

[54] **3-PERFLUOROALKYL-1 PROPENES AND
PROCESS FOR PRODUCING**

[76] Inventors: **Martin Knell**, 4 Possum Rd.,
Ossining, N.Y. 10562; **Neal O.
Brace**, 1202 Howard Cle., Wheaton,
Ill. 60187

[22] Filed: **Sept. 1, 1971**

[21] Appl. No.: **177,091**

[52] U.S. Cl. **260/653.3**

[51] Int. Cl. **C07c 17/00, C07c 21/18**

[58] Field of Search **260/653.3**

[56] **References Cited**

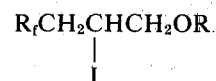
UNITED STATES PATENTS

2,880,247 3/1959 Miller 260/653.3

Primary Examiner—Daniel D. Horwitz
Attorney, Agent, or Firm—Joseph G. Kolodny; Edward
Mc C. Roberts; Prabodh I. Almanla

[57] ABSTRACT

This invention discloses the preparation of 3-perfluoroalkyl-1-propenes with the perfluoroalkyl group containing three to fourteen carbon atoms. These compounds are formed by treatment of



with zinc wherein R_f is perfluoroalkyl, and R is lower alkyl, acyl, benzoyl or aryl.

5 Claims, No Drawings

3-PERFLUOROALKYL-1 PROPENES AND PROCESS FOR PRODUCING

The present invention is directed to a novel process in the preparation of 3-perfluoroalkyl-1-propenes of the formula:



wherein R_f is a long chain straight or branched perfluoroalkyl group of the formula C_nF_{2n+1} , where n is an integer from 3 to 14 and more preferably 6 to 12. There compounds are disclosed in Anello et al U.S. Pat. No. 3,576,858 issued Apr. 27, 1971.

The present compounds are useful intermediates for application in textile finishes. Illustratively, the 3-perfluoroalkyl-1-propenes of the present disclosure may be converted to fluoroalkyl fumarates which may be employed as textile finishes. Reference is made to E. K. Kleiner and M. Knell, U.S. Pat. application Ser. No. 720,370 filed Apr. 10, 1968 for employment of the fluoroalkyl fumarates as soil repellents.

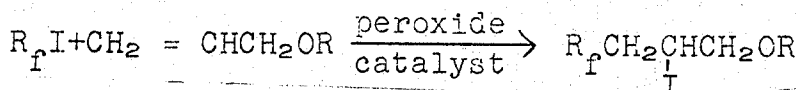
In the technique of this disclosure, the 3-perfluoroalkyl-1-propenes are formed by treatment of specific 3-perfluoroalkyl-2-iodo-1-alkyl ethers or 3-perfluoroalkyl-2-iodo-1-alkyl esters with zinc which re-

point of economic consideration, R_f desirably contains six to 12 carbon atoms. R_f groups containing less than six carbon atoms do provide soil repellency in textile finishes. Nevertheless, due to industry standards of high repellency levels, an additional fluorine content is desirable and therefore the use of R_f groups containing at least six carbon atoms is highly desirable. Illustratively a suitable R_f group contains seven carbon atoms.

The present process is directed to the treatment of the disclosed 3-perfluoroalkyl-2-iodo-1-alkyl ethers or esters with zinc to obtain terminal unsaturation rendering novelty to the present technique. A hydroxylic solvent may be employed in conjunction with the disclosed process.

