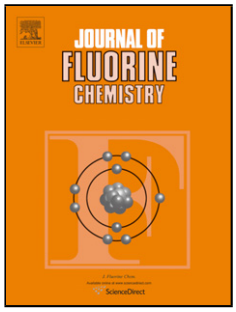

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NUCLEOPHILIC NON-METAL ASSISTED TRIFLUOROMETHYLATION AND PERFLUOROALKYLATION REACTIONS OF ORGANIC SUBSTRATES

NUCLEOPHILIC NON-METAL ASSISTED TRIFLUOROMETHYLATION AND PERFLUOROALKYLATION REACTIONS OF ORGANIC SUBSTRATES

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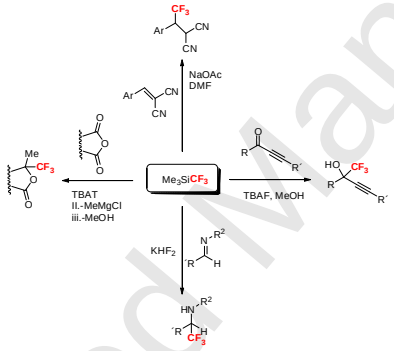
Abstract

Nucleophilic trifluoromethylation and perfluoroalkylation reactions have been the outstanding approach during the last few decades to effect fluoroalkyl group addition or substitution reactions. In most instances, perfluoroalkyl-metal species participate at the beginning of the reactions. In this account, however, the latest nucleophilic *non-metal* assisted or uncatalyzed trifluoromethylation and perfluoroalkylation reactions of substrates bearing biological relevance will be discussed.

Graphical Abstract



Keywords: Nucleophilic trifluoromethylation**,** fluoroform, trimethylsilyltrifluoromethane, fluorinated sulfones, fluorinated sulfoxides, fluorinated sulfides,

1.Introduction

A recent review article by Wu, Beller and collaborators [1], and before that, the seminal *in-depth* review article by Grushin and colleagues [2] appropriately summarize the nucleophilic trifluoromethylation and perfluoroalkylation reactions of organic substrates in the presence of metals. Thus numerous transformations regarding fluorination of both aliphatic and aromatic substrates either with or without formal leaving groups can be

accomplished with the intervention of metals and transition metal complexes which aid in the coupling of the fluoroalkyl moieties that act as nucleophiles onto the organic electrophilic substrates.

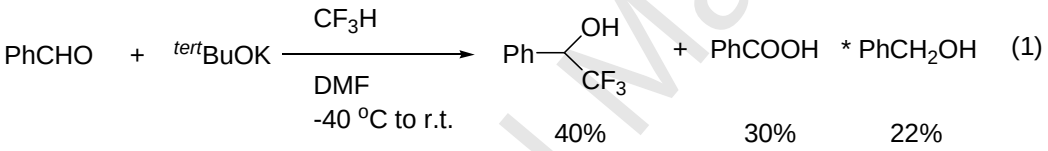
The nucleophilic trifluoromethylation has been extensively studied and reviewed [3]. However, the incorporation of CF_3 groups remains limited by the low stability of the CF_3 anion due to α-elimination to the difluorocarbene [4]. The following sections shall describe diverse sources of trifluoromethylating and perfluoroalkylating reagents such as fluoroform CF_3H, trimethylsilyltrifluoromethane (Me_3SiCF_3), fluorinated sulfones, sulfoxides, sulfides, phosphorous-derived reagents, trifluoroacetate, hexafluoroacetone hydrate salts, and trifluoroacetaldehyde hydrates that can be employed as nucleophilic sources towards a variety of electrophiles, such as carbonyl compounds, thiocarbonyl compounds, halides, imines, hydrazones, nitrones, iminium salts, and azomethine imines .

2.The use of Fluoroform (CF_3H) as Nucleophilic Trifluoromethylating Agent

Fluoroform is a byproduct of Teflon manufacture, but if desired, it could be synthesized as a commodity chemical by fluorine/chlorine exchange of chloroform; a gas with a boiling point of −83 °C. However, until recently, it had attracted little interest as a synthetic fluorinated building block reagent, in spite of various reports by Shono, and Langlois since 1991 [5,6], which employed it for the nucleophilic trifluoromethylation of ketones. These earlier works set the stage for the recent series of important papers by Grushin, Prakash, and Shibata, [7-9] where they have reported the use of fluoroform in a

great variety of nucleophilic trifluoromethylation reactions with the intervention of metals or metalorganic species.

The reaction of fluoroform at room temperature with a deprotonating strong base, leads to rapid decomposition of the trifluoromethyl anion thus formed to a difluorocarbene intermediate. However, addition of 1 equiv. of CF_3H to ^{tert}BuOK in DMF in the presence of benzaldehyde (Barbier conditions) at - 40 °C led to a mixture of the corresponding trifluoromethyl carbinol in 40% yield with 30% of benzoic acid, 22% of benzyl alcohol and 8% of remaining benzaldehyde as described in eq 1. When the same reaction was performed at room temperature as opposed to - 40 °C, only the starting material was recovered [10].

