoromethyl arsine and methyl iodide, which shows no tendency to form a quaternary compound at moderate temperatures, leads to an exchange between methyl and trifluoromethyl radicals. As a result, trifluoroiodomethane and compounds of the type $(CF_3)_n(CH_3)_{3-n}As$ are formed. The compound $(CF_3)_2(CH_3)As$ (bp, 52°) is independently synthesized from methyl magnesium iodide and $(CF_3)_2AsI$, and the identity of products firmly establishes this novel exchange reaction, which is being subjected to detailed examination.

The reaction between antimony and trifluoroiodomethane (*14*) is similar to that with arsenic, the main product, tristrifluoromethyl stibine (bp, 72°), being accompanied by $(CF_3)_2SbI$ and $(CF_3)SbI_2$. The monoiodide, however, is decidedly less stable than its arsenic analog and disproportionates at room temperature, with separation of red crystals of antimony triiodide. The monoiodide reacts readily with mercury to give the distibine $(CF_3)_2SbSb(CF_3)_2$, and with aqueous hydrogen peroxide to give $(CF_3)_2SbOOH$.

The interaction of sulfur and trifluoroiodomethane occurs smoothly at 200°–260° in sealed glass tubes or in an autoclave to give a high yield of a compound $C_2S_2F_6$. The main by-product is thiocarbonyl fluoride, CSF_2, formed in negligible amount under optimum conditions, but in higher yield at more elevated temperatures. Thiocarbonyl fluoride is the analog of the carbonyl fluoride obtained by irradiation of trifluoroiodomethane in the presence of oxygen:

$$CF_3I \xrightarrow{O_2,\ h\nu} COF_2,$$

$$CF_3I \xrightarrow[\text{Heat}]{S} CSF_2.$$

The main product, $C_2S_2F_6$, is a dense liquid, which is stable to glass and to mercury, with a boiling point of 35° and a normal Trouton constant. It is decomposed rapidly by aqueous alkali to give not fluoroform, as found for the majority of the compounds mentioned earlier, but completely fluoride, sulfide, polysulfides, and carbonate.

The structure of this compound is proved by two of its reactions. With chlorine at 330°, approximately 90% of the fluorine may be recovered as CF_3Cl, showing that two CF_3 groups are present in the molecule. This conclusion is supported by the reaction with mercury in ultraviolet light, when a very high yield of the crystalline compound $Hg(SCF_3)_2$ is formed. The structural formula may thus be written as $CF_3—S—S—CF_3$. The infrared spectrum is also consistent with this structure (*15*). In the initial reaction two other products, $(CF_3)_2S_3$ (bp, 86.5°) and $(CF_3)_2S_4$ (bp, 135°), are formed and have been isolated (*16*). It is not known whether these contain a straight or a branched sulfur chain, although by analogy with other polysulfides the former is more likely.

Very few polyhalogenated alkyl sulfides have so far been prepared, and those that are known are clearly less stable than the fluoro compounds. Thus, bistrichloromethyl sulfide, which has been prepared, for example, by the action of chlorine on dimethyl sulfide, is readily decomposed into carbon tetrachloride and thiocarbonyl chloride. Bistrichloromethyl disulfide, which is obtained by the action of zinc dust on perchloromethanethiol:

$$2CCl_3SCl + 2Ag = CCl_3—S—S—CCl_3 + 2AgCl$$

decomposes on distillation at atmospheric pressure:

$$CCl_3SSCCl_3 \rightarrow CCl_3SCl + CSCl_2.$$

On irradiation with ultraviolet light, bistrifluoromethyl disulfide liberates free sulfur and yields quantitatively the monosulfide $(CF_3)_2S$ (bp, −22°). The last compound is extremely inert to aqueous alkali, thus differing sharply from the disulfide and resembling the perfluoro-ethers, such as $(CF_3)_2O$ (*17*), which show a general chemical inertness comparable with that of the fluorocarbons.

The interaction of trifluoroiodomethane with selenium (*14*) differs from that with sulfur in that both the monoselenide, $(CF_3)_2Se$ (bp, −1°), and the diselenide, $(CF_3)_2Se_2$ (bp, 70°), are formed under optimum conditions in an approximate ratio of 2:1. At temperatures above 290° the yield of diselenide diminishes rapidly, because of the reversal of the primary reaction, and, at 300°, bistrifluoromethyl diselenide and iodine give a quantitative yield of trifluoroiodomethane and selenium.