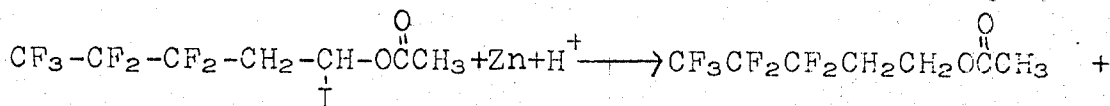
DESCRIPTION OF THE INVENTION

The present process employs the utilization of starting materials comprising fluorinated iodoalkyl ethers and esters with zinc. The fluorinated iodoalkyl compounds utilized in this technique are known in the art and may be prepared in accordance with Brace U.S. Pat. No. 3,145,222 and Brace, J. Org Chem. 27, 3033, (1962), namely:



sults in terminal unsaturation. In contrast, the prior art teaches the treatment of closely related fluorinated iodoalkanes with zinc results in a different reaction, namely replacement of the iodine atom by hydrogen (Haszeldine and Steele, J. Chem. Inc. 1953, 1199; Haszeldine and Steele, J. Chem. Inc. 1953, 1592.)

Also, it is known in the prior art, Brace, J. Org Chem. 27, 3033 (1962), to treat polyfluoro-iodoalkyl acetate with zinc and alcoholic HCl to obtain the following:

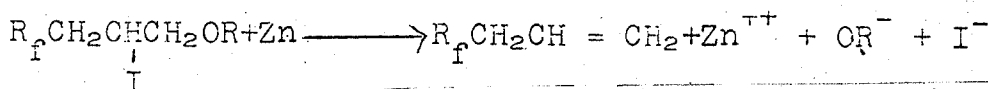


The Brace disclosure illustrates the principle that in reacting fluorinated iodoalkyl esters in the presence of zinc, reduction of the fluorinated alkyl iodide takes place, namely the replacement by iodine by hydrogen.

In contrast to known teachings utilizing fluorinated alkyl iodide constituents and zinc, the present invention employs starting compounds which are closely related to prior art starting compounds but forms a reactant product which is totally unexpected.

SUMMARY OF THE INVENTION

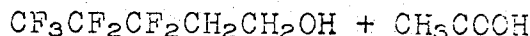
The present process may be summarized by the following equation:



wherein R_f is a long chain perfluoroalkyl group either straight or branched chain of the formula C_nF_{2n+1} , where n is an integer from 3 to 14; R represents lower alkyl containing one to four carbon atoms, lower acyl containing one to four carbon atoms, benzoyl or aryl. For optimum utility in producing textile finishes, it is desirable that R_f be a straight chain although branched chains produce satisfactory results. From the stand-

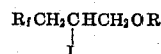
In the present disclosure R_f is a straight or branch chain perfluoroalkyl group containing three to 14 carbon atoms, and more desirably six to 12 carbon atoms.

The reaction to produce the 3-perfluoroalkyl-1 propene is carried out in the presence of zinc. A hydroxylic solvent may be employed. Additionally a proton donor may be used in analogous fashion as prior art disclosures but a different result is obtained in the present use with the present selection of starting compounds. Suitable



solvents include methanol, isopropanol, cellosolves and ethylene glycol, etc. Proton donor systems, if employed, can include hydrogen chloride, formic acid etc. and systems disclosed in the Haszeldine and Steele disclosures, supra.

In the reaction to form the 3-perfluoroalkyl-1-propenes utilizing the starting compounds defined herein, namely



and zinc, it is not directly understood why replacement of the iodine with hydrogen does not take place under

similar reaction conditions as the prior art employing closely related fluorinated iodoalkanes. Nevertheless, in spite of the prior art indication and illustration of the replacement of iodine by hydrogen in the presence of a proton donor, in the present reaction the iodine is not replaced by hydrogen and terminal unsaturation results.

To further illustrate the innovative aspects of the

present invention the following examples are provided:

EXAMPLE 1

Preparation of

1,1,2,3,3-pentahydroperfluoro-1-decene from
1,1,2,3,3-pentahydro-2-iodoperfluoro-1-decyl acetate

19.0 Grams of zinc dust and 20 ml. of anhydrous ethanol are added to a 500 ml. flask and stirred rapidly while 10 ml. of 36 percent hydrochloric acid are added. The reaction mixture is heated to 60°C and 50.0 grams of 1,1,2,3,3-pentahydro-2-iodoperfluoro-1-decyl acetate (prepared according to method of Brace, J. Org Chem. 27, 3033 (1962)) is added with 100 ml. of anhydrous ethanol. The addition of the acetate takes approximately 45 minutes. The reaction mixture is continuously stirred for an additional 2½ hours and the temperature maintained at 60°C. Thereafter the reaction mixture is cooled to room temperature, the unreacted zinc is filtered off and the product washed with 1500 ml. of water. The oily layer is dried over molecular sieve and then distilled through an 18 inch spinning band column; 19.6 grams of product boiling at 142°–144°C/760 mm. is obtained.