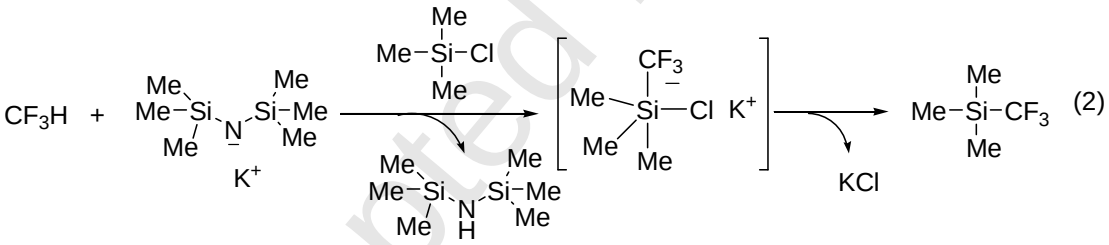


The reaction of fluoroform with metallated dimethyl sulfoxide (dimsyl –K) afforded 65% yield of the trifluoromethyl alcohol derived from benzaldehyde. The mechanism of the reaction could be explained by deprotonation of fluoroform by potassium dimsylate affording the trifluoromethyl anion which was trapped *in situ* by the carbonyl moiety of DMF solvent to form the *gem*-aminoalcoholate **1** (Scheme 1, step **A**). This intermediate is a *masked* and *stable* form of the trifluoromethyl anion at – 22 °C (a CF_3^- synthon), therefore avoiding the degradation of the carbenoid CF_3K [10].

Scheme 1. Mechanism for the trifluoromethylation of benzaldehyde with CF_3H

The nucleophilic adduct between **A** (Scheme 1) and DMF (**1**, Scheme 1) reacts with benzaldehyde to afford the CF_3-alcohol.

Prakash and collaborators [8] have developed a protocol which generates and stabilises the CF_3^- anion to allow direct trifluoromethylation of a range of targets (eq 2). The team initially showed that if CF_3H is dissolved in toluene with potassium hexamethyldisilazide as a stabilizing base, this allows the direct introduction of the CF_3 group into trimethylsilyl chloride (eq 2). Building on this success, the researchers showed that careful optimization of solvent and reaction conditions enables CF_3H to trifluoromethylate a wide range of silicon, boron, sulfur and carbon-based compounds. Besides, the synthesis of the Ruppert reagent, Me_3SiCF_3 (*vide infra*), can easily be prepared

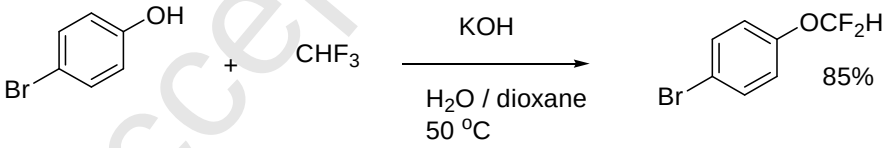


from CF_3H as starting material (eq 2) [8].

Luo and Qu have very recently uncovered [11] the origin of the remarkable effects of alkali metal salts of hexamethyldisilazane in the reaction of fluoroform with electrophiles. The detailed mechanism of trifluoromethylation of Si and C centers in the presence of $(Me_3Si)_2NK$ as a base has been studied using the DFT methods. The authors [11] found that the origin of the so pronounced an effect of the alkali metals is related to the stability of an intermediate MCF_3. More interestingly, a linear relationship has been

encountered between the chemical hardness of M^+ (M = Li, Na, K, Rb, Cs) and the difference between the values of ΔG_{dec} (decomposition Gibbs energy of the key intermediate MCF_3), and ΔG_{tfm} (the relative Gibbs energy barrier for the formation of a Si–CF_3 or C–CF_3 bond) [11]. These results may help to both theoretically and experimentally search for better bases to develop more atom-economic and environmentally benign protocols to achieve trifluoromethylation using CF_3H [11].

Consequently fluoroform can be established as a major option for installing trifluoromethyl groups by nucleophilic addition of metal-mediated coupling [12] onto organic electrophiles given the proper choice of metals. However, very recent examples have appeared in the literature with the use of fluoroform without the assistance of metals or metal complexes, for the difluoromethylation of phenols [13]. The scope of the reaction is represented in Scheme 2 [13].



Scheme 2. Optimized reaction conditions for the difluoromethylation of phenols with CF_3H.

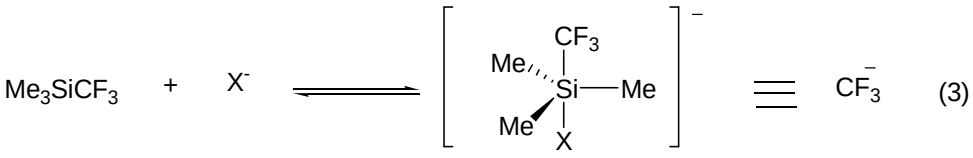
Difluoromethylation reactions of several phenol and thiophenol derivatives such as 4-chlorophenol, 4-methoxyphenol, 4-iodophenol, 2-iodophenol, 2-naphthol, 4-cyanophenol, etc. and their respective thiophenol derivatives were conducted in the presence of fluoroform, yielding the difluoromethyl aryl ethers and thioethers in yields ranging from 41% to 90% [13]. Also recently, the direct trifluoromethylation of Si, B, S, and C centers was achieved by employing fluoroform [8].

Very recently, Mikami and collaborators [14] have come up with an organic base methodology to generate the "trifluoromethyl anion" for carbonyl, ester, acid halide, epoxide, deuterium donor, and carbon dioxide substrates to afford the trifluoromethylation products with good overall efficiency even under organocatalysis conditions. On addition of electrophiles, the trifluoromethylation products were obtained efficiently [14].

3.The Ruppert-Prakash Reagent, Me_3SiCF_3

Prakash and collaborators reviewed, in 1997, the use of Me_3SiCF_3 [15a] as an efficient nucleophilic trifluoromethylating reagent.

