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THE REACTION OF HEXAFLUOROPROPENE OXIDE WITH GRIGNARD REAGENTS

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SUMMARY

The reactions of hexafluoropropene oxide and equimolar amounts of Grignard reagents lead to the formation of 2-halotetrafluoropropanoyl fluorides which were converted to the methyl or ethyl ester for isolation purposes. Treatment of hexafluoropropene oxide with excess Grignard reagent formed an unsaturated ketone of the type $R_2C=CFCOR$ ($R=CH_3$ or CH_2CH_3); a route by which this product is formed is postulated.

INTRODUCTION

The reaction of ethylene oxide with Grignard reagents to form primary alcohols with a two-carbon atom increase in chain length over the alkyl group of the Grignard reagent is a well known reaction in organic chemistry. Treatment of propene oxide with Grignard reagents has been shown to yield secondary alcohols of the type $CH_3CHOHCH_2R$ (R is the alkyl group of the Grignard reagent) formed by attack at the terminal CH_2 group[1]. In certain cases, attack of halide ion from the Grignard reagent on the terminal CH_2 group of propylene oxide also takes place and results in the formation of secondary alcohols of the type $CH_3CHOHCH_2X$ ($X=Cl$, Br)[1,2].

Partly fluorinated epoxides have also been treated with Grignard reagents; thus, McBee and co-workers have reported the following reaction[3]:

$$CF_3CH-CH_2 + CH_3MgBr \rightarrow CF_3CHOHCH_2CH_3$$
$$\underset{\text{O}}{\rule{1.5em}{0pt}}$$

Other nucleophiles such as H^-, $NH(CH_2CH_3)_2$, Br^- and $CH_3CH_2O^-$ also attack the terminal carbon atom of this epoxide to give a secondary alcohol.

Hexafluoropropene oxide, HFPO, on the other hand, has been found by both Sianesi[4] and Knunyants[5] to react with a variety of nucleophiles to give 2-substituted tetrafluoropropanoyl fluorides or other derivatives which are obtained by attack of
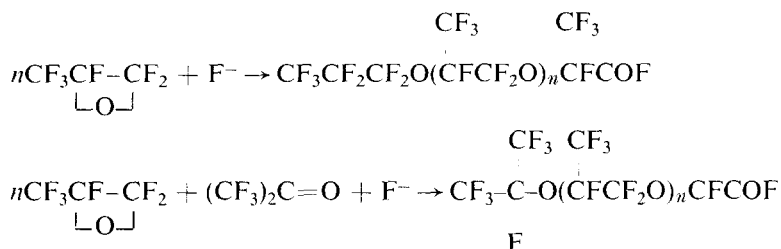
the nucleophile on the central carbon atom. The patent literature contains many references to the use of fluoride ion and R_fO^- as nucleophiles in reactions with HFPO which can lead to relatively high molecular perfluoropolyethers[6-8].
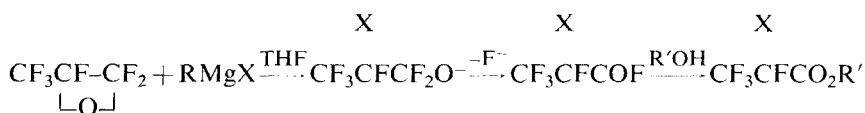
$$nCF_3CF-CF_2 + F^- \rightarrow \overset{CF_3}{CF_3CF_2CF_2O(\overset{|}{C}FCF_2O)_n}\overset{CF_3}{\overset{|}{C}FCOF}$$
$$\lfloor O \rfloor$$

$$nCF_3CF-CF_2 + (CF_3)_2C=O + F^- \rightarrow \overset{CF_3\ CF_3}{CF_3-\overset{|}{C}-O(\overset{|}{C}FCF_2O)_n\overset{}{C}FCOF}$$
$$\lfloor O \rfloor \qquad\qquad F$$

The $-C(CF_3)FCOF$ moiety at the end of the chain has been converted to other groups such as CF_2CF_3, $CF=CF_2$ and $CHFCF_3$[9].

Our interest in HFPO was twofold: (1) the point of attack by organometallic reagents and (2) the possibility that useful monomers could be made using the reaction of HFPO and organometallic reagents.

