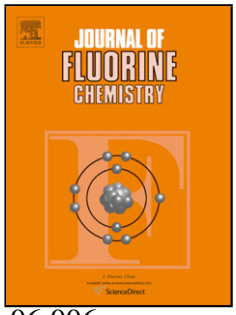

Title: Alcoholysis of Fluoroform

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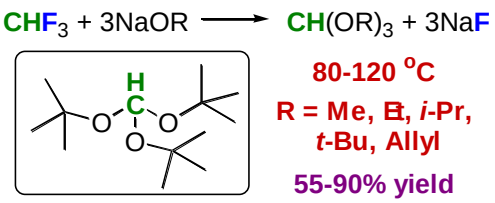
PII: S0022-1139(14)00152-3
DOI: http://dx.doi.org/doi:10.1016/j.jfluchem.2014.06.006
Reference: FLUOR 8335

To appear in: *FLUOR*

Received date: 13-4-2014
Revised date: 2-6-2014
Accepted date: 8-6-2014

Please cite this article as: F.M. Miloserdov, V.V. Grushin, Alcoholysis of Fluoroform, *Journal of Fluorine Chemistry* (2014), http://dx.doi.org/10.1016/j.jfluchem.2014.06.006



Fluoroform (CHF_3) reacts with alkali metal alkoxides MOR (M = Na, K) in the corresponding alcohols ROH (R = Me, Et, *i*-Pr, *t*-Bu, and Allyl) at 80-120 ^oC to give orthoformate esters $HC(OR)_3$ in 55-90% yield. Particularly notable is the formation of $HC(OBu\text{-}t)_3$ in 75-80% yield (62% isolated yield), an exotic organic compound that has been previously synthesized only once (3% yield). Solutions of NaOH in ROH (R = Me, Et, *i*-Pr, *t*-Bu) react with CHF_3 to give NaF, HCOONa, and orthoformates $HC(OR)_3$. Hydrolysis of fluoroform with MOH (M = Na, K) at 140 ^oC produces largely MF and HCOOM along with small quantities of CO.

- CHF_3 reacts with NaOR in ROH at 80-120 ^oC to give $HC(OR)_3$ (55-90% yield).
- Extremely rare and exotic $HC(OBu\text{-}t)_3$ forms in 75-80% yield (62% isolated yield).
- NaOH in ROH reacts with CHF_3 to give NaF, HCOONa, and $HC(OR)_3$.
- Alkaline hydrolysis of CHF_3 produces F^-, HCO_2^-, and small amounts of CO.

For the Special Issue of the Journal of Fluorine Chemistry, dedicated to Dr. Teruo Umemoto

Alcoholysis of Fluoroform

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ABSTRACT

Fluoroform (CHF_3) reacts with alkali metal alkoxides MOR (M = Na, K) in the corresponding alcohols ROH (R = Me, Et, *i*-Pr, *t*-Bu, and Allyl) at 80-120 ^oC to give orthoformate esters $HC(OR)_3$ in 55-90% yield. Particularly notable is the formation of $HC(OBu\text{-}t)_3$ in 75-80% yield (62% isolated yield; X-ray), an exotic organic compound that has been previously synthesized only once (3% yield). Solutions of NaOH in ROH (R = Me, Et, *i*-Pr, *t*-Bu) react with CHF_3 to give NaF, HCOONa, and orthoformates $HC(OR)_3$. Hydrolysis of fluoroform with MOH (M = Na, K) at 140 ^oC produces largely MF and HCOOM along with small quantities of CO.

Keywords:
Fluoroform
CHF_3
HFC-23
Alcoholysis
Orthoformates

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1. Introduction

Fluoroform (CHF_3, trifluoromethane, HFC-23, R-23), a gas (b.p. -82 ^oC) and the lightest member of the haloform family, was first reported by Meslans [1] and Chabrié [2] over 120 years ago. In the 1930's, Henne [3] and Ruff et al. [4] developed efficient synthetic procedures furnishing CHF_3 in sufficient quantities for isolation in pure form and thorough studies. Numerous experiments carried out back then, particularly by Henne [3], established that fluoroform is an exceptionally chemically and biologically inert compound. In addition to being nontoxic and highly unreactive, CHF_3 is ozone-friendly and, consequently, is not on the Montreal Protocol list of chemicals depleting the ozone layer. It is not surprising therefore, that for many decades CHF_3 was considered to be a rather unremarkable, nonhazardous compound. As a result, large quantities of gaseous HFC-23 side-produced by the fluorochemicals and fluoropolymers industries could be disposed of by venting into the atmosphere without much environmental concern. This state of affairs, however, has recently changed dramatically.

