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Authors: Feng-Ling Qing, Jia-Yi Shou, and Xiu-Hua Xu

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COMMUNICATION

Chemoselective Hydro(Chloro)pentafluorosulfanylation of Diazo Compounds with Pentafluorosulfanyl Chloride

Jia-Yi Shou, Xiu-Hua Xu, and Feng-Ling Qing*

[a] J.-Y. Shou, Dr. X.-H. Xu, Prof. Dr. F.-L. Qing
Key Laboratory of Organofluorine Chemistry
Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Science, Chinese Academy of Sciences
345 Lingling Lu, Shanghai 200032, China
E-mail: flq@mail.sioc.ac.cn

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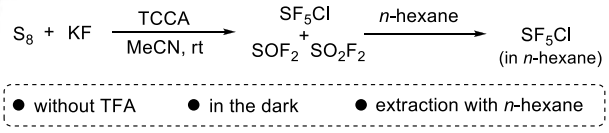
Abstract: Pentafluorosulfanyl chloride (SF_5Cl) is the most prevalent reagent for the incorporation of SF_5 group into organic compounds. However, the preparation of SF_5Cl often relied on hazardous reagents and specialized apparatuses. Herein we described a safe and practical synthesis of a bench-stable and easy-to-handle solution of SF_5Cl in *n*-hexane under gas-reagent-free conditions. The synthetic application of SF_5Cl was demonstrated through the unprecedented reaction with diazo compounds. The chemoselective hydro- and chloropentafluorosulfanylations of α-diazo carbonyl compounds were developed in the presence of K_3PO_4 or copper catalyst respectively. These reactions provide a direct and efficient access to various α-pentafluorosulfanyl carbonyl compounds of high value for potential applications.

The pentafluorosulfanyl (SF_5) group, an unique octahedral geometry around sulfur atom and a square pyramidal array of fluorine atoms, has attracted increasing attention due to its intriguing physicochemical properties, such as strong electron-withdrawing capability, substantial steric hindrance, significant lipophilicity, and high chemical stability.[1] It has been intensively used as a bioisosteric replacement of the CF_3 group in a multitude of drug candidates.[2] Furthermore, the SF_5 group is frequently exploited in the development of new materials, especially in the area of optoelectronic materials.[3] Recently, the application of SF_5 group in the design of molecular catalysts has been developed.[4] Consequently, the considerable advances have been made in the introduction of the SF_5 group into organic molecules in the past decade.[5] To date, most of these synthetic methods focused on the improvement of the fluorination process for the preparation of SF_5-substituted aromatic compounds[6] and transformation of SF_5-containing building blocks.[7] The synthesis of aliphatic pentafluorsulfanylated compounds through direct pentafluorosulfanylation reactions was less developed probably due to a lack of efficient and easily available pentafluorosulfanylating reagents.

Among the reported pentafluorosulfanylating reagents, pentafluorosulfanyl chloride (SF_5Cl) is most extensively used in terms of the balance between reactivity and stability.[8] Especially, it is more stable than pentafluorosulfanyl bromide (SF_5Br)[9] and more reactive than sulfur hexafluoride (SF_6)[10]. However, SF_5Cl is hardly commercially available, and its synthesis is difficult to execute in common organic chemistry laboratories. Normally, SF_5Cl was prepared from the toxic and corrosive sulfur tetrafluoride (SF_4) in an autoclave.[11,12] Recently, more convenient synthetic methods without the use of SF_4 were reported in the patent literatures. Winter disclosed that the reaction of dry KF, sulfur powder, and Cl_2 in the presence of Br_2 afforded SF_5Cl in excellent yield.[13] Togni observed the formation of SF_5Cl from the mixture of sulfur powder, dry KF, and trichloroisocyanuric acid (TCCA) in MeCN using trifluoroacetic acid (TFA) as the catalyst.[14] Although Togni's protocol is very intriguing in terms of gas-reagent-free conditions, neither the yield nor purification process of SF_5Cl was provided. To develop a synthetically useful method in common research laboratories, we optimized Togni's procedure (Scheme 1). It was found that the catalytic amounts of TFA was not necessary for the formation of SF_5Cl,[6e] and the protection from light is crucial for this reaction. The reaction of sulfur powder, dry KF, and TCCA in MeCN under light only afforded the byproducts SO_2F_2 and SOF_2, whereas SF_5Cl was formed in the absence of light along with SO_2F_2 and SOF_2. To our delight, SF_5Cl was easily purified through simple extraction with *n*-hexane. The resulting solution of SF_5Cl in *n*-hexane could be stored on the bench for months without noticeable decomposition. Finally, the reaction was easily scaled up in an average yield of 47% from 0.46 mmol[14] to 32 mmol.