RESULTS AND DISCUSSION

The reaction of Grignard reagents with tetrafluoroethylene oxide has been reported to yield a mixture of products which were not identified[10]. The reaction of HFPO and Grignard reagents has not been reported to date. We wish to report that reactions of equimolar amounts of HFPO and Grignard reagents form, in yields as high as 65%, α-halo derivatives of tetrafluoropropionic acid which were isolated as the methyl or ethyl ester.

$$CF_3CF-CF_2 + RMgX \xrightarrow{THF} \overset{X}{CF_3\overset{|}{C}FCF_2O^-} \xrightarrow{-F^-} \overset{X}{CF_3\overset{|}{C}FCOF} \xrightarrow{R'OH} \overset{X}{CF_3\overset{|}{C}FCO_2R'}$$
$$\lfloor O \rfloor$$

where $R = CH_3$, CH_2CH_3, C_6H_5, C_6F_5, $H_2C=CHCH_2$, $F_2C=CF$; $X = Cl$ or Br and $R' = CH_3$ or CH_2CH_3.

Products in which the alkyl group of the Grignard reagent was incorporated into the HFPO molecule were not detected nor were products formed by attack of fluoride ion on HFPO observed, confirming that bromide and chloride ions are better nucleophiles than fluoride ion.

The esters of 2-halotetrafluoropropanoic acid were identified by elemental and spectroscopic analysis. The CF_3CFBr group shows characteristic ^{19}F NMR absorption (TFA ref.) at *ca.* 0.5 ppm (CF_3, doublet, $J=9.0$ Hz) and 56 ppm (CFBr, quartet, $J=9.0$ Hz), and the CF_3CFCl group shows characteristic ^{19}F absorption at 3.0 ppm (CF_3, doublet, $J=6.5$ Hz) and 55.3 ppm (CFCl, quartet, $J=6.5$ Hz).

It is considered probable that the α-halo derivatives of tetrafluoropropionic acid are formed by nucleophilic attack of halide ion on the central carbon atom of HFPO, which is the most susceptible point towards nucleophilic attack. The source of halide ion is possibly provided by the equilibrium:

$$2RMgX \rightleftharpoons R_2Mg + MgX_2$$

It is also possible that the formation of the products of the type CF_3CFXCO_2R' takes place *via* direct halogenation by the Grignard reagent.

On the basis of these results, it seemed desirable to prepare diethylmagnesium and determine the course of its reaction with HFPO. When the reaction was carried out, a mixture of at least nine components was detected by GLC analysis; these products were not identified.

The reaction of methylmagnesium iodide with HFPO gave a large amount of tar, iodine and a small amount of material which decomposed with the liberation of iodine when isolated. Since it was evident that the reaction was proceeding in some manner by initial attack of iodide ion on HFPO, a study was made of the reaction of HFPO and sodium iodide in acetone. The products of the reaction, which began immediately, were iodine and the acid fluoride (isolated as the ammonium salt) of 2,3,3,3-tetrafluoropropanoic acid. It seems reasonable to assume that the reaction proceeds as follows:

$$CF_3CF\!-\!CF_2 + I^- \longrightarrow CF_3CFICF_2O^- \longrightarrow CF_3CFIC\overset{\displaystyle O}{\overset{\|}{F}}$$
$$\underset{\textstyle \llcorner O \lrcorner}{\qquad}$$

$$CF_3CHF\overset{O}{\overset{\|}{C}}\!-\!OH \xrightarrow{H_2O} CF_3CFHC\overset{O}{\overset{\|}{F}} \xleftarrow{CH_3CCH_3} [CF_3CFC\overset{O}{\overset{\|}{F}}]^- + I_2$$
$$\downarrow NH_3$$
$$CF_3CHFCO_2NH_4$$

The reaction of HFPO with excess Grignard reagents led to the formation of alkylated α,β-unsaturated ketones.

$$CF_3CF\!-\!CF_2 + RMgBr\ (excess) \longrightarrow \overset{\displaystyle R}{\underset{\displaystyle R}{\diagdown}}C\!=\!\overset{\displaystyle F}{\overset{|}{C}}\!-\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!R$$
$$\underset{\textstyle \llcorner O \lrcorner}{\qquad}$$

(R=CH$_3$ or C$_2$H$_5$)

The infrared spectra of these products showed absorption at 5.9 μ (C=O str.) and 6.2 μ (C=C str.). Both ^{1}H and ^{19}F NMR spectra were consistent with the proposed structures; the ^{1}H NMR spectra showed absorptions due to three distinct alkyl groups and the ^{19}F NMR spectra showed a single absorption at *ca.* 50 ppm (TFA ref.).

