The above and other objects may be accomplished in accordance with this invention which comprises compounds of the formula \( \text{HCF}_2\text{CF}_{2}\text{CH}_2X \) wherein \( X \) is a halogen having an atomic weight between 35 and 80, i.e. 3-chloro-1,1,2,2-tetrafluoropropane having the formula \( \text{HCF}_2\text{CF}_{2}\text{Cl} \) and 3-bromo-1,1,2,2-tetrafluoropropane having the formula \( \text{HCF}_2\text{CF}_{2}\text{Br} \).

The compounds of this invention are new compounds which are useful for a wide variety of purposes. They are useful as solvents, heat exchange media, hydraulic fluids, dielectrics, fire extinguishing agents, intermediates for the manufacture of other fluorne-containing compounds, and the like. The 3-bromo-1,1,2,2-tetrafluoropropane is particularly valuable as an inhalation anesthetic, and has unexpectedly unique properties for that purpose as disclosed more fully by Dishart in Patent No. 3,034,959.

The compounds of this invention are nonexplosive and nonflammable in air, and are stable solvents for oils and greases but have little effect on elastomers, plastics, insulation materials and metals. A selective solvent action adapts them for removing oil, grease, and dirt from such objects and equipment as motor stators, electrical controls, optical and precision instruments, gages, and aircraft instruments, without harm to metal or plastic parts. The compounds are preferably used as solvents in closed systems or well ventilated areas. The compounds are also useful as solvent media for the polymerization of perfluoroelins, for example, tetrafluoroethylene.

The bromo- and chlorofluoropropanes of this invention may be used as low boiling dielectric media to provide, for example, insulation and cooling simultaneously through evaporation in equipment fitted with a reflux condenser. The dielectric constants are:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dielectric Constant, 5,000 cycles per sec. at 20° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-bromo-1,1,2,2-tetrafluoropropane</td>
<td>6.9</td>
</tr>
<tr>
<td>3-chloro-1,1,2,2-tetrafluoropropane</td>
<td>6.8</td>
</tr>
</tbody>
</table>

In comparison, petroleum oil that is widely used as a dielectric has a dielectric constant of about 2, and highly chlorinated aromatic hydrocarbons that provide advantages over petroleum oil as dielectrics have a dielectric constant of 5 to 6.

The compounds are effective fire extinguishing agents. For example, a vigorous gasoline fire in an open dish was readily made to subside and to go out by impinging a fine stream of either the bromo- or the chlorofluoropropane onto the burning gasoline. The fire of a well-burning paper and wood-chip mixture was soon smothered and put out with a stream of either compound. A temporary fire-proofing effect was provided, as the wood-chips absorbed the fire extinguishing compound and could not be immediately reignited.

It has been found that the 3-bromo-1,1,2,2-tetrafluoropropane of this invention is especially well adapted for use as an inhalation anesthetic because it smoothly and readily induces a deep anesthesia and its vapors, in concentrations within the anesthetic range, have a pleasant and non-irritating odor. This compound is nonflammable and its vapors, mixed with oxygen in the proportions used for anesthesia, is not flammable or explosive.

In concentrations that produce anesthesia satisfactory for surgical purposes, the compound does not cause convulsions in mice and dogs. It may be administered by various machine techniques with a wide margin of safety and has been observed to produce no pronounced change in respiratory rate or blood pressure in dogs until very deep levels of anesthesia were reached and maintained.
With 3-bromo-1,1,2,2-tetrafluoropropene, a concentration of from about 6% to about 7% by volume in oxygen or air induces a surgical depth of anesthesia in dogs. Such a level is readily maintained with concentrations of from about 4% to about 5% by volume. Concentrations in excess of 8% have been used without fatality. At a given level of anesthesia in dogs, blood pressure depression is generally low.

The compounds of this invention may be considered to be members of series of compounds, the members of which differ from the adjacent members by a CF₂ group, which series may be represented by the formulae H(CF₃)₂CH₂Cl and H(CF₃)₂CH₂Br wherein n represents an integer. Not all members of each series are known. Of those that are known, none, other than the 3-bromo-1,1,2,2-tetrafluoropropene of this invention, has been found suitable as an inhalation anesthetic. For example, the compounds of the formula H(CF₃)₂CH₂Cl and H(CF₃)₂CH₂Br cause convulsions in mice when used in inhalation anesthetic mixtures. The compounds in which n is 6 or higher have too low a vapor pressure at ordinary room temperature to function as inhalation anesthetics. 2-bromo-1,1-difluoroethane (n=1) having the formula HCF₂CH₂Br is unsuitable as an inhalation anesthetic because, when it was so used on dogs, it rendered them rigid, produced convulsions and resulted in cardiac arrhythmia as disclosed by Robbins in J. Pharmacology and Experimental Therapeutics, 86, pp. 197-204 (1946), see particularly page 202.