Scheme 1. Preparation of a solution of SF_5Cl in *n*-hexane.

The reactions of SF_5Cl mainly involve the atom-transfer radical addition (ATRA) with unsaturated compounds, such as alkenes (Scheme 2a)[8,15] and alkynes (Scheme 2b)[7f,16]. The resulting chloropentafluorosulfanylated products are important precursors for the preparation of other SF_5-containing compounds. The transformation of SF_5Cl adducts formed from vinyl esters or ethers is the common approach to α-SF_5 aldehydes, ketones, carboxylic acids, and esters (Scheme 2c).[7a,c,17] Recently, Paquin developed a multistep synthesis of α-SF_5 ketones starting from the addition of SF_5Cl to alkynes (Scheme 2d).[7f] These α-SF_5 carbonyl compounds are valuable building block for further diversification.[7c,d,18] To the best of our knowledge, there was only one example of the direct synthesis of α-SF_5 carbonyl compounds from the addition of SF_5Cl to ketene (Scheme 2e).[19] Inspired by recent advances in radical addition reactions of diazo compounds,[20] which are easily available and versatile intermediates in organic synthesis,[21] herein we disclose the

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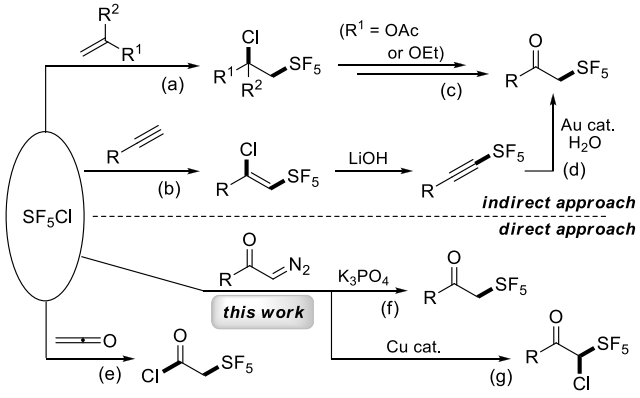
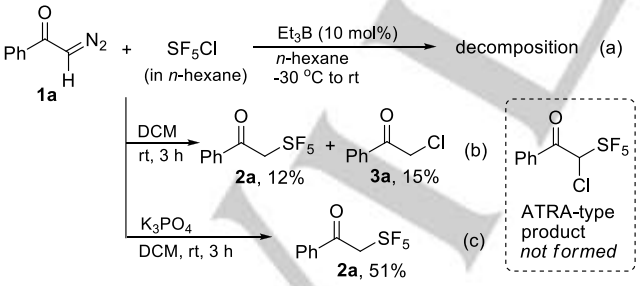
unprecedented reaction of SF_5Cl with diazo compounds. This protocol enables the direct and facile access to α-SF_5 ketones and esters for the first time. Notably, the hydro- and chloropentafluorosulfanylated products were chemoselectively formed in the presence of base (Scheme 2f) or copper catalyst (Scheme 2g), respectively.