It appeared probable that the reaction was proceeding in the following way:

$$CF_3CF\text{-}CF_2 + RMgBr \rightarrow CF_3CFBrCOF$$
$$\qquad \underset{\displaystyle \ \ O\ \ }{\underline{\qquad}}$$

$$CF_3CFBrCOF + RMgBr \rightarrow [CF_3CFCOF]^- \rightarrow F_2C{=}CFCOF$$

$$F_2C{=}CFCOF + RMgBr \rightarrow [RCF_2CFCOF]^- \rightarrow RCF{=}CFCOF$$

$$R_2C{=}CFCOR \leftarrow R_2C{=}CFCOF$$
$$\text{(I)}$$

where $R = CH_3$.

In order to confirm this pathway, $CF_3CFBrCOF$ was prepared and allowed to react with methylmagnesium bromide and the expected product (I) was obtained in 62% yield. Both perfluoroacryloyl fluoride and methyl perfluoroacrylate were also found to give (I) on treatment with methylmagnesium bromide in yields of 35 and 52%, respectively.

The acyl fluoride, $CF_3CFBrCOF$, was made in 92% yield by the reaction of lithium bromide with HFPO in diglyme. Perfluoroacryloyl derivatives proved to be troublesome to make, probably because of the susceptibility of the unsaturated system to attack by even weak nucleophiles[11]. However, the following method adapted from the work of Paleta[12] and Cheburkov[13] was found satisfactory for the preparation of the acid fluoride.

$$CFCl{=}CFCl + CFCl_3 \xrightarrow{AlCl_3} CF_2ClCFClCCl_3 \xrightarrow{Zn} CF_2ClCF{=}CCl_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\downarrow Br_2$$

$$CF_2ClCFBrCOF \xleftarrow{SbF_3Cl_2} CF_2ClCFBrCOCl \xleftarrow{H_2SO_4} CF_2ClCFBrCCl_2Br$$

$$\underset{\xrightarrow{\hspace{1cm}}}{\Big|\ Zn} \quad F_2C{=}CFCOF$$
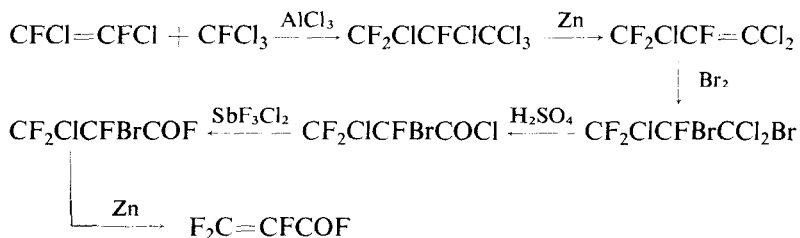
Since the reaction of perfluoroacryloyl fluoride and methanol did not lead to methyl perfluoroacrylate, it was made by the dehalogenation of $CF_2ClCFBrCO_2CH_3$ obtained from $CF_2ClCFBrCOCl$.

Treatment of HFPO with a fourfold excess of trifluorovinylmagnesium bromide yielded only very high boiling material which could not be distilled. It is thus probable that the product $(F_2C{=}CF)_2C{=}CFCOCF{=}CF_2$ undergoes further reaction with Grignard reagent at the CF_2 groups resulting in the formation of high molecular weight material.

It is of interest to note that treatment of the ester $F_2C{=}CFCO_2CH_3$ with excess methylmagnesium bromide gave the ketone in which both fluorine atoms of the CF_2 group were replaced by methyl groups. In contrast, reaction of the ester $F_2C{=}CFCF_2CO_2CH_3$ with excess methylmagnesium bromide yielded the carbinol

$CF_2BrCF=CFC(CH_3)_2OH$ (II). It is unlikely that this reaction takes place *via* attack of bromide ion since no reaction occurred on treatment of the ester $F_2C=CFCF_2CO_2CH_3$ with lithium bromide. It is more likely that the Grignard reagent itself initially brominates the terminal $F_2C=$ group and this is followed by double-bond shift and loss of fluoride ion:

$$F_2C=CFCF_2CO_2CH_3 \xrightarrow{CH_3MgBr} BrCF_2CF=CFCO_2CH_3 \xrightarrow{CH_3MgBr}$$

$$
\begin{array}{ccc}
BrF_2C & & F \\
\diagdown & & \diagup \\
& C=C & \\
\diagup & & \diagdown \\
F & & C(CH_3)_2OH
\end{array}
$$