Without the assistance of metals or metalorganic catalysts, undoubtedly, the Ruppert-Prakash (Me_3SiCF_3) reagent is the most widely commercial approach for nucleophilic trifluoromethylation reactions of electrophiles in conventional laboratories. This latter reagent nucleophilicity is uncovered by Lewis acid activators such as fluoride ions. The Lewis-base mediated reactions of Me_3SiCF_3 proceed through the generation of five-coordinate silicon species, which serve as CF_3 carbanion equivalent (eq 3).



(3)

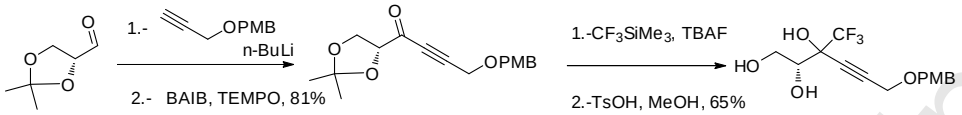
Several electrophilic substrates bearing the C=X (X = heteroatom, O, S, N) double bonds are rendered excellent acceptors of nucleophilic species such as the CF_3^- anion. Under basic conditions the carbonyl carbon of the C=O bond is particularly the best electrophile.

There exist review articles and numerous reports in the literature on trifluoromethylation reactions of carbonyl compounds [15b-d] with the Ruppert reagent. A review article in 2014 on the trifluoromethylation of aldehydes, ketones, and esters with the Ruppert reagent attests to the relevance of the subject [16a].

Shreeve and collaborators [16b] have recently accomplished the trifluoromethylation of a series of aromatic carbonyl compounds in good yields as an entry to the synthesis of α-trifluoromethylated alcohols. The activator in this case is *tetra*butylammonium fluoride (TBAF) in THF as solvent. β-Amino-α-trifluoromethyl alcohols can be synthesized by the trifluoromethylation (Me_3SiCF_3) of aryl glyoxals derivatives (arylglyoxalimines) [17]. The reactions [17] encompass the use of the Ruppert-Prakash reagent, an initiator (CsF or K_2CO_3) in dimethoxyethane as solvent.

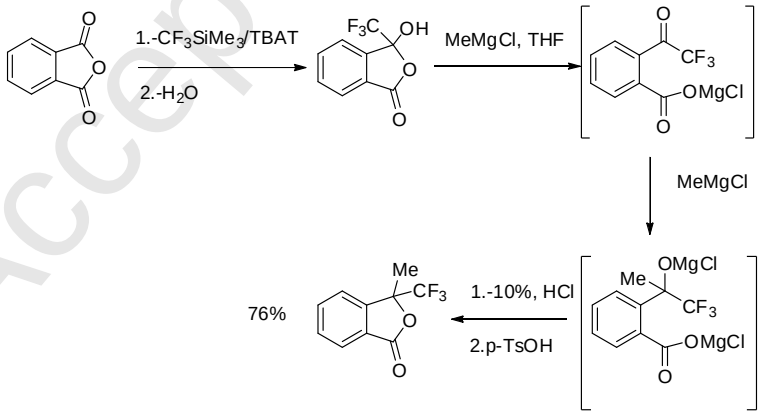
Although the trifluoromethylation of carbonyl compounds has been, as noted, thoroughly reviewed [16a], propargyl ketones constitute a timing recent example of the use of Me_3SiCF_3 on carbonyl acceptors recently published.

Propargyl ketones easily undergo trifluoromethylation with the Ruppert Prakash reagent in good yields, according to Scheme 3 [18].



Scheme 3. Trifluoromethylation reactions of propargyl ketones with the Ruppert Prakash reagent

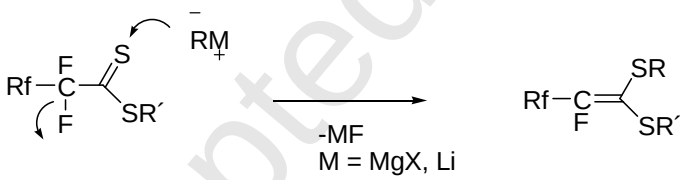
Pohmakotr and collaborators have very recently accomplished the trifluoromethylation of anhydrides employing Me_3SiCF_3 towards the synthesis of γ-trifluoromethylated-γ-butyrolactones [19], according to Scheme 4.



Scheme 4. Trifluoromethylation of anhydrides followed by nucleophilic addition with Grignard reagent. TBAT = *tetra*butyl ammonium *tri*phenyldifluorosilicate. *p*-TsOH : *p*-toluensulfonic acid.

This constitutes a fluoride ion-catalyzed nucleophilic addition of Me_3SiCF_3 to anhydrides which provides γ-hydroxy-γ-trifluoromethyl-γ-butyrolactones that can be transformed to γ-trifluoromethylated-γ-butyrolactones upon treatment with Grignard reagents and ulterior lactonization [19].

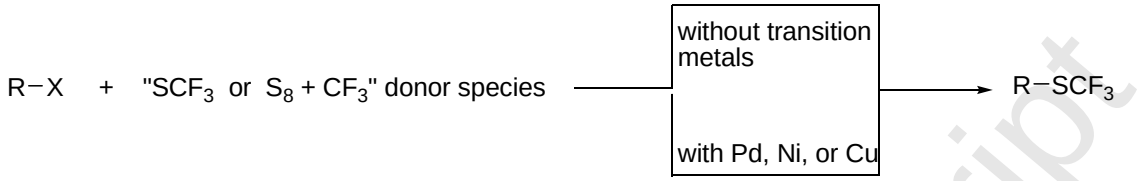
Alkyl perfluorodithioesters and analogues react with various nucleophiles at sulfur of the thiocarbonyl group (thiophilic attack) with subsequent β-elimination of a fluoride [20], according to Scheme 5.