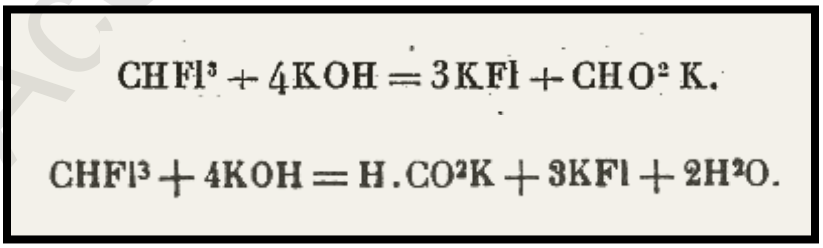
In recent years, CHF_3 has become a center of attention as a potent greenhouse gas with the second highest global warming potential of 11,700 (100 years) and a long, 264-year atmospheric lifetime [5-8]. The release of HFC-23 into the atmosphere should be stopped as otherwise it would likely lead to an ecological disaster [9]. Therefore, the large quantities of the side-generated fluoroform should be destroyed or utilized. As fluoroform currently lacks industrial applications on a scale comparable with that of its production, the destruction of HFC-23 is the only viable solution to the problem [5]. The available methods to eliminate large quantities of fluoroform, a flame retardant, are thermal oxidation, catalytic hydrolysis, and plasma destruction. All of these processes are costly and none of them are free from considerable drawbacks.

Utilizing HFC-23 waste streams as a chemical feedstock would provide an ideal solution to the problem. However, the exceptional inertness of fluoroform makes its use as a reagent a considerable challenge. This task is further complicated by the requirements of industrially viable conditions and sufficiently low-cost chemicals and materials for converting CHF_3 to useful products on a scale commensurate with that of its side-production, ca. 20000-25000 metric tons annually. Since 1990's, considerable progress has been made toward the development of new chemical transformations of fluoroform. Strong bases have been demonstrated to deprotonate CHF_3, a weak acid (pK_a = 27 in H_2O) [10], to generate CF_3^- carbanion equivalents, e.g., for trifluoromethylation of carbonyl compounds and some other electrophiles [11-23]. These reactions have been reviewed [24-26]. Over the last few years, a novel approach to H-CF_3 activation has emerged, employing transition metals [27-36]. Although none of these reactions [11-36] have been commercialized for various reasons, some seem to hold promise [22, 30-34, 36]. A number of high-temperature transformations of fluoroform have also been developed, including the gas-phase flow pyrolysis to CF_2=CF_2 (TFE) and hydrogenolysis to mixtures of hydrofluorocarbons (HFC's) [37], the catalytic iodination to CF_3I [38, 39], and the co-pyrolysis with TFE yielding hexafluoropropylene [40] and with methane to produce various fluorinated products [41-44].

In the current work, we studied reactions of fluoroform with simple bases such as NaOH and KOH as well as with alkali metal alkoxides in the corresponding alcohols under mild conditions. Surprisingly little has been reported on such reactions, although mineralization of CHF_3 with solid alkali metal hydroxides and alkali and alkaline earth metal carbonates at 200-400 ^oC has recently been investigated in considerable detail [45].