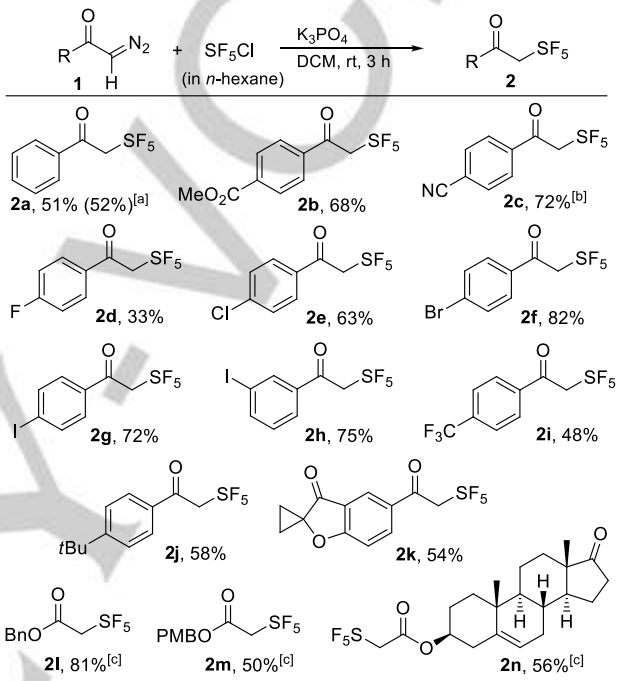
Scheme 2. Preparation of α-SF_5 carbonyl compounds with SF_5Cl.

Initially, 2-diazo-1-phenylethanone (**1a**) was chosen as the model substrate to react with SF_5Cl under Et_3B-catalyzed conditions developed by Dolbier in 2002.[22] However, no SF_5-containing product was observed (Scheme 3a). Unexpectedly, the reaction of **1a** and SF_5Cl in DCM without any additive afforded the hydropentafluorosulfanylated product α-pentafluorosulfanylketone (**2a**), α-chloroketone (**3a**), and other byproducts (Scheme 3b). The expected ATRA-type chloropentafluorosulfanylated product was not formed. Encouraged by this result, the reaction conditions were optimized to improve the yield of **2a** (see the Supporting Information). Previous studies showed that the byproduct **3a** was presumably formed from the reaction of **1a** and in situ generated HCl.[23] Consequently, different bases were added to suppress the formation of **3a**. To our delight, the addition of K_3PO_4 afforded **2a** in 51% yield, and no **3a** was detected (Scheme 3c).



Scheme 3. Reaction of **1a** and SF_5Cl.

Then, the substrate scope of hydropentafluorosulfanylation of diazo compounds with SF_5Cl was examined (Scheme 4). α-Diazoketones **1b**-**i** bearing electron-withdrawing groups reacted efficiently to afford the corresponding products in moderate to excellent yields. The substituents including ester (**1b**), nitrile (**1c**), halogen (**1d-h**), and trifluoromethyl (**1i**) at different positions of the aromatic ring were all well tolerated. The presence of electron-donating groups, such as alkoxyl and amino, on the phenyl ring was harmful to this reaction, probably due to the competing electrophilic chlorination reaction.[24] Notably, terminal alkenyl- and alkynyl-substituted substrates were not suitable for this reaction. Sterically hindered (**1j**) and polysubstituted (**1k**) substrates furinshed the desired products in moderate yields. α-Diazoesters **1l** and **1m** were also compatible with the reaction conditions. Dehydroepiandrosterone-derived substrate **1n** underwent the reaction smoothly, delivering **2n** in 56% yield. The reaction of **1a** was scaled up to 1.25 mmol without erosion of the yield.



Scheme 4. Substrate scope of hydropentafluorosulfanylation of diazo compounds. Reaction conditions: **1** (0.1 mmol), SF_5Cl (0.15 mmol), K_3PO_4 (0.15 mmol), DCM (2.0 mL), N_2, rt, 3 h, isolated yields. [a] Reaction was performed on a 1.25 mmol scale. [b] Reaction time 12 h. [c] **1** (0.15 mmol), SF_5Cl (0.1 mmol).

To gain insight into the mechanism of the hydropentafluorosulfanylation reaction, several control experiments were performed. When ethynylbenzene was added to the standard reaction of **1a**, the hydropentafluorosulfanylated product **2a** was not formed, whereas ethynylbenzene-derived chloropentafluorosulfanylated product **4** was obatined in low yield (Scheme 5a). These results indicated that SF_5 radical was probably generated as the key intermediate and the reaction of SF_5 radical with alkynes should be faster than that with diazo compounds. Furthermore, the deuteration experiments were performed in DCM-d_2 (Scheme 5b) or using a solution of SF_5Cl in *n*-hexane-d_{14} (Scheme 5c), respectively. The deuterated product **[D]2a** was observed in the presence of *n*-hexane-d_{14}, demonstrating that *n*-hexane acts as a hydrogen atom donor. Notably, a chlorination product from *n*-hexane was also detected in the reaction mixture, which supports the formation of hexyl radical. On the basis of the above results and previous reports,[5,20] a plausible reaction mechanism for hydropentafluorosulfanylation of diazo compounds was proposed in Scheme 5d. Initially, SF_5 radical is generated from SF_5Cl by the reaction with diazo compounds **1**[25] or photo-irradiation. Then, the addition of SF_5