Analysis for $C_{10}H_5F_{15}$:

	C	H	F
Calc.:	29.35;	1.12;	69.49
Found:	29.35;	1.32;	70.17

EXAMPLE 2

Preparation of

1,1,2,3,3-pentahydroperfluoro-1-decene from
1,1,2,3,3-pentahydro-2-iodoperfluoro-1-decyl
hydroxyethyl ether

A slurry of 8.0 grams (.122 mole) of zinc dust in 80 ml. of acetic acid and 55 ml. of ether is heated to reflux with stirring and a solution of 50.0 grams (0.083 mole) of 1,1,2,3,3-pentahydro-2-iodoperfluoro-1-decyl hydroxyethyl ether (prepared from perfluoroheptyl iodide and allyl hydroxyethyl ether according to the method of Brace, J. Org Chem. 27, 3033 (1962)) in 25 ml. of ether is added dropwise. Reflux with stirring is continued for about 12 hours. The clear colorless solution is then separated from the unreacted zinc; water and sodium bicarbonate is added to neutralize the acetic acid. The ether solution is dried over anhydrous magnesium sulfate and the ether removed with the aid of a water pump. The residue is then fractionally distilled through a short Vigreux column. The first fraction, boiling at 46°–47.5° at 16 mm. pressure, weighs 22.3 grams and is shown to be 1,1,2,3,3-pentahydroperfluoro-1-decene.

EXAMPLE 3

Preparation of

Bis(1,1,2,2,3,3-hexahydroperfluoro-1-decyl) Fumarate
a) 1,1,2,2,3,3-Hexahydroperfluoro-1-Bromodecane

15.6 Grams of 1,1,2,3,3-pentahydroperfluoro-1-decene are added to a quartz glass Fischer Porter tube and brought to boiling to remove any possible trapped air. It is then closed off, cooled to the temperature of liquid nitrogen and 7.0 grams of dry hydrogen bromide added. The reaction mixture is allowed to warm to room temperature and it is then placed 15 centimeters from a 250 watt UV light source for 4½ hours. The ex-

cess hydrogen bromide is permitted to escape and the product is then washed with 50 ml. of water to remove any trapped hydrogen bromide. It is then washed with 25 ml. of a 10 percent solution of sodium thiosulfate and dried over molecular sieve. Distillation yields 16.8 grams of product boiling mainly at 95°–96°C./24 mm.

Analysis for $C_{10}H_6BrF_{15}$:

	C	H	Br	F
Calc.:	24.46;	1.23;	16.27;	58.04
Found:	24.31;	1.27;	17.50;	58.10

EXAMPLE 4

b) Bis(1,1,2,2,3,3-Hexahydroperfluoro-1-decyl)
Fumarate

14.7 Grams of 1,1,2,2,3,3-Hexahydroperfluoro-1-bromodecane and 13.0 grams of montriethylammonium fumarate are charged to a reaction flask and heated with constant stirring at 150°C for 7 hours. Thereafter volatiles are stripped off and the reaction mixture cooled to room temperature. The product is extracted with chloroform and washed with water to remove the triethylammonium hydrobromide salt. Thereafter the chloroform is stripped off in a rotary evaporator. The product is distilled, yielding 8.65 grams, boiling at 190°–195°C/100 mm. The melting point is 75°–78°C.