2. Results and Discussion

In their original publications on the synthesis of fluoroform, both Meslans [1] and Chabrié [2] mentioned that CHF_3 reacted with alcoholic KOH to give a mixture of potassium fluoride and potassium formate (Fig. 1). Meslans conducted the hydrolysis in a sealed tube at 160 ^{o}C [1], whereas in Chabrié's report, the reaction conditions were not specified [2]. In 1956, Hine et al. published a detailed kinetic study of alkaline hydrolysis of six haloforms in 2:1 dioxane-water to determine the following order of reactivity $CHBrClF >> CHBrCl_2 > CHBr_2Cl \approx CHCl_2I > CHBr_3 > CHCl_3 >> CHF_3$, also reporting that "the reaction of fluoroform was too slow to measure" [46]. Hine's observations are consistent with the fact that fluoroform is ca. 10^6 times less reactive than chloroform toward H/D exchange with aqueous alkali [10]. Very recently, Thomoson and Dolbier [22] demonstrated that CHF_3 reacts with KOH in aqueous dioxane or acetonitrile in the presence of phenols or thiophenols to give $ArOCF_2H$ and $ArSCF_2H$, respectively. It was concluded that "The mechanism of the reaction almost certainly involves the intermediacy of difluorocarbene, which would be formed by deprotonation of CHF_3 by hydroxide followed by loss of fluoride ion" [22].



$$CHFl^3 + 4KOH = 3KFl + CHO^2K.$$

$$CHFl^3 + 4KOH = H.CO^2K + 3KFl + 2H^2O.$$

Fig. 1. The chemical equations for the reaction of CHF_3 with KOH, exactly as they appear in the original articles by Meslans [1] (1890; top) and Chabrié [2] (1892; bottom). Note the old symbol "Fl" used for fluorine.

We first confirmed that CHF_3 reacted with NaOH or KOH under solvent-free conditions to give the corresponding formate salt (Table 1, entries 1-3; Eq. (1)). These reactions were carried out with freshly ground (in air) NaOH or KOH, in Fischer-Porter tubes at 140 ^oC under initial CHF_3 pressure of 50 psi (3.45 bar). The products were analyzed by ^1H and ^{19}F NMR, using sodium acetate and sodium trifluoroacetate as internal standards for the aqueous phase and 1,3-benzodioxole and benzotrifluoride for the organic extracts (see the Experimental section for details). With ca. 85% KOH (eutectic, m.p. = ca. 100 ^oC [47]), the reaction occurred in the melt, whereas NaOH remained solid throughout the experiment and, therefore, agitation was especially important for faster CHF_3 hydrolysis with sodium hydroxide (Table 1, entries 1 and 3). After 65-75% conversion was reached at stirring, the reaction virtually stopped. It is unlikely that considerably higher conversions could be achieved under such conditions because as the reaction occurs, water is produced, diminishing the basicity and reactivity of the alkali in the system. The yield of the formate anion (55-65%) was roughly 10% lower than that of fluoride because of the competing reaction leading to CO (Eq. (2)), in accord with the literature data [45]. The formation of CO was confirmed by GC analysis of the gas phase after the reaction.

$$CHF_3 + 4MOH \xrightarrow{140\ ^oC} HCO_2M + 3MF + 2H_2O \qquad (1)$$

M = Na, K

$$CHF_3 + 3MOH \xrightarrow{140\ ^oC} CO + 3MF + 2H_2O \qquad (2)$$

M = Na, K

Table 1

Reactions of fluoroform with alkali metal hydroxides and alkoxides.[a]

Entry	Base (g)	Solvent (mL)	T, °C	Conversion of base, %	Yield of HCO_2M, %	$HC(OR)_3$ (yield, %)
1	NaOH (0.82)	-	140	75	65	
2	KOH (1.32)	-	140	65	55	
3 [b]	NaOH (0.82)	-	140	30	20	
4	NaOH (0.82)	MeOH (1.5)	120	60	35	$CH(OMe)_3$ (15)
5	NaOH (0.82)	EtOH (1.5)	120	45	15	$CH(OEt)_3$ (20)
6	NaOH (0.82)	*i*-PrOH (1.5)	120	50	40	$CH(OPr\text{-}i)_3$ (10)
7	NaOH (0.82)	*t*-BuOH (5.0)	80	55	50	$CH(OBu\text{-}t)_3$ (<0.5)
8	MeONa (1.08)	MeOH (1.5)	120	75		$CH(OMe)_3$ (55)
9	MeONa (1.08)	diglyme (1.5)	120	90		$CH(OMe)_3$ (70)
10	EtONa (1.36)	EtOH (1.5)	120	55		$CH(OEt)_3$ (55)
11	*i*-PrONa (1.64) [c]	*i*-PrOH (5.0)	120	90		$CH(OPr\text{-}i)_3$ (90)
12	*t*-BuONa (1.92)	*t*-BuOH (5.0)	80	80		$CH(OBu\text{-}t)_3$ (80)
13	*t*-BuOK (2.24)	*t*-BuOH (5.0)	80	85		$CH(OBu\text{-}t)_3$ (75)
14	CH_2=$CHCH_2ONa$ (1.60) [c]	CH_2=$CHCH_2OH$ (5.0)	120	60		$CH(OCH_2CH{=}CH_2)_3$ (60)