Bistrifluoromethyl selenide is stable to acids and alkalis at room temperature but gives almost a quantitative yield of fluoroform when treated with concentrated alcoholic potash at 100°. There is little reaction with chlorine at temperatures up to 100° in the dark, but exposure of a mixture of the monoselenide and chlorine to filtered ultraviolet light brings about a rapid and quantitative conversion to trifluoromethyl selenium trichloride, CF_3SeCl_3 and CF_3Cl. The trichloride is a white crystalline solid with a sublimation point of 180°/760 mm which hydrolyzes rapidly on exposure to moist air and forms trifluoromethyl seleninic acid, $CF_3SeO(OH)$, a white crystalline solid with a melting point of 118°, shown by titration to be a strong monobasic acid. The marked inductive effect of the trifluoromethyl groups is shown by the failure of bistrifluoromethyl selenide to give the reactions with reagents such as nitric acid, methyl iodide, and heavy metal salts, which are characteristic of the methyl analog. This difference is indeed common to the methyl and trifluoromethyl derivatives of all the elements so far studied.

Bistrifluoromethyl diselenide is stable to water and to dilute acids but is readily hydrolyzed to fluoride, carbonate, and selenide by aqueous potassium hydroxide at room temperature. Reaction with chlorine occurs at temperatures below −10° and yields a mixture of CF_3SeCl_3 and the monochloride, CF_3SeCl, which is a red liquid boiling at 32°, converted by an excess of chlorine to the trichloride CF_3SeCl_3. The chlorine atom in the monochloride may readily be replaced by other groups by reaction with silver or mercury salts. Its reaction with mercury gives bis-(trifluoromethylseleno)mercury, $Hg(SeCF_3)_2$, a white crystalline solid of low melting point (*ca.* 40°), which is soluble in water and may readily be sublimed, as well as the compound $CF_3SeHgCl$. The dimercurial is the analog of the sulfur compound $Hg(SCF_3)_2$, which has already been mentioned, and, indeed, may be produced in a similar way from the diselenide, $(CF_3)_2Se_2$, by reaction with mercury in ultraviolet light. The bromination of the diselenide at 150° gives only selenium tetrabromide and bromotrifluoromethane, but at lower temperatures CF_3SeBr_3 and CF_3SeBr can be isolated.

Although indications have already been obtained that the preparation of other fluorinated organometallic compounds of other elements (e.g., Al, Ga) will be possible by the general method described above, it is questionable if this approach will prove satisfactory in all cases. Indeed, it is already known that the more reactive electropositive metals react readily with free fluoroalkyl radicals and are converted to fluorides. There is thus a need for other approaches to this problem. One, which is of considerable interest from the point of view of reaction mechanism, is the use of radical exchange reactions, as illustrated by the work already mentioned on the preparation of arsenicals containing both alkyl and fluoroalkyl radicals. A more general solution to the problem is now available, however, with the successful preparation of perfluoroalkyl Grignard reagents (*18*). It has already been shown that these compounds, although appreciably more difficult to manipulate than their hydrocarbon analogs, can under suitable conditions react with organic functional groups such as —CHO, $>C=O$, —COOR, —CN, —COCl. Furthermore, reaction of trifluoromethyl magnesium iodide with silicon tetrachloride yields, with related compounds, bistrifluoromethyl silicon dichloride $(CF_3)_2SiCl_2$ (*19*). This opens up interesting possibilities in the field of perfluorosilicones.

The above account does no more than outline the present state of knowledge. The perfluoroalkyl derivatives of the elements other than carbon constitute a vast new branch of chemistry, the study of which is only just beginning. It is already apparent, however, that such a study will throw considerable light on the current theories of chemical reactivity, as well as providing compounds of value in both the academic and industrial worlds.

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The International Astronomical Union

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THE International Astronomical Union held its eighth general assembly in Rome, September 3–13. Founded in 1919 by the International Research Council (now the International Council of Scientific Unions), it is the oldest among the scientific unions of the world. Because the earth is a sphere and at any one place on its surface only half the sky is observable, astronomers have since ancient times depended more than other research workers upon international cooperation.

The Astronomical Union is unusual in another respect—it is the only union in which the USSR takes an official part, with 32 other participating countries. This is a source of professional gratification to the astronomers of the United States; it is also the origin of a large number of thorny problems. To deal with the latter, as well as with the more ordinary problems that confront all unions, the Department of State, working with the National Research Council, appointed a delegation to the Rome meeting, which consisted of J. J. Nassau, I. S. Bowen, G. M. Clemence, D. Brouwer, and F. L. Whipple as members. G. P. Kuiper was appointed as an alternate. I was named as chairman of the delegation.

The United States delegation held conferences in

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[1] The views expressed in this article are my own. I present them as an American astronomer, and not as the president of the International Astronomical Union.