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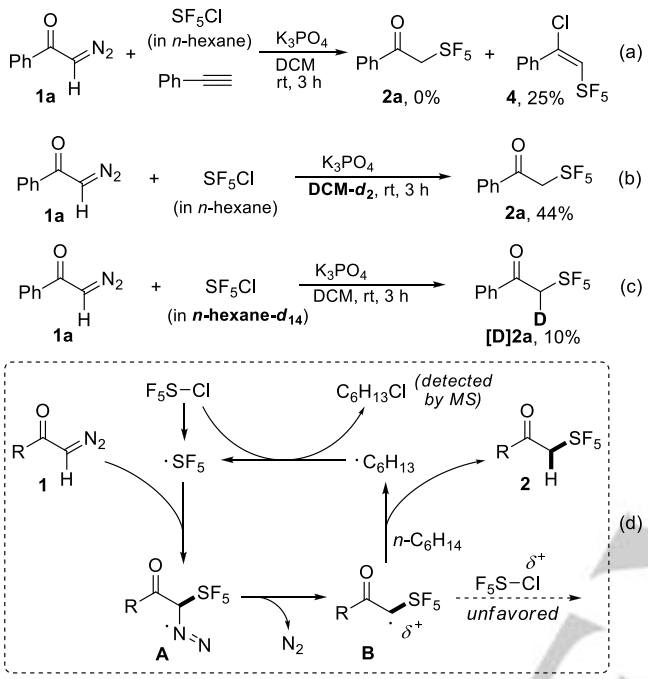
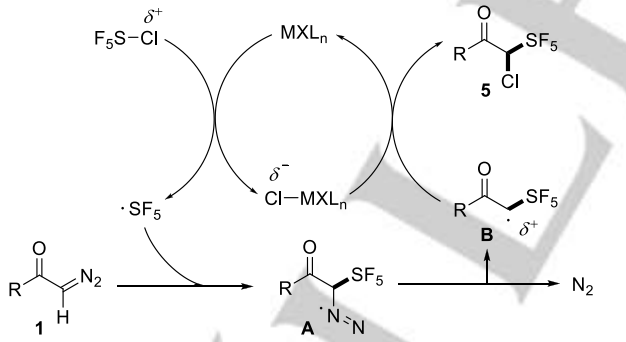
radical to diazo compounds **1** gives radical intermediate **A**, which releases of one molecule of N_2 to afford radical intermediate **B**. The presence of adjacent electron-withdrawing SF_5 and carbonyl groups makes radical **B** highly electrophilic. Thus, the abstraction of electrophilic Cl atom from SF_5Cl by electrophilic radical **B** is unfavorable. Instead, radical **B** abstracts hydrogen atom from *n*-hexane to furnish the hydropentafluorosulfanylated products **2**. On the other hand, hexyl radical is formed, and then reacts with SF_5Cl to give chlorohexane and SF_5 radical.



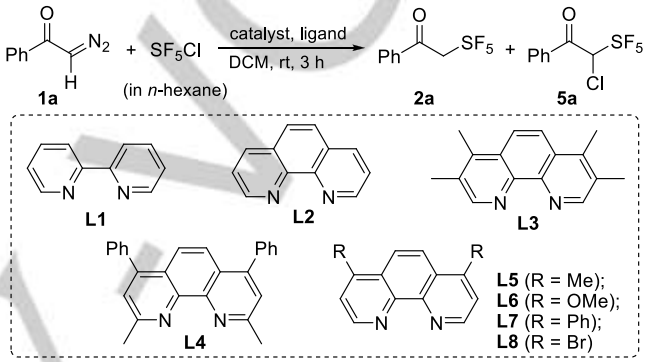
Scheme 5. Investigations of hydropentafluorosulfanylation reaction.