[a] Reaction conditions: base (20 mmol), CHF_3 (initial pressure 50 psi), 90-mL Fisher-Porter tube, 24 h. All yields are NMR yields (±5%) calculated using Eqs. (1-3) on the total amount of base used for the reaction (see the Experimental section for details). [b] Without agitation. [c] Generated *in situ* by adding 0.8 g of NaH (60% suspension in mineral oil) to the specified amount of the corresponding alcohol.

We then studied reactions of fluoroform with NaOH in various alcohols, ROH (Table 1, entries 4-7). These reactions occurred in the temperature range of 80-120 ^{o}C to give NaF, HCO_2Na, and the corresponding orthoformate $HC(OR)_3$ as a result of a competition between the two processes shown in Eq. (1) and Eq. (3). We are unaware of publications reporting the formation of orthoformates from fluoroform, although the reaction of chloroform with alkali metal alkoxides is widely used to prepare the corresponding orthoformate esters [48]. The conversion of the base did not exceed 45-60%, with the yield of the orthoformate decreasing in the order R = Et (20%) > Me (15%) > *i*-Pr (10%) > *t*-Bu (<0.5%). The formation of small quantities of the corresponding $CHF_2(OR)$ (ca. 0.5%) was observed in all of these reactions.

$$CHF_3 + 3NaOH + 3ROH \xrightarrow{80\text{-}120\ ^{o}C} HC(OR)_3 + 3NaF + 3H_2O \qquad (3)$$

R = Me, Et, *i*-Pr, *t*-Bu

Orthoformates are valuable reagents that find numerous applications in organic synthesis [48]. To favor the formation of orthoformates from fluoroform, NaOH was replaced with alkali metal alkoxides under anhydrous conditions (Table 1, entries 8-14; Eq. (4)). With MeONa in MeOH (entry 8), the reaction gave $HC(OMe)_3$ in 55% yield, along with 75% of NaF. Although the yield of methyl orthoformate increased to 70% at ca. 90% conversion in diglyme (entry 9), C2 products $(MeO)_2C{=}C(OMe)_2$ (ca. 2%) and $(MeO)_3C\text{-}CH(OMe)_2$ (ca. 10%) were detected by GC-MS in the reaction mixture. This is apparently because the slower formation of $HC(OMe)_3$ at the lower overall concentration of MeOX (X = Na, H) favored dimerization of the carbene intermediates.

$$CHF_3 + 3NaOR \xrightarrow{80\text{-}120\ ^oC} HC(OR)_3 + 3NaF \qquad (4)$$

R = Me, Et, *i*-Pr, *t*-Bu, CH_2=CH-CH_2

The reactions of EtONa and *i*-PrONa in the corresponding alcohols furnished the corresponding orthoformate esters in 55% and 90% yield, respectively (entries 10 and 11). Likewise, allyl orthoformate was produced in 60% yield under similar conditions (entry 14). Of special interest, however, is the reaction of fluoroform with *t*-BuOM (M = Na, K) in *t*-BuOH (entries 12 and 13). These reactions afforded, in 75-80% yield, tri-*tert*-butyl orthoformate $HC(OBu\text{-}t)_3$, a simple yet exceedingly rare and exotic compound. This bulkiest orthoformate ester has appeared only once in the chemical literature. In 1969, Hine et al. [49] reported the synthesis and isolation of $HC(OBu\text{-}t)_3$ in only 3% yield from the reaction of $CHFCl_2$ with *t*-BuOK in *t*-BuOH. In their article, Hine, Dalsin, and Schreck also noted that "in the preparation of orthoformates from haloforms and alkali metal alkoxides, dichlorofluoromethane is the haloform of choice" and that "fluoroform is relatively unreactive" under such conditions [49]. As can be seen from our results (entries 12 and 13), fluoroform can be successfully used to produce $HC(OBu\text{-}t)_3$ in >75% yield. In a scale-up of the reaction of CHF_3 with *t*-BuONa (0.1 mol) in *tert*-butanol, NMR-spectroscopically pure $HC(OBu\text{-}t)_3$ was isolated in 62% yield as a white, low-melting (m.p. 25-26 ^oC [49]) crystalline solid. The structure of $HC(OBu\text{-}t)_3$ was confirmed by a single crystal diffraction study (Fig. 2) [50]. Also interesting is the fact that in all our reactions of ROM/ROH with CHF_3, the corresponding difluoromethyl ethers CHF_2OR were formed in only small amounts (0.5-1.5%), whereas similar transformations of haloforms bearing two fluorine atoms have been reported to conventionally produce large quantities of such difluoromethyl ethers [51-53].