Scheme 5. Thiophilic nucleophilic addition-β-elimination sequence for perfluorodithioesters.

The introduction of the SCF_3 group into organic substrates is a challenging task because of harsh or specific synthetic methods. However, recent advances in the formation

of C-SCF_3 bonds include the trifluoromethylthiolation with transition-metal-free systems or in the presence of palladium, nickel, or copper catalysts (Scheme 6) [21a,22].



Scheme 6. Trifluoromethylthiolation of RX under various reaction conditions

However, most of the reagents employed for the trifluoromethylthiolation are electrophilic in nature, such as trifluoromethanesulfenamide, which is able to trifluoromethylthiolate an array of carbon and nitrogen nucleophiles [21b]. Most successful nucleophilic trifluoromethylthiolation reactions are conducted in the presence of metals or metalorganic species [21c]. The sulfur-derived nucleophilic fluoroalkylating reagents that are able to react with diverse electrophiles such as carbonyl compounds, imines derivatives, aziridine rings, epoxides, and olefins are discussed in section 4.

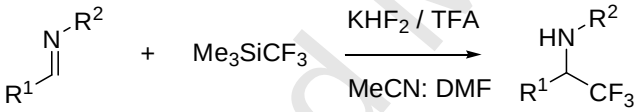
Due to the high polarizability of sulfur, sulfur-containing organic compounds exhibit a versatile chemistry. Thus both carbophilic and thiophilic addition can be observed. The reaction of dithiomalonate **2**, Scheme 7 [22], uses catalytic amounts of *tetra*-methylammonium fluoride (TMAF) as initiator.

Scheme 7. Reaction of α-hydroxy dithioester with Me_3SiCF_3

Following in nucleophilicity order, the C=N bond in imines are quite good candidates for nucleophilic fluoroalkylation reactions. Strained imines are the most reactive within the group, following perfluoroalkyl *N*-substituted imines > sulfonimines > *N*-aryl substituted imines > *N*-alkyl substituted imines as the least reactive in the series.

A recent review article on the trifluoromethylation of imine systems with the above reagent accounts for the convenience of this reaction [16a], where imines, hydrazones, nitrones, iminium salts, and azomethine imines are shown to be trifluoromethylated conveniently, in the presence of a base and an activator [23].

Dilman, Tartakovsky and collaborators [24] have reported in 2008 a nucleophilic trifluoromethylation of imines in the presence of strong protic acids. Thus a series of

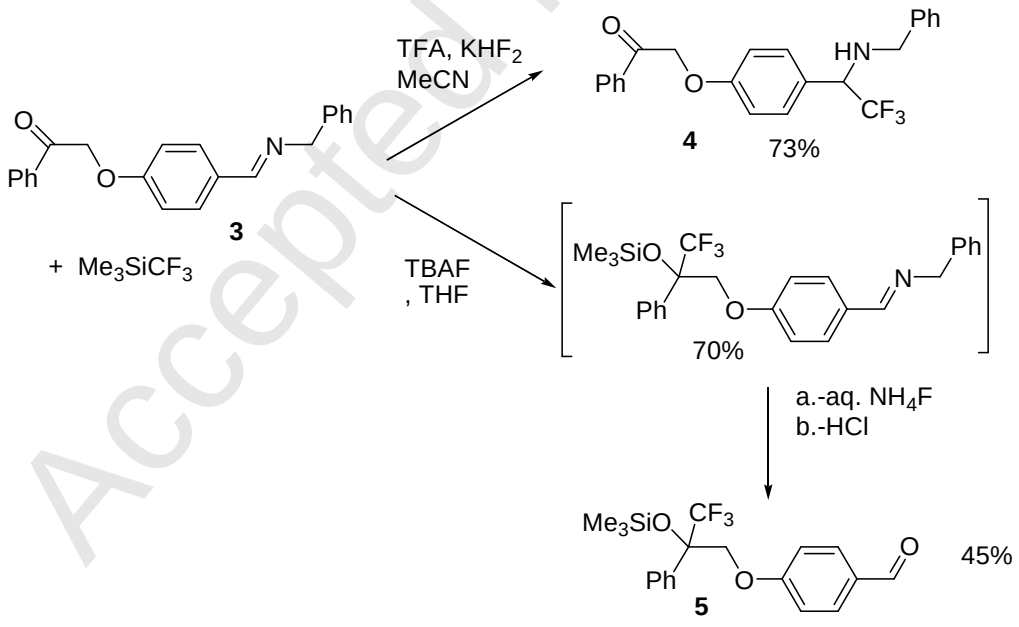


aromatic imines could be trifluoromethylated using trifluoroacetic acid in a mixture of acetonitrile-dimethylformamide (DMF) with KHF_2 as the fluoride source, according to Scheme 8.

