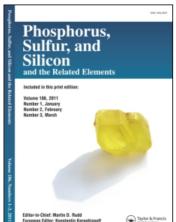
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A NEW CONVENIENT AND INEXPENSIVE METHOD FOR PREPARATION OF ALKYL- ARYLTRIFLUOROMETHYL SULFIDES IN REDUCTIVE MEDIUM

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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 CF₂-S-radical is extremely lipophilic. That is the reason why it is widely used in pharmaceutical drugs and in agrochemical compounds¹.

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.

CF₄I used by HASZELDINE⁶ 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 CF₂Br 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 CF₃Br 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 thiocyanate⁹

$$R-X$$
 \xrightarrow{MSCN} $R-S-S-R$ \xrightarrow{NaOH} $R-S-S-R$ $\xrightarrow{MSCN/H_2O_2}$

• by the reaction of a nucleophile on sulfur monochloride (S₂Cl₂) ¹⁰

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

$$R-S-S-R$$

$$: Nu$$

$$+E$$

$$R-S-E$$

$$R-S-E$$

$$R-S-R'$$

Sources of $^{\circ}$ CF3 ($^{\circ}$ R' = $^{\circ}$ CF3)

The preparation of "CF₃" equivalent is carrying out mainly starting from expensive reagents and by using laboratory methods.

$$CF_3I$$
 $M = Hg^{11}$; Cu^{12} ; $Si \leq {}^{13}$
 CF_3M
 CF_3Br_3
 CF_3M
 CF_3M
 CF_3M
 CF_3M
 CF_3M
 CG_3M
 CG_3M

Among the different methods proposed in the litterature for the generation of CF₃. 5, 15-19 Wakselman's is undoubtedly the simplest one. It is based on the following principle:

$$Zn + SO_2$$
 \longrightarrow $SO_2^{+} + "Zn^{+}"$
 $CF_3Br + SO_2^{-}$ \longrightarrow $SO_2 + ^{\circ}CF_3 + Br^{-}$

Other well known sources of SO₂ radical anion are dithionite and hydroxymethyl-sulfinates:

$$Zn/SO_2$$
 $Na_2 S_2 O_4$
 SO_2^{-}
 SO_2^{-}

These three systems have been tested for the reduction of CF₃Br and in the synthesis of alkyl or aryltrifluoromethylsulfides starting from the corresponding disulfides.

RESULTS

a. with the Na₂S₂O₄ or HO SO₂ systems

$$R-S-S-R = \frac{\text{Na}_2 S_2 O_4}{\text{or HO} \sim SO_2^- \text{Na}} \qquad R-S-CF_3$$

$$CF_3Br/DMF/H_2 O/Base$$

TRIALS	$(R-S)_{\overline{2}}$	Na ₂ S ₂ O ₄	HO SO ₂ Na	RR
1	$(\emptyset - S)_2$	X		65 %
2	$(\varnothing - S -)_2$		X	93 %
3	$(EtO_2 c \sim S)_2$		X	55 %
4	$(\sim s)_2$		X	31 %

b. with the Zn/SO₂ system

$$R-S-S-R \xrightarrow{Zn/SO_2} R-S-CF_3$$

$$DMF$$

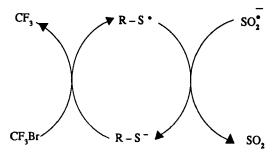
TRIALS	$(R-S)_{\overline{2}}$	RR
6	$(\varnothing - S \rightarrow 2$	LOW

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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