(II)
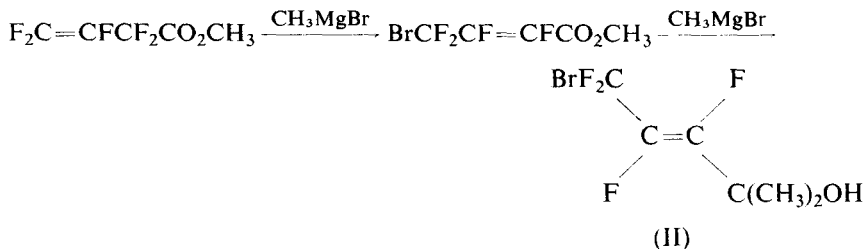
Reaction of the ester grouping with the Grignard reagent to form the carbinol may take place before or after reaction at the $F_2C=$ group. The structure of the carbinol (II) is supported by elemental analysis and spectral data. Mass spectrometry indicated the presence of bromine, infrared spectroscopy showed absorptions at 2.95 μ (OH str.), 3.35 μ (CH str.), 5.9 μ (C=C str.), and in the region 8.0–9.0 μ (CF str.). The ^{19}F NMR spectrum of (II) showed *trans*-F–F coupling of 134.0 Hz. ^{19}F NMR absorption assigned to the CF_2Br group occurred at -27.1 ppm (TFA ref.); this is consistent with ^{19}F NMR absorption due to the CF_2Br group of $CF_2BrCFBrCF_2CFBrCl$ which occurs at -23.1 ppm[14].

Replacement of one fluorine atom of a $F_2C=$ group by bromine has previously been reported in the reaction of allylmagnesium bromide and tetrafluoroethylene which gives, as the major product, 1-bromo-1,2-difluoro-1,4-pentadiene, $H_2C=CHCH_2CF=CFBr$[15].

It is noteworthy that the carbinol (II) consisted only of the *trans* form. This is unusual since it has been observed that 1-fluoro-2-halo-olefins are generally more stable in the *cis* form[16]. Previous work in this laboratory has also indicated the preferential formation of *cis* products in the reaction of $CF_3CF=CFLi$ with various substrates[17].

EXPERIMENTAL

Preparation of hexafluoropropene oxide (HFPO)

Methanol (1350 ml, technical grade) was placed in a flask fitted with a stirrer, thermometer and a Dry Ice/acetone condenser. Potassium hydroxide (112 g) was dissolved in water (178 ml) and added to the flask. The reaction mixture was cooled to $-45°$ and hydrogen peroxide (675 ml, 50% aqueous) was added slowly, the temperature being maintained at or below $-45°$. Hexafluoropropene (135 g, 0.81 mole) was added to the flask in one portion as a liquid. The flask was warmed until the mixture refluxed violently at $-20°$ (10 min), then cooled to $-40°$, the

reflux condenser exchanged for a gas outlet tube and the temperature slowly raised. Impure HFPO was collected in traps cooled to $-78°$ and was purified by passage through bromine (10 ml) in 1,2-dibromohexafluoropropane (100 ml) then through sodium thiosulphate (5% aqueous). The gas was dried by passage through anhydrous calcium sulphate and carbon dioxide was removed *in vacuo*. HFPO (53.0 g, 0.32 mole, 40%) was identified by infrared spectroscopy.

Reaction of HFPO and Grignard reagents

General procedure

Grignard reagents were prepared in the conventional way by addition of the appropriate halogen compound to a rapidly stirred suspension of magnesium metal in THF (dried by distillation from $LiAlH_4$) or diethyl ether. The solution of Grignard reagent was cooled to $0°$ and HFPO bubbled into the solution slowly. A Dry Ice/ acetone condenser was fitted to the reaction flask to return unreacted HFPO. The reaction mixture was stirred at room temperature (10 h), cooled to $-10°$ and methanol or ethanol (20 ml) added, then stirred at room temperature (1 h). After washing with dilute hydrochloric acid, the organic material was extracted with ether, the ether extract was dried ($CaSO_4$) and ether removed by distillation. Fractional distillation of the remaining material yielded the products indicated below.