50-90%

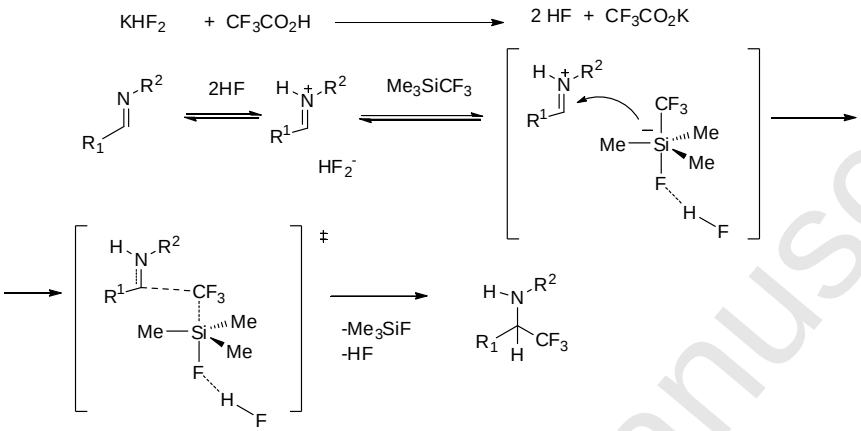
Scheme 8. Trifluoromethylation of aromatic imines using trifluoroacetic acid (TFA) in a mixture of acetonitrile-dimethylformamide (DMF) with KHF_2 as the fluoride source. R_1 substituents are Ph, 2-methoxyphenyl, 4-methoxyphenyl, 3,4,5-trimethoxyphenol, 2,4-dichlorophenyl, 4-chlorophenyl, furanyl. R_2 substituents are: benzyl, propyl, allyl, ^{tert}butyl, cyclohexyl.

The authors [24] found that DMF exhibits an accelerating effect on the trifluoromethylation. Substrates bearing benzyl, alkyl, cycloalkyl, and allyl substituents at the nitrogen atom also work well in the reaction. Imines derived from tertiary and α-branched aliphatic aldehydes also gave good yields of trifluoromethylated products. When a substrate contains both a carbonyl group and the imino functionality, as being the former more reactive than the C=N bond in the presence of basic activators for Me_3SiCF_3 nucleophilic trifluoromethylations, it was found [24] that substrate **3** (Scheme 9), in the presence of TFA/KHF_2, affords the amino ketone **4** (Scheme 9). In contrast, the reaction mediated by Bu_4NF (TBAF) affected only the keto group to afford the silyl ether **5** (Scheme 9).



Scheme 9. Chemoselective trifluoromethylation

The authors [24] postulated a mechanism such as that in Scheme 10, where the protonated imine is the potential electrophile which develops into a transition-state complex from where elimination of Me_3SiF ensues, producing the trifluoromethylated-α-amino compound.



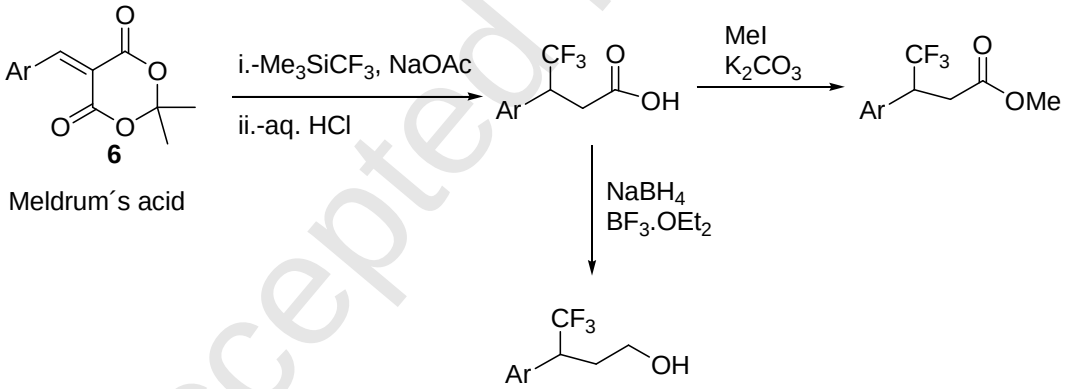
Scheme 10. Reaction mechanism for the acid-catalyzed trifluoromethylation of imines.

The trifluoromethylation of arylidenemalononitriles using Me_3SiCF_3 in the presence of sodium acetate as Lewis base affords products of Michael addition in high yields [25]. The authors noted that the efficiency of trifluoromethylation depends on the electrophilicity of the alkene substrate. Interestingly, in the case of a substrate possessing two sites for possible nucleophilic attack, only one product, corresponding to the attack at the position adjacent to the malononitrile moiety was obtained. The scope of the reaction is depicted in Scheme 11.

75-98%

Scheme 11. Trifluoromethylation of arylidenemalononitriles. The Ar substituents are: 4-methoxyphenyl, 3,4-dimethoxyphenyl, 2-methoxyphenyl, 4-nitrophenyl, 3-bromophenyl, naphthyl, cynnamyl.

A method for the trifluoromethylation of arylidene Meldrum's acids **6** (Scheme 12) using Me_3SiCF_3 followed by transformation of the initial products to CF_3-substituted esters and alcohols has been described by Dilman and Tartakovsky [26]. The sequence of reactions is performed without isolation of intermediate compounds furnishing the final products in good overall yields (Scheme 12).

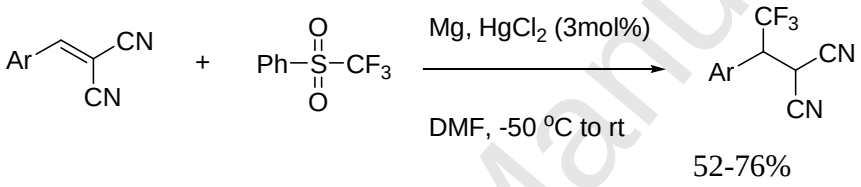


Scheme 12. Trifluoromethylation of arylidene Meldrum's acids using Me_3SiCF_3 followed by transformation of the initial products to CF_3-substituted esters and alcohols

4.Fluoroalkylation with Fluorinated Sulfones, Sulfoxides, Sulfides, and Phosphorous-derived Reagents.