Robbins (loc. cit.) tested 2-chloro-1,1-difluoroethane (n=1) having the formula HCF₂CH₂Cl as an inhalation anesthetic on mice and found that it had an AD 50 value (the dose in volume percent in an air atmosphere required to induce anesthesia in 50% of the mice upon ten minutes exposure) of 2.15% and an FD value (the dose in volume percent that caused death in 50% of the mice in ten minutes) of 7.5 (page 198), but did not consider it to show sufficient promise to warrant testing it with dogs or other animals. On the other hand, as shown by Dishar in Patent No. 3,034,959, 3-bromo-1,1,2,2-tetrafluoropropene has an AD 50 value in mice of 0.5%. Thus, the anesthetic dose (AD) of HCF₂CH₂Cl is more than 4 times that for 3-bromo-1,1,2,2-tetrafluoropropene.

A convenient method for preparing the compounds of this invention is to form a p-toluenesulfonic acid ester of 2,2,3,3-tetrafluoro-1-propanol following the procedure of Tiers et al. (JACS, 75, 5978 (1953)) and then to react the resultant ester with the appropriate potassium halide to yield 3-bromo-(or 3-chloro-) 1,1,2,2-tetrafluoro propane following the procedure of Fauro et al. (JACS, 78, 4999 (1956)). Another method of preparation is to react the sodium derivative of 2,2,3,3-tetrafluoro-1-propanol with sulfuryl chloride and to convert the resultant chloro-sulfonate or sulfite ester to the required chloro- or bromo-tetrafluoropropene by reaction with lithium halide. A direct method for preparing the 3-chloro-1,1,2,2-tetrafluoropropene is to feed 2,2,3,3-tetrafluoro-1-propanol to a refluxing mixture of thionyl chloride and pyridine, continue the refluxing, and then distill the 3-chloro-1,1,2,2-tetrafluoropropene from the reaction mixture.

In order to more clearly illustrate the preparation of the compounds of this invention, the following examples are given in which the proportions are by weight except where it is specifically indicated otherwise.

EXAMPLE 1
Preparation of 2,2,3,3-Tetrafluoropropyl Chlorosulfonate
Sulfuryl chloride (168.5 g., 1.25 mol), dissolved in 2,2,3,3-tetrafluoro-1-propanol (132 g., 1 mol), was added dropwise at 45°C to 65°C to a solution prepared by reacting sodium wire (23 g., 1 mol) with 2,2,3,3-tetrafluoro-1-propanol (330 g., 2.5 mol). At the end of one-half hour's stirring, the solution was acidic. The reaction mixture was filtered to remove sodium chloride, and the filtrate was distilled. The fraction distilling at 142°C to 145°C (127.5 g.) was the desired 2,2,3,3-tetrafluoropropyl chlorosulfonate and had an index of refraction (nD²θ) of 1.3710.

Analysis — Calculated for CH₃O₂SF₂Cl: C, 15.61; S, 13.87; Cl, 15.39. Found: C, 15.55; S, 13.5; Cl, 15.25.

Conversion to 3-Chloro-1,1,2,2-Tetrafluoropropene
Lithium chloride (25.4 g., 0.6 mol) was heated in 75 ml of diethyleneglycol to 125°C in a flask fitted with a water separator-condenser unit. 2,2,3,3-tetrafluoro-1-propanol (58 g., 0.25 mol) was added dropwise while stirring the reaction mixture. The product began to distill at the start of addition and continued to distill throughout the reaction. The pot temperature was raised to 170°C before cooling. The crude distillate, collecting in the water separator, weighed 33 g. After being washed with ice water, drying over anhydrous MgSO₄ and distilling, 3-chloro-1,1,2,2-tetrafluoropropene was obtained in 61% yield (23 g.). By further fractional distillation and passage through columns of alumina activated by heating in an air oven at 200°C for four days, a high quality compound was provided. Its physical properties and the result of chemical analysis are: M.P. 108°C, B.P. at 760 mm. 55°C, sp. gr. 20/4 = 1.43, nD²θ 1.3281; calculated chloride content 23.58%, found 23.4% CI.