Scheme 6. Transition-metal-catalyzed polarity reversal strategy for chloropentafluorosulfanylation reaction.

To overcome the challenges for the chloropentafluorosulfanylation of diazo compounds and inspired by recent progress in transition-metal-catalyzed ATRA reactions,[26,27] a transition-metal-catalytic strategy for the reaction of SF_5Cl with diazo compound was proposed in Scheme 6. We reasoned that the single electron transfer (SET) reaction of SF_5Cl and MXL_n would afford SF_5 radical and $ClMXL_n$. In this process, the polarity of Cl atom is reversed, thus enabling the transfer of Cl atom from $ClMXL_n$ to electrophilic radical **B** for the formation of chloropentafluorosulfanylated products **5**. To test our hypothesis, several transition metal catalysts including $FeCl_2$, $CoCl_2$, $NiCl_2$, and $CuCl_2$ were added to the reaction mixture (Table 1, entries 1-4). Only the reaction in the presence of $CuCl_2$ afforded the desired chloropentafluorosulfanylated product **5a** in low yield, along with the hydropentafluorosulfanylated product **2a** (entry 4). Further screening of different copper catalysts demonstrated that $Cu(MeCN)_4PF_6$ led to the selective formation of **5a** (entries 5-8). Subsequently, a variety of *N*,*N*-bidentate ligands including 2,2'-bipyridine (**L1**), 1,10-phenanthrolines (**L2**-**8**) were employed (entries 9-16). Pleasingly, all of them promoted the desired chloropentafluorosulfanylation reaction. Among them, ligand **L7** was optimal to give **5a** in 84% yield (entry 15).

Table 1. Optimization of the reaction conditions[a]

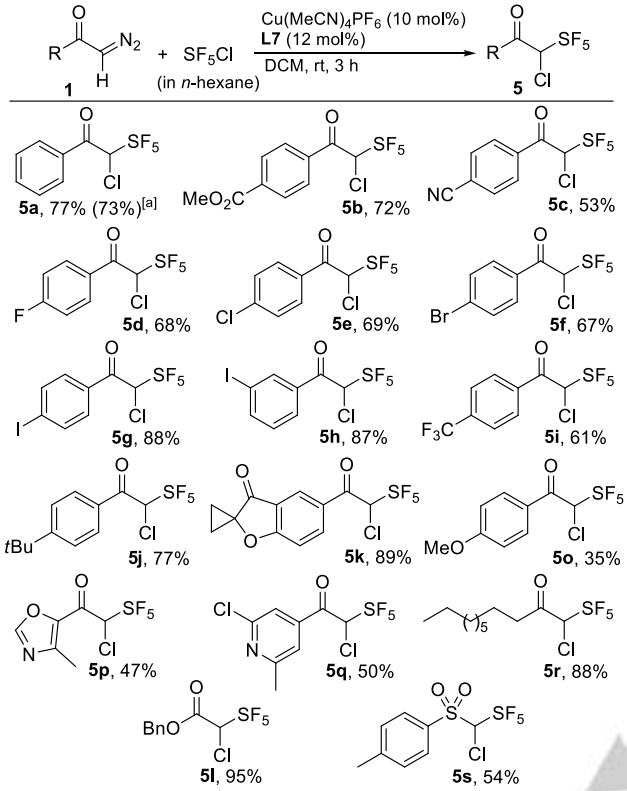


Entry	Catalyst	Ligand	Yield (**2a**/**5a**, %)[b]
1	$FeCl_2$	—	5/0
2	$CoCl_2$	—	0/0
3	$NiCl_2$	—	3/0
4	$CuCl_2$	—	11/2
5	$Cu(OAc)_2$	—	17/trace
6	$Cu(acac)_2$	—	17/0
7	CuCl	—	10/trace
8	$Cu(MeCN)_4PF_6$	—	0/5
9	$Cu(MeCN)_4PF_6$	**L1**	0/42
10	$Cu(MeCN)_4PF_6$	**L2**	0/45
11	$Cu(MeCN)_4PF_6$	**L3**	0/74
12	$Cu(MeCN)_4PF_6$	**L4**	0/44
13	$Cu(MeCN)_4PF_6$	**L5**	0/78
14	$Cu(MeCN)_4PF_6$	**L6**	0/31
15	$Cu(MeCN)_4PF_6$	**L7**	0/84
16	$Cu(MeCN)_4PF_6$	**L8**	0/60

[a] Reaction conditions: **1a** (0.2 mmol), SF_5Cl (0.1 mmol), catalyst (0.01 mmol), ligand (0.012 mmol), DCM (2.0 mL), N_2, rt, 3 h. [b] Yields determined by ^{19}F NMR spectroscopy using trifluoromethylbenzene as an internal standard.