Analysis for $C_{24}H_{14}F_{30}O_4$:

	C	H	F
Calc.:	30.78;	1.51;	60.87
Found:	31.08;	1.62;	60.83

EXAMPLE 5

Preparation of

1,1,2,3,3-pentahydro-2-iodo-perfluoro-1-decylphenyl
ether ($C_6H_5OCH_2CHICH_2C_7F_{15}$)

Allyl phenyl ether (Aldrich, 13.4g, 0.100 mol), 1-iodoperfluoroheptane (redistilled, bp 70°/70 mm, n_D^{25} 1.3286; 49.6g, 0.100 mol) and azobisisobutyronitrile (0.456g, 0.00278 mol) were charged to a Fischer Porter aerosol tube, cooled to -78°, evacuated and filled three times with nitrogen, sealed and heated at 70.0° for 21 hr. An orange, cloudy mixture formed, which was cooled to 20°, filtered through a sintered disc into a distillation flask (62.5g) and distilled in a two-foot platinum spinning band column (Column A). 1-iodoperfluoroheptane (bp 36°/10 mm, n_D^{25} 1.3308, 21.5g), allyl phenyl ether (bp 39°/10.20 mm, n_D^{25} 1.5184, 4.72g) and the adduct ($C_6H_5OCH_2CHICH_2C_7F_{15}$, bp 96–99°/0.14 mm, n_D^{25} 1.4245, 29.55g), a residual brown oil (4.0g) and trap liquid (2.0g, n_D^{25} 1.3794, mostly $C_7F_{15}I$) were obtained. The yield of the adduct was 89 percent, and conversion was 47 percent based on recovered starting materials.

Analysis for $C_{10}H_{10}F_{15}IO$:

	C	H	F	I
Calc.:	30.49;	1.60;	45.27;	20.14
Found:	30.66;	1.65;	45.10;	20.10

EXAMPLE 6

Preparation of 1,1,2,3,3-pentahydro-perfluoro-1-decene ($C_7F_{15}CH_2CH=CH_2$)

from $C_6H_5OCH_2CHICH_2C_7F_{15}$

Zinc powder (9.2g, 0.14 mol, 60-200 mesh size), was added to a solution of 50 ml of ethanol and 10 ml of 36 percent hydrochloric acid in a 500 ml r.b. flask fitted with a paddle stirrer, reflux condenser and dropping funnel, and heated to 60°. A solution of $C_6H_5OCH_2CHICH_2C_7F_{15}$ (28.5g, 0.0470 mol) in ethanol (50 ml) was added during 1 hr at 60°-70° while stirring. A gray cloudy slurry formed with an exothermic reaction. Stirring was continued for 2.0 hr at 70°; 5 ml of 36 percent HCl was added, and stirred for 2.5 hr at 70°. The reaction mixture had separated into 2 layers. To the cooled reaction mixture, decanted from zinc, was added 200 ml of water, and the lower layer removed (17.1g, 88 percent crude yield). The aqueous layer was extracted twice with dichloromethane and the combined organic layers allowed to stand over $MgSO_4$. Since the filtered solution contained phenol (strong odor), pellets of sodium hydroxide and solid $CaSO_4$ (Drierite) were placed in the solution and again allowed to stand. The entire slurry was placed on Column A and after solvent was removed, the product ($C_7F_{15}CH_2CH=CH_2$) distilled, bp 55°/20 mm, n_D^{25} 1.3090, 14.2g (73 percent yield). The trap contained additional product (0.71g, by gas chromatography). Total yield 14.9g (77 percent).

