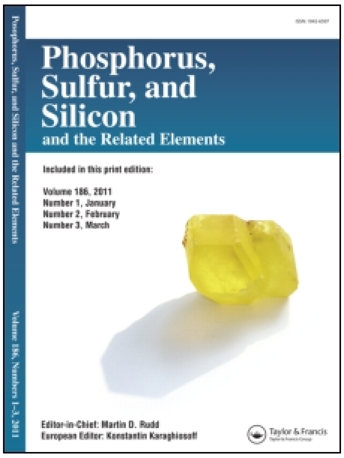

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ORGANOSULFUR TRANSFER WITH DISULFIDES IN THE PRESENCE OF CCl_4

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ORGANOSULFUR TRANSFER WITH DISULFIDES IN THE PRESENCE OF CCl_4

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Abstract Thiols and protic nucleophiles undergo sulfur-element bond formation in the presence of CCl_4/base. Sulfenylation of CH-acidic compounds with thiols occur via disulfides, formed in a preliminary step. Uses and advantages of this organosulfur transfer are described.

INTRODUCTION

The reaction of thiols and bases like NEt_3, NaOEt, NaOH etc. with CCl_4 is a suitable route of mild oxidation into the corresponding disulfides (eq.1)[1].

$$2\ RSH + CCl_4 \xrightarrow[-\ base\cdot HCl]{base} RSSR + CHCl_3 \qquad (1)$$

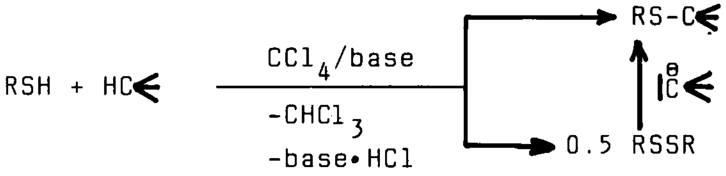
R □ alkyl, aryl

In order to use this type of reaction for sulfur-element bond formation in general, we have investigated other protic nucleophiles (HNu) instead of thiols under comparable conditions (eq.2).

$$RSH + HNu + CCl_4 \xrightarrow[-\ base\cdot HCl]{base} RS\text{-}Nu + CHCl_3 \qquad (2)$$

HNu □ HSR, HC<

Besides organylthiolation the formation of disulfides was observed in all reactions influenced by CCl_4/base [2]. It was therefore interesting to explore, whether disulfides originate from a first step of the reaction or as a competitive product (eq.3).



(3)

In the following parts the reaction route of the sulfenylation of CH-acidic compounds with thiols and the use of disulfides as organosulfur transfer reagents, influenced by CCl_4/base, are described[3].

SULFENYLATION OF PENTANE-2.4-DIONE WITH ARYLTHIOLS

Reactions of thiophenol and 4-chloro-thiophenol with pentane-2.4-dione (Hacac) have been carried out in DMF at 20^0 and 60^0C in the presence of CCl_4/base. The concentration gradients of the sulfur compounds thiols, disuldides and 3-arylthiopentane-2.4-diones have been followed time dependent by means of GC. Before sulfenylated compounds were detectible, always the formation of disulfides took place. Organylthiolation of CH-acidic compounds with thiols and CCl_4/base therefore proceed via disulfides, which are the real sulfur transfer reagents (eq.3).

ORGANOSULFUR TRANSFER WITH DISULFIDES

In principle sulfur-carbon bond formation resulting from the reaction of disulfides and carbanionsis known [4]. According to eq.4 the sulfur of disulfides is used only to 50 % maximum. Sometimes a sulfur-carbon bond cleavage from the reaction of the sulfenylated species and thiolate ions immediatly yields the starting materials (eq.4)[5].

$$\mathrm{RSSR} + |\overset{\ominus}{\mathrm{C}}< \;\rightleftharpoons\; \mathrm{RS{-}C}< + \mathrm{RS}^{\ominus} \qquad (4)$$

Therefore we were interested to check, whether the efficiency of this reaction could be increased in the presence of CCl_4/base (eq.5).

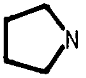
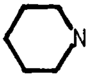
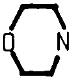
$$RSSR + 2\ HC\!\lessdot \xrightarrow[-CHCl_3/-base\bullet HCl]{CCl_4/base} 2\ RS\text{-}C\!\lessdot \qquad (5)$$

Hitherto we have used diaryldisulfides and thiuramdisulfides as organosulfur transfer raegents for several CH-acidic compounds.

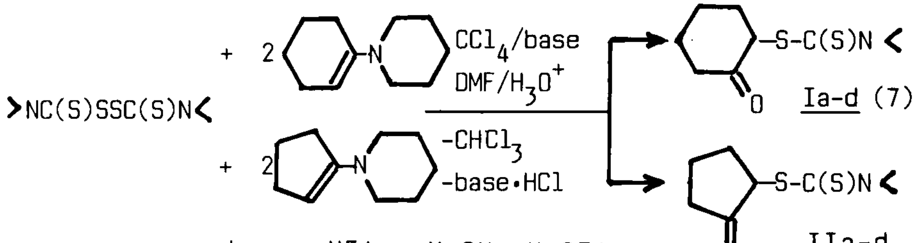
With pentane-2.4-dione the sulfenylated species were formed in yields between 47 and 91 % (eq.6).

$$RSSR + 2\ H_2C(COMe)_2 + CCl_4 \xrightarrow[-\ NaCl]{NaOH(DMF/H_2O)} 2\ RSCH(COMe)_2 + CHCl_3 \qquad (6)$$

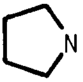
R = Ph (88%), 4-ClC$_6$H$_4$ (91%), 4-MeC$_6$H$_4$ (63%);

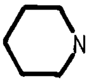
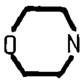
R = >NC(S): >N = Me$_2$N (58%), Et$_2$N (59%),  (72%),  (47,5%),  (48%).

In the result of enamine sulfenylation, e.g. of piperidinocyclohexene or -pentene resp. with thiuramdisulfides [6] and CCl$_4$/base the corresponding cyclohexane-2-one or cyclopentane-2-one esters of dithiocarbamic acids have been isolated after acidic hydrolysis (eq.7).



base: NEt$_3$, NaOH, NaOEt

>N: Me$_2$N(Ia 65%, IIa 48%);  (Ib 61%, IIb 31%);

 (Ic 50%, IIc 45%); (Id 32%, IId 28%).

SUMMARY

Diaryldisulfide formation is the first step of sulfenylation reactions of CH-acidic compounds with arylthiols and CCl_4/base. Thus organylthiolated species are formed from disulfides and carbanions together with thiolate ions (eq.4). The latter are oxidized by CCl_4 again. Therefore organosulfur transfer from disulfides to CH-nucleophiles offers the following advantages:

- Thiolate ions are removed by oxidation with CCl_4 and cannot cause a sulfur-bond fission (back reaction),
- the yields of sulfenylated compounds in relationship to the disulfides used are generally higher than 50% causing a much better utilization of sulfur.

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