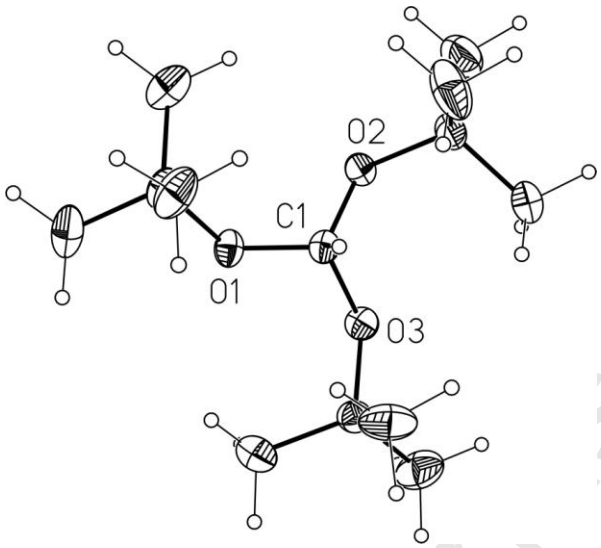
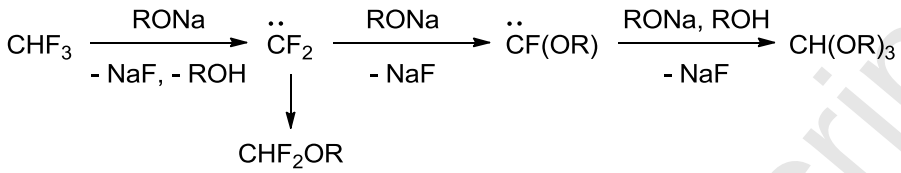


Fig. 2. ORTEP drawing of HC(OBu-*t*)$_3$ with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (^{o}): O1-C1 1.390(5), O2-C1 1.399(5), O3-C1 1.398(5), O1-C1-O2 108.1(3), O1-C1-O3 107.4(3), O2-C1-O3 106.8(3).

We also probed the reactivity of CHF_3 toward $Mg(OEt)_2$ and $Al(OPr\text{-}i)_3$ with CHF_3 in EtOH and *i*-PrOH, respectively. At temperatures up to 120 ^{o}C, no reaction was observed with these much less basic alkoxides. On the other hand, the pyrrolide anion generated from pyrrole and NaH reacted with fluoroform at 120 ^{o}C to give NaF (30%), three isomers of $HC(C_4H_4N)_3$ in a 5:3:2 ratio, and ca. 1% of $(C_4H_4N)CHF_2$ (one isomer), as detected by GC-MS.

The reactions described above likely involve the intermediacy of difluorocarbene CF_2 [49, 51-54]. A plausible mechanism for the formation of $HC(OR)_3$ as the main product and of the small quantities of CHF_2OR is presented in Scheme 1. It is conceivable that the CF(OR) carbene proposed by Hine [51-53] is converted to $C(OR)_2$ that, as has been shown by Moss et al. for R = Me [55], readily reacts with ROH to give $HC(OR)_3$. The difluoromethyl ethers CHF_2OR

produced in only 0.2-1.5% yield in the reactions, are most likely end products rather than intermediates in the formation of the orthoformates [52].



Scheme 1. Proposed mechanism for the formation of orthoformate esters from CHF_3.