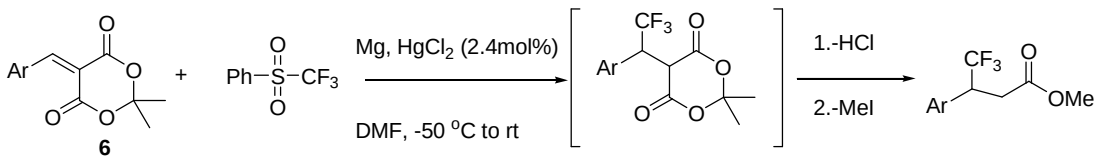
A recent review article by Prakash and Hu [27] explores the sulfur-derived nucleophilic fluoroalkylating reagents that are able to react with diverse electrophiles such as carbonyl compounds, imines derivatives, aziridine rings, epoxides, and olefins.

Very recently, Petersen and co-workers have accomplished the trifluoromethylation of conjugate acceptors via phenyl trifluoromethyl sulfone [28]. Thus, the trifluoromethylation of arylidenemalononitriles can be accomplished in excellent yields, as indicated in Scheme 13.



Scheme 13. Trifluoromethylation of arylindenemalononitriles in DMF as solvent (Ar: aryl, naphthyl, biphenyl)

While direct additions of the trifluoromethyl anion to a carbonyl moiety are well studied using a variety of sources, conjugate additions are rare. In another work [28], the arylidene derivative of Meldrum´s acid **6** (Scheme 14), which is highly electrophilic, undergoes trifluoromethylation reaction efficiently, according to Scheme 14.



6

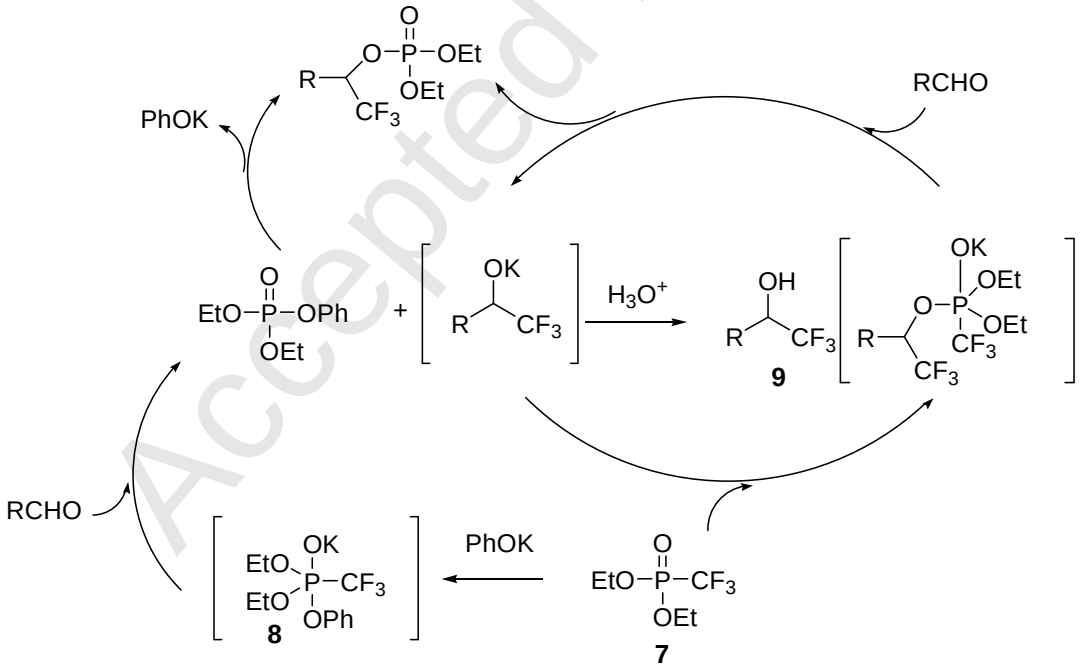
Meldrum´s acid

52-68%

Scheme 14. Trifluoromethylation of arylidene Meldrum´s acid **6**. Ar: phenyl, 2-furanyl, 2-thiophyl.

The use of phosphorous-containing nucleophilic trifluoromethylating reagent diethyl trifluoromethylphosphonate **7** (Scheme 15) allows the synthesis of trifluoromethyl alcohols and diethylphosphate trifluoromethyl esters in high yields [29]. This reagent is used in conjunction with potassium *tert*butoxide or potassium phenolate as bases.

The authors postulate a plausible mechanism for the trifluoromethylation reaction of aldehydes and ketones with reagent **7** such as that depicted in Scheme 15.

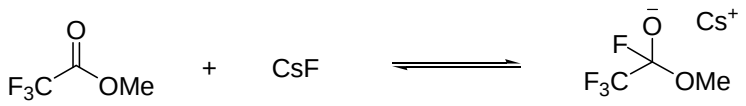


Scheme 15. Plausible mechanism for the trifluoromethylation of aldehydes with diethyl trifluoromethylphosphonate in the presence of potassium phenolate.