EXAMPLE 2
Preparation of Bis(2,2,3,3-Tetrafluoropropyl)Sulfate
Sodium wire (23 g., 1 mol) was reacted at 80°C to 95°C in excess 2,2,3,3-tetrafluoro-1-propanol (330 g., 2.5 mol). To this solution, sulfuryl chloride (67.5 g., 0.5 mol), dissolved in 2,2,3,3-tetrafluoro-1-propanol (132 g., 1 mol), was added slowly at 70°C to 85°C. A white precipitate of sodium chloride formed. After standing for about 48 hours at room temperature, the strongly acidic mixture was filtered to remove the salt. The filtrate was distilled at 107°C to 112°C to remove unreacted fluoroketanol. The residue from the first distillation consisted of two immiscible phases which were then fractionally distilled under vacuum. The desired bis(2,2,3,3-tetrafluoropropyl)sulfate distills at 90°C to 91°C/6 mm. (61.5 g.); nD²θ 1.3498.

Analysis — Calculated for CH₃O₂S₂F₂: C, 22.1; H, 1.84; F, 46.62; S, 9.81. Found: C, 22.7; H, 2.1; F, 45.1; S, 9.9.

Conversion to 3-Bromo-1,1,2,2-Tetrafluoropropene
Lithium bromide (14.5 g., 0.167 mol) and bis(2,2,3,3-tetrafluoropropyl)sulfate (27.5 g., 0.083 mol) were heated in 50 ml diethyleneglycol in a flask fitted with a water separator-condenser unit. The product began to distill when the mixture reached 125°C and continued to come over as the reaction temperature rose. The pot temperature was raised to 165°C before cooling. The crude distillate, collecting in the water separator, weighed 15.5 g. After being washed twice with ice water, drying over anhydrous MgSO₄, fractionally distilling, and passing through columns of alumina as in Example 1, pure 3-bromo-1,1,2,2-tetrafluoropropene was obtained. Its physical properties and the result of chemical analysis are: M.P. 70°C, B.P. at 760 mm. 74°C, sp. gr. 20/4 = 1.81, nD²θ 1.3558; calculated bromine content 41.01%, found 40.3% bromine.

EXAMPLE 3
Preparation of 2,2,3,3-Tetrafluoropropyl p-Toluenesulfonate
With 79 g. of 2,2,3,3-tetrafluoro-1-propanol was mixed 120 ml of pyridine, and the mixture was heated at 45°C to 10°C. To the cooled mixture was added slowly over a period of one hour 190 g. of p-toluenesulfonyl chloride, and the reaction mass was left at room temperature.
overnight. The resultant mass was then poured into a mixture of ice and sodium bicarbonate. The ester crystallized and was collected by filtration. The ester was then dissolved in methanol, dried over anhydrous magnesium sulfate and filtered. The methanol was removed from the filtered solution by distillation at atmospheric pressure, and 142 g. of the desired ester collected as distillate at 124° C. to 126° C. at 2 mm. mercury pressure. The ester melts at 14° C. to 16° C., has nD\text{20} = 1.4600 and sp. gr. 20/4 = 1.397.

**Analysis.**—Calculated for C\text{10}H\text{15}F\text{4}O\text{2}S: C, 42.15; H, 3.5; F, 26.6; S, 11.2. Found: C, 41.9; H, 3.6; F, 26.0; S, 11.2.

**Conversion to 3-Bromo-1,1,2,2-Tetrafluoropropane**

By the procedure of Tiers et al. (J.A.C.S., 75, 5979, 1953)), 142.8 g. (0.5 mol) of the above 2,2,3,3-tetrafluoropropyl p-toluenesulfonate, 43.4 g. (0.5 mol) of lithium bromide and 150 ml. of diethylene glycol were heated together with a rise of temperature to 190° C. over a period of 2 hours. An additional 9 g. portion of lithium bromide was added and the mass kept at about 190° C. for another 6 hours. A total of 90 g. of product distilled from the reaction mass and was collected. The product was washed twice with water, dried over anhydrous magnesium sulfate, fractionally distilled, and passed through columns of activated alumina. The final product had a boiling point of 74° C. at 760 mm., sp. gr. 20/4 of 1.81, and refractive index nD\text{20} of 1.3558.

It will be understood that the foregoing examples are given for illustrative purposes solely and that this invention is not limited to the specific embodiments described therein. On the other hand, it will be apparent to those skilled in the art that variations and modifications can be made therein, particularly in the materials, proportions and conditions employed without departing from the spirit and scope of this invention.

From all of the above, it will be apparent that this invention provides novel compounds which are valuable for a variety of purposes. Particularly, the 3-bromo-1,1,2,2-tetrafluoropropane has unexpectedly unique properties whereby it is outstanding as an inhalation anesthetic. Therefore, this invention constitutes a valuable advance in and contribution to the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A fluorine-containing compound having the formula HCF\text{2}CF\text{2}CH\text{2}X wherein X represents a halogen atom having an atomic weight between 35 and 80.
2. 3-chloro-1,1,2,2-tetrafluoropropane.
3. 3-bromo-1,1,2,2-tetrafluoropropane.

**References** Cited in the file of this patent