3. Conclusions

In this work, we have confirmed that, in full accord with the original early 1890's reports by Meslans [1] and Chabrié [2], fluoroform reacts with NaOH or KOH at 140 ^{o}C to give mixtures of the corresponding metal fluoride and formate. Solutions of NaOH in various alcohols ROH (R = Me, Et, *i*-Pr, *t*-Bu) also hydrolyze CHF_3 to NaF and HCOONa. Importantly, however, the corresponding orthoformate (up to 20%) is also produced in these reactions. Against previously reported observations [49, 51-53], fluoroform can be sufficiently reactive toward MOR (M = Na, K) in ROH (R = Me, Et, *i*-Pr, *t*-Bu, and Allyl) to give the corresponding orthoformate esters in 55-90% yield, provided the reactions are carried out at 80-120 ^{o}C. Of particular interest is the formation of $HC(OBu\text{-}t)_3$ (70-80% yield), a simple yet extremely rare and poorly accessible organic compound that has been previously synthesized only once and in only 3% yield. A scale-up of the reaction of CHF_3 with *t*-BuONa (0.1 mol) in *tert*-butanol produced pure $HC(OBu\text{-}t)_3$ that has been isolated in 62% yield and structurally characterized. It is hoped that the overall simple, low-cost transformations developed in the current work may contribute to a solution for the HFC-23 ecological problem.

4. Experimental

Chemicals were purchased from Aldrich (EtONa, *t*-BuONa, $(EtO)_2Mg$, $(i\text{-}PrO)_3Al$, pyrrole, allyl alcohol, CF_3CO_2Na, 1,3-benzodioxole, $PhCF_3$), Alfa Aesar (MeONa, *t*-BuOK, *t*-BuOH, CH_3CO_2Na), Acros (NaH, 60% suspension in mineral oil), Apollo Scientific (CHF_3), Panreac (NaOH, 98%), and Carlo Erba (KOH, 85%). Methanol, ethanol, isopropanol, *tert*-butanol, toluene, and pentane were used as received, unless otherwise noted. Anhydrous MeOH, EtOH, *i*-PrOH, *t*-BuOH, allyl alcohol, and pyrrole were distilled from CaH_2 under argon and stored over freshly activated 4 Å molecular sieves in an argon glove-box. Sodium trifluoroacetate was dried at 130 ^oC under vacuum (0.05 mmHg) and stored in the glovebox. ^1H and ^{19}F NMR spectra were recorded on a Bruker Avance 400 Ultrashield NMR spectrometer. 1,3-Benzodioxole, benzotrifluoride, sodium acetate, and sodium trifluoroacetate were used as internal standards for quantitative ^1H and ^{19}F (D1 = 5 s) NMR analysis. Agilent Technologies 7890A-5975C and 7890B instruments were used for GC-MS and GC-TCD analyses, respectively.

Alkaline hydrolysis of CHF_3 (Table 1, entries 1-3). A 90-mL Fisher-Porter tube containing a Teflon-coated magnetic stirbar was charged, in air, with freshly ground alkali (20 mmol; calculated on the MOH assay in the reagent used), evacuated, and pressurized with CHF_3 to 50 psi. After 24 h of heating at 140 ^oC (oil bath; see Table 1 for specifics), the tube was allowed to cool to room temperature and the gas phase was analyzed for CO by GC-TCD. To the contents of the tube, were added water (100 mL), sodium acetate, and sodium trifluoroacetate as internal standards (Table 2). A ca. 0.6-mL aliquot of the resultant aqueous solution was admixed with D_2O (0.1 mL) and quantitatively analyzed by ^1H (for HCO_2^-) and ^{19}F (for F^-) NMR (see Tables 1

and 2). The amount of the base consumed in the reaction was calculated using the stoichiometry displayed in Eq. (1) and Eq. (2), as a sum of the amounts of the F^- and HCO_2^- produced.