Analysis for $C_{10}H_5F_{15}$:

Calc.: C, 29.35; H, 1.12; F, 60.49
Found: C, 29.52; H, 1.32; F, 67.93

EXAMPLE 7

Preparation of

2-Iodo-4-trifluoromethyl-4,5,5,5-tetrafluoro-1-pentyl acetate ($(CF_3)_2CFCH_2CHICH_2O_2CCH_3$)

2-Iodoperfluoropropane (29.6g, 0.100 mol), allyl acetate (10.0g, 0.100 mol) and azobisisobutyronitrile (0.328g, 2.00 mmol) were charged to a Fischer Porter aerosol tube; after the usual procedure, the tube was heated at 70.0° for 15 hr. Distillation in Column A gave $(CF_3)_2CFCH_2CHICH_2O_2CCH_3$, bp 70°/4.3 mm, n_D^{25} 1.4069, 34.60g (in 3 cuts); an impure higher boiling mixture, bp 72-69°/0.15 mm, n_D^{25} 1.4292, 1.05g, and a residue, 0.5g. The -78° trap contained two layers (5.0g), recovered $(CF_3)_2CFI$ and allyl acetate. The conversion to product was 87.5 percent.

Analysis for $C_8H_8F_7IO_2$:

Calc.: C, 24.26; H, 2.03; F, 33.58; I, 32.04
Found: C, 24.09; H, 2.17; F, 32.76, 33.00; I, 31.95

EXAMPLE 8

Preparation of

4-Trifluoromethyl-4,5,5,5-tetrafluoro-1-pentene

$(CF_3)_2CFCH_2CH=CH_2$ from

$(CF_3)_2CFCH_2CHICH_2O_2CCH_3$

$(CF_3)_2CFCH_2CHICH_2O_2CCH_3$ (30.0g, 0.0756 mole)

was added slowly from a Varibor dropping funnel to a slurry of zinc (10.0g, 0.153g-atom) in oxydiethanol (diethylene glycol, 20 ml), while stirring by a magnet in a total reflux, partial take-off distilling apparatus connected to a Dry-Ice trap. The iodo acetate was added to the reaction flask during 1 hr at 116°-130° bath temperature (internal temperature, 110°-118°) while $(CF_3)_2CFCH_2CH=CH_2$ distilled, bp 46°-50°, 15.5g (99 percent). The distillate was dried over Drierite, and a check by glpc showed only one peak. The product was redistilled in a 6-inch Podbielniak Heligrid Column, bp 52°, n_D^{25} ca. 1.2980, 12.8g. An NMR spectrum show proton resonance for $CFCH_2CH=$ at 2.85 p.p.m. from tetramethyl silane as a doublet of doublets; and for $CH=CH_2$ at 5.05 to 6.25 p.p.m., as a multiplet. These data were consistent for $(CF_3)_2CFCH_2CH=CH_2$.

Analysis for $C_8H_5F_7$:

Calc.: C, 34.30; H, 2.40
Found: C, 30.76; H, 2.20

The volatility of the sample caused elemental analysis to be inaccurate.

EXAMPLE 9

Free Radical Addition of R_1I ($R=C_8, C_{10}, C_{12}$) to Allyl Acetate; Preparation of