In this mechanism diethyl trifluoromethylphosphonate **7** (Scheme 15) reacts with PhOK to form an adduct **8** (Scheme 15) that acts as a CF_3^- synthon in the presence of carbonyl compounds, affording the trifluoromethylated alcohol **9** (Scheme 15). The nucleophilic addition also proceeds in the presence of benzophenone derivatives to afford 1,1-diaryl trifluoromethyl carbinols in good yields [29].

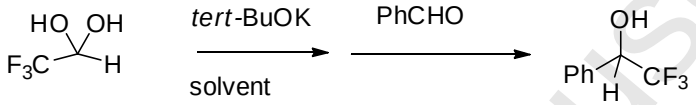
5.Trifluoromethylation with Methyl trifluoroacetate, Hexafluoroacetone Hydrate Salts, and Trifluoroacetaldehyde Hydrate

Methyl trifluoroacetate, in conjunction with an alkaline halide, such as cesium chloride, is an efficient protocol which enables the trifluoromethylation of (hetero)aromatic iodides and bromides [16b]. Langlois and collaborators [16c] propose the intervention of an adduct, such as that in eq 4, responsible for the trifluoromethylation reaction. The solvent of choice was DMF



(4)

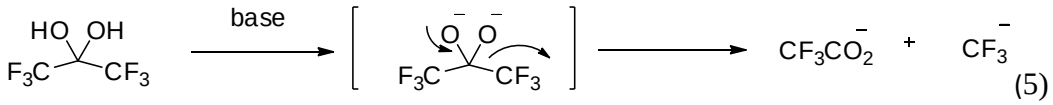
Trifluoroacetaldehyde hydrate has been recently used as an atom-economical trifluoromethyl source for the nucleophilic trifluoromethylation of carbonyl compounds [30]. Thus, the authors found that the trifluoromethylation of aldehydes using trifluoromethylacetaldehyde hydrate, with ^{tert}butoxide as base in DMF as solvent at low temperature, affords α-trifluoromethyl carbinols in fairly good yields, as indicated in Scheme 16.



Scheme 16. Trifluoromethylation of benzaldehyde with trifluoromethyl acetaldehyde with ^{tert}BuOK in DMF as solvent.

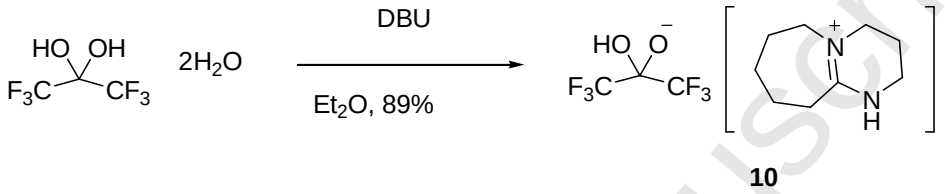
As for the substrate scope, the steric hindrance of substituents did not play a major role in the reactivity of substrates. However, the trifluoromethylation of enolizable hydrogens was a very unproductive reaction. Benzophenone derivatives also afford trifluoromethylated alcohols under this protocol with high efficiency [30].

The amidate salts of hexafluoroacetone hydrate has recently been used for the nucleophilic trifluoromethylation of aromatic carbonyl compounds, employing ^{tert}BuOK, *n*-Bu_4NCl, in DMF as solvent [31]. This reagent (amidate salts of hexafluoroacetate hydrate) came up as a valid alternative to an anhydrous form of the acidic hexafluoroacetone hydrate protons , eq 5.



(5)

(pKa1 = 6.76, and pKa2 = 13.53). Thus the salt **10** in Scheme 17 does not contain water.



10

Scheme 17. Hexafluoroacetone hydrate amidate salt

This salt **10** (Scheme 17) does not contain water, it is not hygroscopic, and can be exposed to air. Thus, a series of aromatic aldehydes can be trifluoromethylated with this reagent in good yield. The optimized reaction conditions [31] involve 1.2 equiv of salt **10** (Scheme 17), ^{tert}BuOK as base, and *n*-Bu_4NCl as additive in DMF as solvent. A byproduct of the reaction is trifluoroacetate, which causes no concern to the environment. Also aromatic ketones can be trifluoromethylated with this reagent.

CONCLUSIONS

Though the nucleophilic trifluoromethylation and perfluoroalkylation reactions constitute one of the first approaches toward the synthesis of fluorinated organic compounds, new fluorinating reagents and improved nucleophilic methods have become available in the last

few years to overcome the instability of CF_3 anion and the scope of electrophiles that are made react. Thus, new protocols employing trifluoromethane, trimethylsilyltrifluoromethane, and trifluoromethyl sulfides, sulfoxides and sulfones broaden the scope of the array of electrophiles that can be fluorinated. The introduction of trifluoroacetaldehyde and hexafluoroacetone derivatives as potential nucleophilic trifluoromethylating sources constitute alternatives of nucleophilic fluoroalkylation reactions, and address some environmental concerns regarding the toxicity, handling and disposal of trifluoromethylating reagents and by-products.

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ABBREVIATIONS

BAIB	=	*bis*(acetoxy)iodobenzene
DMF	=	*N*,*N*-dimethylformamide
DFT	=	Density Functional Theory
MF	=	metal fluoride
OPMB	=	4-methoxybenzyloxy

R_f	=	perfluoroalkyl
TBAF	=	*tetra*butyl ammonium fluoride
TBAT	=	*tetra*butyl ammonium *tri*phenyldifluorosilicate
TEMPO	=	(2,2,6,6-tetramethyl-piperidin-1-yl)-oxyl)
TFA	=	trifluoroacetic acid
THF	=	tetrahydrofuran
TMAF	=	*tetra*-methylammonium fluoride
TsOH	=	*p*-toluensulfonic acid

References

[1] X-F. Wu, H. Neumann, M. Beller, *Chem.Asian J.* 7 (2012) 1744-1754.

