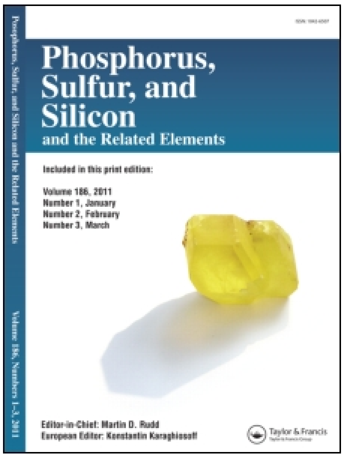

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A NEW CONVENIENT AND INEXPENSIVE METHOD FOR PREPARATION OF ALKYL- ARYLTRIFLUOROMETHYL SULFIDES IN REDUCTIVE MEDIUM

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A NEW CONVENIENT AND INEXPENSIVE METHOD FOR PREPARATION OF ALKYL- ARYLTRIFLUOROMETHYL SULFIDES IN REDUCTIVE MEDIUM

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Abstract A new convenient and general method for preparation of alkyl or aryltrifluoromethyl sulfides is described.

INTRODUCTION

The CF_3-S-radical is extremely lipophilic. That is the reason why it is widely used in pharmaceutical drugs and in agrochemical compounds[1].

Several methods describe the access to alkyl or aryltrifluoromethylsulfides but none of them gives complete satisfaction.

KF or HF exchange on the corresponding trichloromethyl group requires very strong conditions and therefore can not be applied to fragile molecules [2].

CF_3 - S-M (M = Hg, Cu, Ag, Zn, Cd) or CF_3- S - X (X = Cl ; - S - CF_3) react respectively only with an electrophile and a nucleophile.

It is very difficult to prepare these compounds and all of them are toxic [3-4].

UMEMOTO's [5], approach effectively leads to both alkyl or aryltrifluoromethylsulfides starting from the corresponding disulfides but he uses a sophisticated reagent.

CF_3I used by HASZELDINE[6] is very expensive and it is not an industrial compound. Moreover, the reaction takes place in liquid ammonia under UV irradiation. At last Wakselman's [7-8] method is very interesting because he uses CF_3Br as a trifluoromethylating agent ; this is an industrial, inexpensive and non toxic reagent : in this work we describe the access to both alkyl or aryltrifluoromethylsulfides indifferently using a single method.

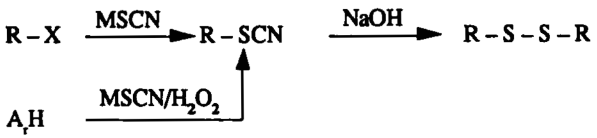
This method consists in reacting CF_3Br with a disulfide (alkyl or aryldisulfide) in reductive medium.

DISCUSSION AND METHODOLOGY

Why disulfides as starting materials ?

a. Because they are readily available in both the alkyl or aryl series :

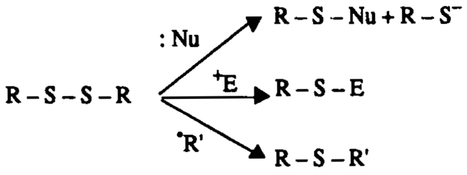
- by hydrolysis of the corresponding thiocyanate[9]



- by the reaction of a nucleophile on sulfur monochloride (S_2Cl_2) [10]

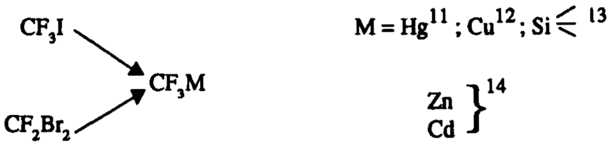
$$2NuH + S_2Cl_2 \longrightarrow Nu-S-S-Nu + 2\,HCl$$

b. Because they can react :
- toward a nucleophile
- toward an electrophile
- toward a radical



Sources of •CF3 (•R' = •CF3)

The preparation of "⁻CF$_3$" equivalent is carrying out mainly starting from expensive reagents and by using laboratory methods.

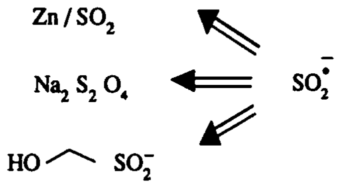


Among the different methods proposed in the litterature for the generation of $CF_3^{\bullet}$ [5, 15-19] Wakselman's is undoubtedly the simplest one. It is based on the following principle :

$$Zn + SO_2 \longrightarrow SO_2^{\bullet-} + \text{"}Zn^{+}\text{"}$$

$$CF_3Br + SO_2^{\bullet-} \longrightarrow SO_2 + {}^{\bullet}CF_3 + Br^{-}$$

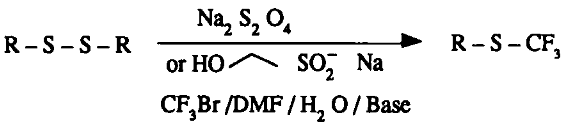
Other well known sources of SO_2 radical anion are dithionite and hydroxymethylsulfinates :

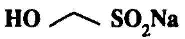
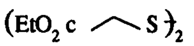
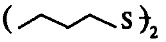


These three systems have been tested for the reduction of CF_3Br and in the synthesis of alkyl or aryltrifluoromethylsulfides starting from the corresponding disulfides.

RESULTS

a. with the $Na_2S_2O_4$ or HO ⌒ SO_2^- systems



TRIALS	$(R-S)_2$	$Na_2S_2O_4$		RR
1	$(Ø-S)_2$	X		65 %
2	$(Ø-S-)_2$		X	93 %
3			X	55 %
4			X	31 %

b. with the Zn/SO_2 system

$$R-S-S-R \xrightarrow[\substack{CF_3Br \\ DMF}]{Zn/SO_2} R-S-CF_3$$

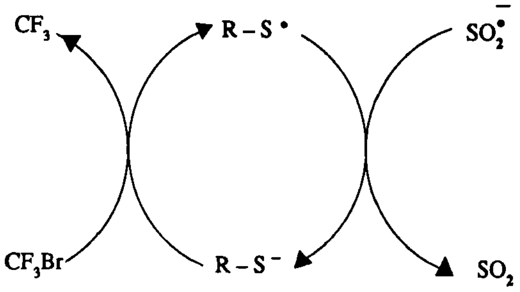
TRIALS	$(R-S)_2$	RR
6	$(Ø-S)_2$	LOW

c. Prosposed mechanism

$$CF_3Br + SO_2^{\bullet -} \longrightarrow CF_3^{\bullet} + Br^- + SO_2$$

$$R-S-S-R + CF_3^{\bullet} \longrightarrow R-S-CF_3 + R-S^{\bullet}$$

$$2R-S^{\bullet} \longrightarrow R-S-S-R$$



CONCLUSION

In conclusion, we can say that we now have a convenient, general and inexpensive method for the preparation of alkyl or aryltrifluoromethylsulfides starting from the always readily available corresponding disulfides.

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