Methylmagnesium bromide

Reaction of methylmagnesium bromide (0.2 mole) in THF and HFPO (33.2 g, 0.20 mole) followed by addition of methanol (20 ml) yielded methyl 2-bromotetrafluoropropanoate (III) (31.0 g, 0.13 mole, 65%), b.p. 104–105° (lit.[18] b.p. 105–107°). (Found: C, 20.2; H, 1.24; F, 31.8%. $C_4H_3BrF_4O_2$ requires C, 20.1; H, 1.25; F, 31.8%.) ^{1}H NMR: singlet 5.68 τ; ^{19}F NMR (TFA ref.): doublet 0.56 ppm (CF_3, $J=9.0$ Hz) and quartet 57.2 ppm ($CFBr$, $J=9.0$ Hz). Infrared and mass spectrometry were consistent with the proposed structure.

Ethylmagnesium bromide

Reaction of ethylmagnesium bromide (0.2 mole) in THF and HFPO (33.2 g, 0.20 mole) followed by addition of ethanol (20 ml) yielded ethyl 2-bromotetrafluoropropanoate (31.0 g, 0.12 mole, 61%), b.p. 123–124° (lit.[4] b.p. 122–123°). (Found: C, 23.9; H, 1.93; F, 29.8%. $C_5H_5BrF_4O_2$ requires C, 23.7; H, 1.98; F, 30.0%.) ^{1}H NMR: triplet 8.32 τ and quartet 5.26 τ; ^{19}F NMR (TFA ref.): doublet 0.5 ppm (CF_3, $J=9.0$ Hz) and quartet 56.7 ppm ($CFBr$, $J=9.0$ Hz). Infrared and mass spectra were consistent with the proposed structure.

Phenylmagnesium bromide

Reaction of phenylmagnesium bromide (0.2 mole) in THF and HFPO (33.2 g, 0.20 mole) followed by addition of methanol (20 ml) yielded (III) (27.7 g, 0.116 mole, 58%) which was identified by comparison with a known pure sample.

Phenylmagnesium chloride

Reaction of phenylmagnesium chloride (0.2 mole) in THF and HFPO (33.2 g, 0.20 mole) followed by addition of methanol (20 ml) yielded methyl 2-chlorotetra-fluoropropanoate (nc) (20.2 g, 0.105 mole, 52%), b.p. 92–94°. (Found: C, 24.7; H, 1.50; F, 38.6%. $C_4H_4ClF_4O_2$ requires C, 24.7; H, 1.54; F, 39.1%.) ^{1}H NMR: singlet 6.36 τ. ^{19}F NMR (TFA ref.): doublet 3.0 ppm (CF_3, $J=6.5$ Hz) and quartet 55.3 ppm (CFCl, $J=6.5$ Hz). Infrared and mass spectral data confirmed the proposed structure.

Pentafluorophenylmagnesium bromide

Reaction of pentafluorophenylmagnesium bromide (0.2 mole) in diethyl ether and HFPO (33.2 g, 0.20 mole) followed by addition of methanol (20 ml) yielded (III) (12.2 g, 0.51 mole, 26%) which was identified by comparison with a known pure sample.

Allylmagnesium bromide

Reaction of allylmagnesium bromide (0.2 mole) in THF and HFPO (33.2 g, 0.20 mole) followed by addition of methanol (20 ml) yielded (III) (20.2 g, 0.084 mole, 42%) which was identified by comparison with a known pure sample.

Trifluorovinylmagnesium bromide

Reaction of trifluorovinylmagnesium bromide (0.2 mole) in THF with HFPO (33.2 g, 0.20 mole) followed by addition of methanol (20 ml) to the reaction mixture yielded (III) (30.0 g, 0.125 mole, 62%) which was identified by comparison with a known pure sample.

Methylmagnesium iodide

Reaction of methylmagnesium iodide (0.2 mole) and HFPO (33.2 g, 0.20 mole) in diethyl ether was carried out in a steel autoclave. After rocking at room temperature (24 h), unreacted HFPO (10.5 g) was vented from the autoclave into a trap cooled to $-78°$. The material remaining in the autoclave was treated with methanol (20 ml) and added to water; a viscous tarry material was present. The non-aqueous layer was separated and dried ($CaSO_4$). During distillation to remove ether, some decomposition with the liberation of iodine took place. On attempted distillation at reduced pressure complete decomposition of the remaining material occurred.