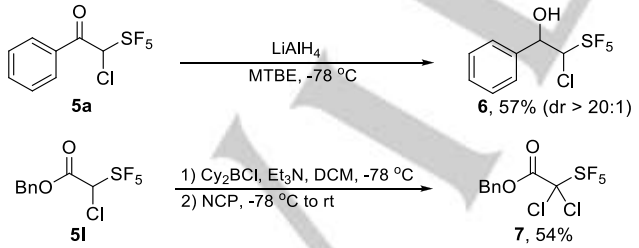
The substrate scope of copper-catalyzed chloropentafluorosulfanylation of diazo compounds was also investigated. As shown in Scheme 7, a range of diazo compounds **1** were converted to the chloropentafluorosulfanylated products **5** in moderate to excellent yields. In general, the yields are higher than those of hydropentafluorosulfanylation reactions. The mild conditions allow the tolerance of both of electron-withdrawing and electron-donating group. Heteroaryl (**1p**,**q**) and alky (**1r**) ketone derivatives were also suitable substrates. Furthermore, α-diazosulfone **1s** underwent the reaction smoothly to give **5s** in 54% yield. However, other diazo compounds, such as diaryl

diazomethanes, failed to yield the desired products. The structure of **5f** was confirmed by X-ray crystallographic analysis.



Scheme 7. Substrate scope of chloropentafluorosulfanylation of diazo compounds. Reaction conditions: **1** (0.2 mmol), SF_5Cl (0.1 mmol), $Cu(MeCN)_4PF_6$ (0.01 mmol), **L7** (0.012 mmol), DCM (2.0 mL), N_2, rt, 3 h, isolated yields. [a] Reaction was performed on a 1.25 mmol scale.

Finally, the transformation of previously unknown α-chloro-α-pentafluorosulfanyl carbonyl compounds **5** was launched. Reduction of α-pentafluorosulfanylketone **5a** with $LiAlH_4$ afforded the corresponding alcohol **6** in 57% yield (Scheme 8a). Treatment of α-pentafluorosulfanylester **5l** with Cy_2BCl/Et_3N, followed by chlorination with *N*-chlorophthalimide (NCP) gave pentafluorosulfanyldichloroacetate **7** in 54% yield (Scheme 8b).



Scheme 8. Transformation of products **5**.

In summary, we have developed a practical synthesis and new reactions of SF_5Cl. The reaction of sulfur powder, dry KF, and TCCA in MeCN followed by extraction with *n*-hexane afforded a bench-stable and easy-to-handle solution of SF_5Cl in *n*-hexane. Under K_3PO_4-promoted or copper-catalyzed conditions, the reaction of SF_5Cl with diazo compounds selectively furnished hydro- and chloropentafluorosulfanylated products respectively. This work represents the rare examples of 1,1-difunctionalized pentafluorosulfanylation reactions and affords the direct synthetic route to the valuable α-pentafluorosulfanyl carbonyl compounds.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: pentafluorosulfanylation • diazo compounds • pentafluorosulfanyl chloride • copper • radical reactions

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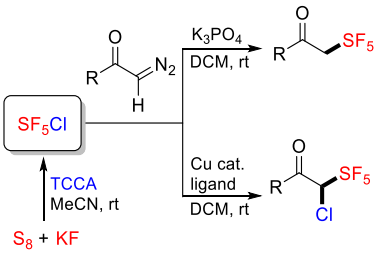

A practical synthesis of SF_5Cl from sulfur powder, dry KF, and trichloroisocyanuric acid (TCCA) in MeCN is described. The new synthetic utility of SF_5Cl is well demonstrated by the chemoselective hydro(chloro)pentafluorosulfanylation of diazo compounds.