2-iodo-3-perfluoroalkyl-1-propyl acetate
 $(R_1CH_2CHICH_2O_2CCH_3)$

Perfluoroalkyl iodide mixture was fractionally distilled and a solid residue was obtained having the composition by glpc analysis: R_1I , $R=C_8F_{17}I$, 11.5 percent; $C_{10}F_{21}I$, 83.8 percent and $C_{12}F_{25}I$, 2.3 percent. There were several unknown substances present in small amount. This material was used in the following preparation. R_1I (64.6g, ca. 0.100 mol) and benzoyl peroxide (0.484g, 2.00 mmol) were placed in a 100 ml r.b. flask fitted with a nitrogen inlet, reflux condenser, Varibor dropping funnel, and stirred by a magnet while heated in an oil bath. Allyl acetate (10.0g, 0.100 mol) was added dropwise during 35 min at 97°-102° (inside), cooling as necessary to maintain reaction temperature at $100 \pm 2^\circ$. Heating in the bath at 100° was continued for 3 hr, and allowed to stand overnight. A solid mass of crystals formed, which would not distill at 100° (12 mm pressure); m.p. (sinter 54°) 56°-59°; ir showed $\gamma C=O$ 1750 cm^{-1} , heavy γCF and other bands anticipated for the adduct $R_1CH_2CHICH_2O_2CCH_3$. A 5.0g portion of the product was recrystallized from ca. 50 ml of ligroine (60°-90° bp). Fractions collected were: (1) 1.8g, mp 63°-64°; (2) 2.5g (after chilling, and evaporation), mp 63°-64°; (3) 0.9g, mp 55°-58°; (4) 0.8g, soft solid. VPC analysis of the mixture showed $R_1CH_2CHICH_2O_2CCH_3R=C_8F_{13}$, 0.2 percent; C_8F_{17} , 12.6 percent and $C_{10}F_{21}$, 76.6 percent. After recrystallization $R=C_8F_{17}$, 4.8 percent; $C_{10}F_{21}$, 83.0 percent. An nmr spectrum agreed with structure.

Analysis for $C_{15}H_8F_{21}IO_2$:

Calc.: C, 24.15; H, 1.08; F, 53.48; I, 17.01
Found: C, 23.33; H, 1.07; F, 54.58; I, 16.92

EXAMPLE 10

Preparation of

1,1,2,3,3-pentahydro-perfluoro-1-tridecene
($C_{10}F_{21}CH_2CH=CH_2$) from
2-iodo-3-(perfluorodecyl)-1-propyl acetate

The crude adduct ($R_1CH_2CHICH_2O_2CCH_3$, mp $56^\circ-59^\circ$, 37.3g, 0.0500 mol) was dissolved in 80 ml of hot ethanol, and added during 25 min at $76^\circ-78^\circ$ to a slurry of zinc dust (9.8g, 0.15 g-atom), ethanol (15 ml) and 36 percent hydrochloric acid (5ml). There was some exothermic reaction. After 1 hr further at 78° the two layers which had formed were poured into water (100 ml) and extracted with dichloromethane (100 ml). Three layers now formed. The lowest layer was removed (14.6g), which solidified at room temperature; mp ca. 30° . It was distilled under reduced pressure in a variable take off still without a column; bp $85^\circ-99^\circ/9.0$ mm, $n_D^{27} 1.3100$, 8.5g. Solid formed in the still head (1.0g recovered), and remained in the pot flask (2.35g). The dichloromethane extract was washed further with dilute sodium sulfite solution, dried over $MgSO_4$ and distilled. Product, bp $88^\circ-93^\circ/9.0$ mm, $n_D^{25} 1.3135$, 5.2g was again obtained. (Total yield of distilled product 55 percent) A residue of 3.2g solid remained. An NMR spectrum agreed with structure, $R_1CH_2CH=CH_2$.

Analysis for $C_{13}H_5F_{21}$:

Calc.:	C, 27.87;	H, 0.90;	F, 71.23
Found:	C, 24.63;	H, 0.86;	F, 71.06

EXAMPLE 11

Addition of $C_7F_{15}I$ to Allyl Benzoate;
1,1,2,3,3-penta-hydro-2-iodo-perfluoro-1-decyl
benzoate ($C_7F_{15}CH_2CHICH_2O_2CC_6H_5$)