Reactions of CHF_3 with NaOH in alcohols (Table 1, entries 4-7). A 90-mL Fisher-Porter tube containing a Teflon-coated magnetic stirbar was charged in air with freshly ground NaOH (98% purity; 0.82 g; 20 mmol) and an alcohol (see Table 1 for specifics), quickly evacuated, and pressurized with CHF_3 to 50 psi. After 24 h of agitation at 80 ^oC or 120 ^oC (oil bath; see Table 1), the tube was allowed to cool to room temperature, unsealed, and its contents were treated with toluene (40 mL) containing 1,3-benzodioxole (200 μL; 237 mg) and benzotrifluoride (50 μL; 58 mg) as internal standards. Upon agitation, a solid inorganic phase and a liquid organic phase were produced. A ca. 0.6-mL aliquot of the organic phase was filtered through Celite and the filtrate was admixed with C_6D_6 (0.1 mL) and analyzed, within an hour, first by ^1H and ^{19}F NMR and then by GC-MS. (A longer delay in carrying out the analysis may produce incorrect data because of partial slow hydrolysis of the orthoformate product with residual moisture in the toluene solvent and in the atmosphere). The solid inorganic phase was separated by filtration, washed with toluene (3 × 15 mL), and dissolved in water (200 mL). Sodium acetate and sodium trifluoroacetate were added as internal standards. A ca. 0.6-mL aliquot of this aqueous solution was admixed with D_2O (0.1 mL) and quantitatively analyzed by ^1H and ^{19}F NMR (see Tables 1 and 2). The amount of the base consumed in the reaction was calculated using the stoichiometry displayed in Eq. (1) and Eq. (3), as a sum of the amounts of the F^- and HCO_2^- produced.

Reactions of CHF_3 with MOR in alcohols (Table 1, entries 8, 10, 12, and 13). A 90-mL Fisher-Porter tube containing a Teflon-coated magnetic stirbar was charged, in a glovebox, with

a metal alkoxide (20 mmol) and the corresponding anhydrous alcohol (see Table 1 for specifics), brought out, quickly evacuated, and pressurized with CHF_3 to 50 psi. After 24 h of agitation at 80 ^oC or 120 ^oC (oil bath; see Table 1), the tube was allowed to cool to room temperature, unsealed, and its contents were treated with toluene (40 mL) containing 1,3-benzodioxole (200 μL; 237 mg) and benzotrifluoride (50 μL; 58 mg) as internal standards. A ca. 0.6-mL aliquot of the resultant suspension was filtered through Celite and the filtrate was admixed with C_6D_6 (0.1 mL) and analyzed, within an hour, first by ^1H and ^{19}F NMR and then by GC-MS. (A longer delay in carrying out the analysis may produce incorrect data because of partial slow hydrolysis of the orthoformate product with residual moisture in the toluene solvent and in the atmosphere). To the rest of the reaction mixture, were added water (200 mL) and sodium trifluoroacetate as an internal standard. A ca. 0.6-mL aliquot of this aqueous solution was admixed with D_2O (0.1 mL) and quantitatively analyzed by ^1H and ^{19}F NMR (see Tables 1 and 2).

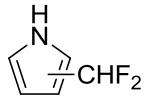
Reactions of CHF_3 with NaOR generated in situ from NaH in ROH (Table 1, entries 11 and 14). A 90-mL Fisher-Porter tube containing a Teflon-coated magnetic stirbar was charged, in a glovebox, with NaH (60% suspension in mineral oil; 0.80 g; 20 mmol) and anhydrous *i*-PrOH or allyl alcohol (see Table 1 for specifics) and brought out. After stirring for 30 min at 120 ^oC (oil bath), the tube was cooled to room temperature, quickly evacuated, and pressurized with CHF_3 to 50 psi. After 24 of agitation at 120 ^oC (oil bath; see Table 1), the tube was allowed to cool to room temperature, unsealed, and its contents were treated with toluene (40 mL) containing 1,3-benzodioxole (200 μL; 237 mg) and benzotrifluoride (50 μL; 58 mg) as internal standards. A ca. 0.6-mL aliquot of the resultant suspension was filtered through Celite and the filtrate was admixed with C_6D_6 (0.1 mL) and analyzed, within an hour, first by ^1H and ^{19}F NMR and then by

GC-MS. (A longer delay in carrying out the analysis may produce incorrect data because of partial slow hydrolysis of the orthoformate product with residual moisture in the toluene solvent and in the atmosphere). To the rest of the reaction mixture, were added water (200 mL) and sodium trifluoroacetate as an internal standard. A ca. 0.6-mL aliquot of this aqueous solution was admixed with D_2O (0.1 mL) and quantitatively analyzed by ^{1}H and ^{19}F NMR (see Tables 1 and 2).