Reaction of excess methylmagnesium bromide and HFPO

Reaction of methylmagnesium bromide (0.8 mole) and HFPO (33.2 g, 0.20 mole) in THF followed by addition of ethanol (20 ml) yielded 3-fluoro-4-methylpent-3-ene-2-one (nc) (I) (11.2 g, 0.096 mole, 48%) b.p. 67–68° at 15 mmHg. (Found: C, 62.14; H, 7.81; F, 16.2%. C_6H_9FO requires C, 62.05; H, 7.76; F, 16.4%.) The infrared spectrum showed absorption at 2.4 μ (C–H str.), 5.9 μ (C=O str.), 6.13 μ (C=C str.) and in the region 7.8–9.0 μ (C–F str.). ^{1}H NMR indicated the

presence of three distinct methyl groups at 7.82 τ (doublet, $J = 5.6$ Hz), 7.96 τ (doublet, $J = 3.4$ Hz) and 8.20 τ (doublet, $J = 4.5$ Hz). ^{19}F NMR showed a complex multiplet at 46.0 ppm (TFA ref.).

Reaction of excess ethylmagnesium bromide and HFPO

Reaction of ethylmagnesium bromide (0.8 mole) and HFPO (33.2 g, 0.20 mole) in THF followed by addition of methanol (20 ml) yielded 4-fluoro-5-ethylhept-4-ene-3-one (nc) (17.4 g, 0.11 mole, 55%) b.p. 69–71° at 20 mmHg. (Found: C, 69.1; H, 9.9; F, 11.8%. $C_9H_{15}FO$ requires C, 68.4; H, 9.5; F, 12.0%.) The infrared spectrum showed absorptions at 3.35–3.5 μ (C–H str.), 5.9 μ (C=O str.), 6.2 μ (C=C str.) and in the region 8.1–8.8 μ (C–F str.). ^{1}H NMR indicated the presence of three distinct ethyl groups. ^{19}F NMR consisted of a complex multiplet at 51.0 ppm (TFA ref.).

Reaction of excess trifluorovinylmagnesium bromide and HFPO

Reaction of trifluorovinylmagnesium bromide (0.8 mole) and HFPO (33.2 g, 0.20 mole) in THF (600 ml) at *ca.* $-10°$, followed by work-up in the usual way, yielded only viscous tarry material which could not be distilled even at 0.1 mmHg pressure.

Reaction of 2-bromotetrafluoropropanoyl fluoride and methylmagnesium bromide

Addition of the acyl fluoride (21.1 g, 0.10 mole) to a solution of methylmagnesium bromide (0.3 mole) in dry ether at $-50°$, followed by addition of methanol (20 ml) and work-up in the usual way yielded 3-fluoro-4-methylpent-3-ene-2-one (I) (7.2 g, 0.062 mole, 62%) which was characterized by comparison with a known pure sample. Methyl 2-bromotetrafluoropropanoate (3.9 g, 0.016 mole, 16%) was also isolated from this reaction.

Reaction of the ester $F_2C = CFCF_2CO_2CH_3$ and methylmagnesium bromide

Reaction of $F_2C = CFCF_2CO_2CH_3$ (38.0 g, 0.20 mole) and methylmagnesium bromide (0.8 mole) in ether at $-30°$, after work-up in the usual way, gave the carbinol $CF_2BrCF = CFC(CH_3)_2OH$ (nc) (22.5 g, 0.09 mole, 45%) b.p. 71–72° at 22 mmHg. (Found: C, 28.67; H, 2.65; F, 30.24%. $C_6H_7BrF_4O$ requires C, 28.7; H, 2.79; F, 30.25%.) ^{1}H NMR showed absorption at 8.18 τ (triplet, 6H, $J = 2.0$ Hz) and 5.04 τ (singlet, OH). ^{19}F NMR (TFA ref.) showed absorption at -27.1 ppm (doublet of doublets, 2F, $J = 34.0$ and 17.0 Hz), 66.0 ppm (doublet of triplets, 1F, $J = 134.0$ and 34.0 Hz) and 83.2 ppm (doublet of triplets, 1F, $J = 134.0$ and 17.0 Hz).

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