Allyl benzoate was prepared from allyl alcohol and benzoyl chloride, bp $102^\circ-104^\circ/13$ mm, $n_D^{25} 1.5165$ lit.*, bp $106^\circ/12$ mm, $n_D^{20} 1.5174$. A Fischer Porter aerosol tube was charged with allyl benzoate (16.2 g, 0.100 mol), 1-iodoperfluoroheptane (49.6 g, 0.100 mol, and azobisisobutyronitrile (0.328 g, 2.00 mmol). After the usual procedure the tube was heated at 70° for 12 hr, the reaction product (two layers) filtered through a sintered disc and distilled without a column, using a variable take-off head. $C_7F_{15}I$ (15.1 g, 30 percent recovery) and allyl benzoate (1.7 g) were removed. The residue was placed on column A and more allyl benzoate (1.7 g, total 21 percent recovery), $C_7F_{15}CH_2CHICH_2O_2C_6H_5$, bp $104^\circ-107^\circ/0.30$ mm, $n_D^{25} 1.4290$, and bp $111^\circ-112^\circ/0.25$ mm, $n_D^{25} 1.4286$, 49.96 g (76 percent conversion, 96 percent yield, based on recovered allyl benzoate), and a residual oil (6.8 g) were obtained. The product turned solid when cooled to 10° . *

Hurd and Filachione, J. Am. Chem. Soc., 61, 1156 (1939); Tommila, Ann. Acad. Sci., Fenn., [A], 59, No. 3, 7 (1942); Beilstein, Vol IX, EIII, p. 402.

Analysis for $C_{17}H_{10}F_{15}O_2$:

Calc.:	C, 31.02;	H, 1.53;	F, 43.30
Found:	C, 30.96;	H, 1.63;	F, 43.66

EXAMPLE 12

Preparation of

1,1,2,3,3-pentahydroperfluoro-1-decene
5 ($C_7F_{15}CH_2CH=CH_2$) from $C_7F_{15}CH_2CHICH_2O_2CC_6H_5$

Using a procedure similar to that for $(CF_3)_2CFCH_2CH=CH_2$, a slurry of zinc dust (9.2 g, 0.14 g-atom) and 2,2'-oxydiethanol (20 ml) was heated to $115^\circ-122^\circ$ (inside) while $C_7F_{15}CH_2CHICH_2O_2CC_6H_5$ (35.0 g, 0.053 mol) was added during a half hr. After the first 15 min, a water pump was attached to reduce the pressure; $C_7F_{15}CH_2CH=CH_2$ distilled, bp $86^\circ-88^\circ/110$ mm, $n_D^{25} 1.3076$, 18.5 g. After all the olefin was obtained the pressure was reduced further during 20 min to strip any remaining product from the pot liquid. The final pot temperature was 138° at 10 mm pressure. The cold trap contained 1.4 g; total 19.9 g (91.5 percent yield). The product was dried over a little Drierite. A check by glpc (6 ft Carbowax 20M, 10 percent on Chromosorb W, at 68° and 15 psi helium pressure) showed one peak at 1.2 minutes. An infrared spectrum was identical to that of $C_7F_{15}CH_2CH=CH_2$ previously prepared.

EXAMPLE 13

Free Radical Addition of 1-Iodoperfluoroheptane to
Allyl Propyl Ether; Propyl

2-Iodo-1,1,2,3,3-pentahydro-perfluoro-1-decyl Ether
30 ($C_7F_{15}CH_2CHICH_2OCH_2CH_2CH_3$)

1-Iodoperfluoroheptane (49.6g, 0.100 mole), allyl propyl ether (15.0g, 0.150 mole, Chem Samples Co., 97 percent) and azobisisobutyronitrile (0.328g, 2.00 mmole) were charged to a Fischer-Porter aerosol tube. After the usual procedure the tube was heated for 12 hrs. at 70° . The colorless clear mixture became cloudy. It was filtered through a sintered glass disc and distilled in column A. A mixture of $C_7F_{15}I$ and allyl propyl ether (6.57g, $n_D^{25} 1.3905$), and $C_7F_{15}I$ (9.27g, $n_D^{25} 1.3300$) were recovered; $C_7F_{15}CH_2CHICH_2OCH_2CH_2CH_3$ distilled, bp $81^\circ-83^\circ/0.85$ mm, $n_D^{25} 1.3767$, 42.65g (71.5 percent conversion). A residue of 1.0g remained. The trap contained 2.50g of starting materials ($n_D^{25} 1.3500$).