Preparation of HC(OBu-*t*)$_3$. A 450-mL Fisher-Porter bottle containing a Teflon-coated magnetic stirbar was charged, in a glovebox, with *t*-BuONa (9.60 g; 100 mmol) and *t*-BuOH (25 mL), brought out, quickly evacuated, and pressurized with CHF_3 to 50 psi. After 21 h of agitation at 80 ^{o}C (oil bath), the bottle was allowed to cool to room temperature and opened to air. Pentane (60 mL) was added and the mixture was transferred to a 250-mL flask. The bottle was rinsed with pentane (3 × 30 mL) and the combined reaction mixture and the washings were evaporated on a rotary evaporator to remove the pentane and *t*-BuOH. Vacuum transfer of the residue at ca. 0.06 mmHg with gentle heating, followed by drying on a rotary evaporator (ca. 50 mbar at 40 ^{o}C for 1 h) gave 4.81 g (62%) of HC(OBu-*t*)$_3$ as a colorless liquid that crystallized on cooling to +8 ^{o}C. The compound was spectroscopically pure. ^{1}H NMR (dry $CDCl_3$), δ: 1.27 (s, 27H), 5.67 (s, 1H) [49]. ^{13}C NMR (dry $CDCl_3$), δ: 29.5, 73.7, 104.4.

Table 2

NMR data for compounds obtained and for internal standards (in reaction mixtures).

Compound	^{1}H NMR, δ	^{19}F NMR, δ
1,3-benzodioxole	5.45 (s, 2H), 6.70-6.79 (m, 4H)	-
$CH(OMe)_3$	3.25 (s, 9H), 4.91 (s, 1H)	-
$CH(OEt)_3$	1.24 (t, J = 7 Hz, 9H), 3.63 (q, J = 7 Hz, 6H), 5.18 (s, 1H)	-
$CH(OPr\text{-}i)_3$	1.27 (d, J = 6 Hz, 18H), 4.07 (sept, J = 6 Hz, 3H), 5.39 (s, 1H)	-
$CH(OBu\text{-}t)_3$	1.37 (s, 27H), 5.78 (s, 1H)	-
$CH(Oallyl)_3$	4.12 (m, 6H), 5.15 (m), [a] 5.25-5.50 (m), [a] 5.92 (m, 3H)	-
CH_3CO_2Na	1.90	-
HCO_2Na	8.44	
$PhCF_3$	-	-63.7
CHF_2OMe	5.74 (t, $J_{F,H}$ = 75 Hz)	-87.5 (d, $J_{F,H}$ = 75 Hz)
CHF_2OEt	5.82 (t, $J_{F,H}$ = 75 Hz)	-84.7 (d, $J_{F,H}$ = 75 Hz)
$CHF_2OPr\text{-}i$	5.89 (t, $J_{F,H}$ = 76 Hz)	-81.7 (d, $J_{F,H}$ = 76 Hz)
$CHF_2OBu\text{-}t$	6.05 (t, $J_{F,H}$ = 77 Hz)	-77.3 (d, $J_{F,H}$ = 77 Hz)
$CHF_2Oallyl$	- [b]	-84.9 (d, $J_{F,H}$ = 75 Hz)
	- [b]	-89.1 (d, $J_{F,H}$ = 62 Hz)
CF_3CO_2Na	-	-75.5
F^-	-	-120.1

[a] Signals overlapped with those from the residual allyl alcohol. [b] Although the ^{1}H NMR signals could not be observed because of their low intensity and overlap with other resonances, the presence of these products was confirmed by ^{19}F NMR and GC-MS.

Acknowledgments

We thank Drs. Jordi Benet Buchholz and Eddy Martin for the crystallographic study of $HC(OBu\text{-}t)_3$. This work was supported by the ICIQ Foundation and the Spanish Government (Grant CTQ2011-25418). F.M. thanks the Government of Spain (MICINN) for the FPI PhD Scholarship (BES-2012-054922). Dr. Carolina Gimbert-Suriñach's assistance with the GC-TCD analysis is thankfully acknowledged.

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