[2] O.A. Tomashenko, V.V. Grushin, *Chem. Rev.* 111 (2011) 4475-4521.

[3] B.R. Langlois, T. Billard, S. Roussel, *J.Fluorine Chem*. 126 (2005) 173-179.

[4] D. J. Burton, Z.-Y. Yang, *Tetrahedron* 48 (1992) 189-275.

[5] T. Shono, M. Ishifune, T. Okada, S. Kashimura, *J.Org.Chem*. 56 (1991) 2-4.

[6] B.R. Langlois, T. Billard, *Synthesis* 2003, 185-194.

[7] P. Novak, A. Lishchynskyi, V.V. Grushin, *J.Am.Chem.Soc*. 134 (2012) 16167-16170.

[8] G.K.S. Prakash, P.V. Jog, P.T.D. Batamak, G.A. Olah, *Science* 338 (2012) 1324-1327.

[9] H. Kawai, Z.E.Yuan, E. Tokunaga, N. Shibata, *Org.Biomol.Chem*. 11 (2013) 1446-1450.

[10] B. Folle´as, I. Marek, J-F. Normant, L. Saint-Jalmes, *Tetrahedron* 56 (2000) 275–283.

[11] G.Y. Luo, J. Qu, *New J. Chem*. 37 (2013) 3274-3280.

[12] A. Zanardi, M.A. Novikov, E. Martin, J. Benet-Buchholz, V.V. Grushin, *J.Am.Chem.Soc*. 133 (2011) 20901-20913.

[13] C.S. Thomoson, W.R. Dolbier, Jr. *J.Org.Chem*. 78 (2013) 8904-8908.

[14] Y. Zhang, M. Fujiu, H. Serizawa, K. Mikami, *J.Fluorine Chem*. 156 (2013) 367-371.

[15] (a) G.K.S. Prakash, A.K. Yudin, *Chem. Rev*. 97 (1997) 757-786. (b) N. Boechat, M.M. Bastos, *Curr.Org.Chem*. 7 (2010) 403-413. (c) T. Billard, S. Bruns, B.R. Langlois, *Org.Lett*. 2 (2000) 2101-2103. (d) S. Large, N. Roques, B.R. Langlois, *J.Org.Chem*. 65 (2000) 8846-8856,

[16] (a) G. Rubiales, C. Alonso, E. Martinez de Marigorta, F. Palacios, Arkivoc (2014) 362-405 (b) R.P. Singh, J.M. Shreeve, *J.Fluorine Chem*. 133 (2012) 20-26. (c) B.R. Langlois, N. Roques, *J.Fluorine .Chem*. 128 (2007) 1318-1325.

[17] G. Mloston, E. Obijalska, H. Heimgartner, *J. Fluorine Chem.* 132 (2011) 951-955.

[18] J.-L.Cheng, L. Chu, F.-L. Qing, *J. Fluorine Chem.* 152 (2013) 70-76.

[19] C. Masusai, D. Soorukram, C. Kuhakarn, P. Tuchinda, V. Reutrakul, M. Pohmakotr, *J. Fluorine Chem*. 154 (2013) 37-42.

[20] V.M. Timoshenko, C. Portella, *J.Fluorine Chem*. 130 (2009) 586-590.

[21] (a) A. Tlili, T. Billard, *Angew.Chemie.Intern.Ed*. 52 (2013) 6818-6819. (b) S. Alazet, K. Ollivier, T. Billard, *Beilstein J. Org. Chem.* 9 (2013) 2354–2357. (c) D. Kong, Z. Jiang, S. Xin, Z. Bai, Y. Yuan, Z. Weng, *J.Fluorine Chem*. 69 (2013) 6046-6050.

[22] S. Gouault-Bironneau, V.M. Timoshenko, F. Grellepois, C. Portella, *J.Fluorine Chem*. 134 (2012) 164-171.

[23] A.D. Dilman, V.V. Levin, *Eur.J.Org.Chem*. 2011 (2011) 831-841.

[24] V.V. Levin, A.D. Dilman, P.A. Belyakov, M.I. Struchkova, V.A. Tartakovsky, *Eur.J.Org.Chem*. 2008 (2008) 5226-5230.

[25] A.D. Dilman, V.V. Levin, P.A. Belyakov, M.I. Struchkova, V.A. Tartakovsky, *Tetrahedron Lett*. 49 (2008) 4352-4354.

[26] A.A. Zemtsov, V.V. Levin, A.D. Dilman, M.I. Struchkova, P.A. Belyakov, V.A. Tartakovsky, *Tetrahedron Lett*. 50 (2009) 2998-3000.

[27] G.K.S. Prakash, J. Hu, *Acc.Chem.Res*. 40 (2007) 921-930.

[28] K. Sakavuyi, K.S. Petersen, *Tetrahedron Lett*. 54 (2013) 6129-6132.

[29] P. Cherkupally, P. Beier, *Tetrahedron Lett*. 51 (2010) 252-255.

[30] G.K. Surya, Z. Zhang, F. Wang, S. Muñoz, G.A. Olah, *J.Org.Chem*. 78 (2013) 3300-3305.

[31] M.V. Rioski, A.D. Hart, D.A. Colby, *Org.Lett*. 15 (2013) 208-211.