Analysis for $C_{15}H_{12}F_{15}OI$:

Calc.:	C, 26.19;	H, 2.03;	F, 47.81;	I, 21.29
Found:	C, 26.50;	H, 2.10;	F, 47.08;	I, 21.31

EXAMPLE 14

Preparation of

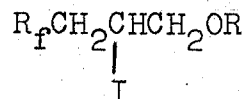
1,1,2,3,3-pentahydro-perfluoro-1-decene
($C_7F_{15}CH_2CH=CH_2$) from
 $C_7F_{15}CH_2CHICH_2O(CH_2)_2CH_3$

Using a procedure similar to that for $C_7F_{15}CH_2CHICH_2O_2CC_6H_5$, a slurry of zinc dust (9.2g, 0.14g-atom) and 2,2'-oxydiethanol (30 ml) was heated to $115^\circ-146^\circ$ (inside), while the pressure was kept at 60 mm and $C_7F_{15}CH_2CHICH_2O(CH_2)_2CH_3$ (38.0g, 0.064 mole) was dropped in slowly during a half hr. Product distilled over slowly at first (bp $45^\circ-102^\circ/60$ mm), and as the reaction temperature reached 146° , more rapidly. Heating at $146^\circ-150^\circ$ was continued for a half

hour under 60 mm pressure. The distillate consisted of two layers (19.4g); the -78° trap liquid (2.86g) also formed two layers. After drying over MgSO₄, distillation in column A gave the following: I, bp 44°/60 mm, (n_D²⁵ not taken), 1.40, 2 layers; II, bp 68°-73°/60 mm, n_D²⁵ 1.3143, 0.40 g; III, bp 73°-74°/60 mm, n_D²⁵ 1.3084, 4.20g, C₇F₁₅CH₂CH=CH₂; IV, bp 74°/60 mm to 56°/21 mm, n_D²⁵ 1.3070, 4.24g, C₇F₁₅CH₂CH=CH₂; V, bp 94°/21 mm, n_D²⁵ 1.3155; 0.80g; VI, bp 94°/21 mm to 87°/6 mm, n_D²⁵ 1.3361, 0.95 g; and VII, bp 85°/1.1 mm, n_D²⁵ 1.3694, 3.75g, recovered C₇F₁₅CH₂CHICH₂O(CH₂)₂CH₃. There was no residue. The infrared spectrum of fraction VII was identical to that of the starting material. The retention time of the peak in glpc analyses of fractions III and IV was identical to that of C₇F₁₅CH₂CH=CH₂ previously prepared. The conversion to C₇F₁₅CH₂CH=CH₂ was 34 percent; the recovery of starting material was 12 percent. Undoubtedly more starting material remained in the reaction mixture which could have been recovered. Nevertheless, reaction of this ether appeared to be more sluggish than that of the benzoate or acetate esters.

What is claimed is:

1. A process for the preparation of 3-perfluoroalkyl-1-propene which comprises treating



where R_f is CnF_{2n+1}

n is an integer from 3 to 14

and R is lower alkyl, lower carboxylacyl, benzoyl or aryl, with zinc in the presence of an alkanol of one to three carbon atoms, a glycol of up to three carbon atoms, ethylene glycol or diethylene glycol.

2. The process of claim 1 wherein n is an integer from 6 to 12.

3. The process of claim 1 wherein R is lower alkyl.

4. The process of claim 1 wherein R is lower carboxylacyl.

5. The process of claim 1 wherein the reaction is effected in the presence of an acid.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,843,735 Dated October 22, 1974

Inventor(s) MARTIN KNELL ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In column 10, claim 1, lines 12 and 13, after the phrase "three carbon atoms," delete "a glycol of up to three carbon atoms, ethylene glycol or diethylene glycol" and insert therefor -- ethylene glycol or diethylene glycol at a temperature of 60°C to the reflux temperature of the system --.

Signed and sealed this 31st day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents