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Silicon Assisted Sulfuration: Tetrachlorosilane-Sodium Sulfide-A New Potent Thionating Reagent for Carbonyl Compounds

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ABSTRACT- *A combination of tetrachlorosilane and sodium sulphide in acetonitrile was found to be an efficient thionating reagent for aromatic aldehydes giving the corresponding thioaldehydes as trimers in good yields as well as for α,β-unsaturated ketones under the catalysis of cobalt(II) chloride giving β-mercaptoketones that subsequently auto-oxidized yielding the respective disulfides in moderate yields at ambient temperature. No reaction was observed with aryl methyl ketones.*

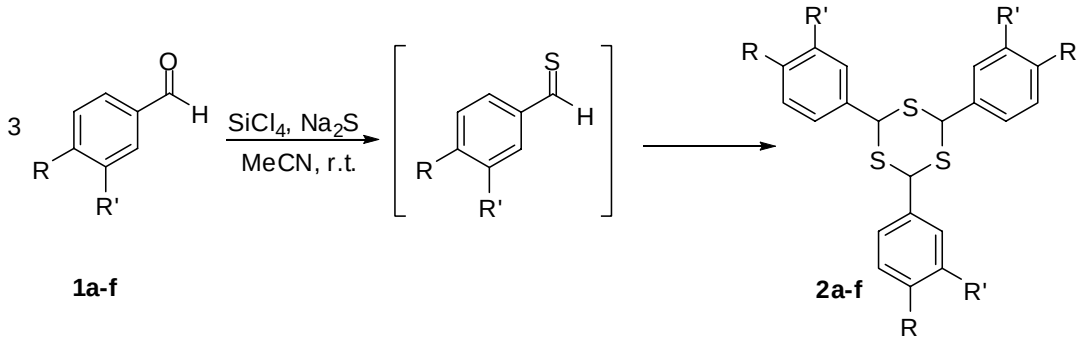
INTRODUCTION

Thio-compounds are important intermediates in the synthesis of various biologically active molecules as well as in industry. Though a variety of thionating reagents such as elemental sulfur, phosphorus pentasulfide, Lawesson's reagent and thiosilanes are reported in the literature, work in development of thionation methods for synthesis of organo-sulfur compounds is essential.[1] Within the framework of the utilization of tetrachlorosilane (TCS)[2] for synthetic purposes in organic chemistry, we present herein a new *in situ* thiosilane system derived from the cheap and readily available tetrachlorosilane and sodium sulfide that converts aromatic aldehydes to their corresponding thioaldehydes which obtained as trimers in good yield at room temperature using acetonitrile as solvent without need of any catalyst. Under these exceptionally mild conditions, α,β-unsaturated ketones react with $SiCl_4$-Na_2S in the presence of a catalytic amount of $CoCl_2.6H_2O$ to give thiol derivatives that subsequently auto-oxidized giving the respective disulfides. However, unfortunately no reaction was observed with aryl methyl ketones.

RESULTS AND DISCUSSION

The reaction of aldehydes with $SiCl_4$-Na_2S works well without further addition of any catalyst giving good yields of respective thioaldehydes which obtained as trimers (Scheme 1, Table1). The structure of isolated trithioaldehydes was assigned based on

their spectral analyses as well as by matching their melting points with reported analogues which showed that the products **2** are being in the trans form.



1a, 2a; R' = R = H
1b, 2b; R' =H, R = Cl,
1c, 2c; R' = H, R = Br,
1d, 2d; R' = H, R = Me,
1e, 2e; R' = H, R = OMe,
1f, 2f; R' = Br, R = H

Scheme 1

Table 1. Reaction of aryl aldehydes with TCS-Na_2S reagent

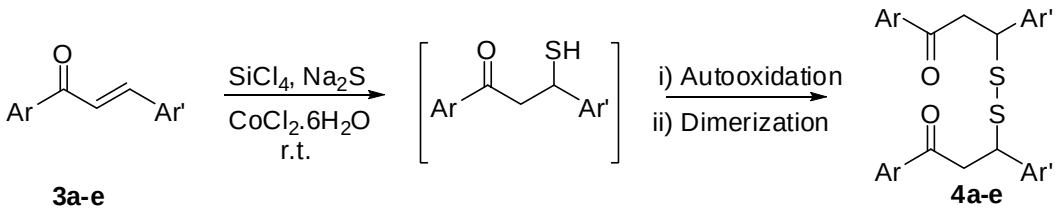
Entry	Substrate	Product	Time (h)	Yield (%)[a]
1	Benzaldehyde	9	**2a**	82
2	4-Methylbenzaldehyde	10	**2b**	77
3	4-Methoxybenzaldehyde	8	**2c**	79
4	4-Chlorobenzaldehyde	12	**2d**	68
5	4-Bromobenzaldehyde	14	**2e**	72
6	3-Bromobenzaldehyde	18	**2f**	63

[a] Isolated yield

The driving force for the present reaction is the net formation of the stronger Si-O bond where the difference in Si-O and Si-S bond energies is ≈ 34 kcal[3] promotes the easy addition of thiosilane to the carbonyl group of aldehyde with the formation of kinetically controlled products.

Applying the present reaction to aryl methyl ketones failed to get the corresponding thioketones even with use of a catalyst and/or heating. This led us to try the reaction with α,β-unsaturated ketones reasoning that the 1,4-addition might be a favourable process. Thus, α,β-unsaturated ketones were found to react with TCS-Na_2S in the presence of catalytic amount of $CoCl_2.6H_2O$ to give 1,4-adducts (presumably the thiols **C**) but, as it is well known, such thiols undergoe auto-oxidative dimerization with such ease giving only the disulphide **4.**[4] It is noteworthy to mention that no

reaction was observed in the absence of either the catalyst or $SiCl_4$. The generality of the process was examined through applying the reaction to various examples of α,β-unsaturated ketones, however, unfortunately, bischalcones gave a complex mixture with no preparative value. For example, dibenzalacetone and 2,6-bis(4-methoxybenzal) cyclohexanone gave no discrete products (Scheme 2, Table 2).



3a, 4a; Ar = Ar' = Ph
3b, 4b; Ar = Ph, Ar' = 4-BrC_6H_4-
3c, 4c; Ar = Ph, Ar' = 4-MeC_6H_4-
3d, 4d; Ar = 4-MeC_6H_4-, Ar' = 4-BrC_6H_4-
3e, 4e; Ar = Ar' = 4-MeC_6H_4-

Scheme 2

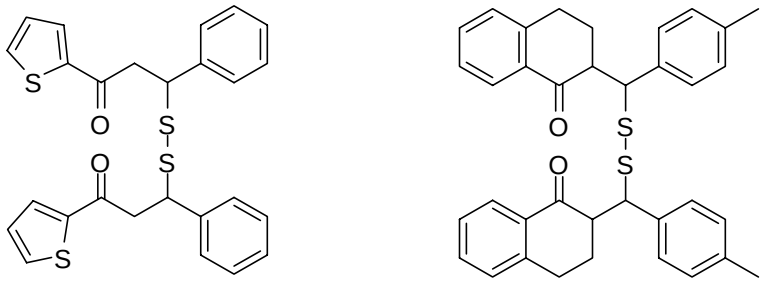


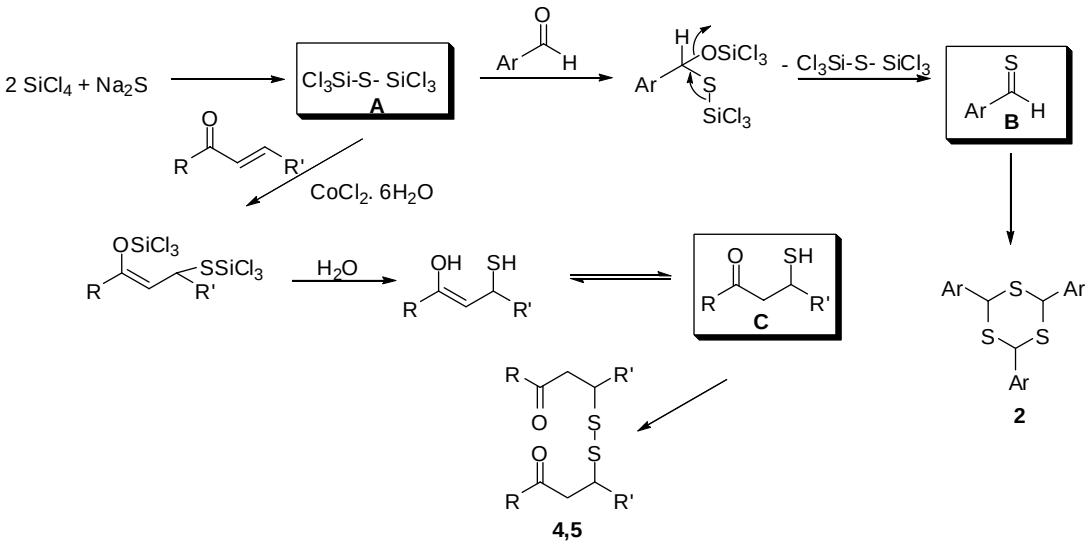
Fig. 1

Table 2. Reaction of α, β-unsaturated ketones with TCS-Na_2S reagent in the presence of $CoCl_2.6H_2O$

Entry	Substrate	Time (h)	Product	Yield (%)
1	Benzalacetophenone	12	**4a**	71
2	4-Bromobenzalacetophenone	14	**4b**	63
3	4-Methylbenzal-acetophenone	12	**4c**	72
4	4-Bromobenzal-4'-methylacetophenone	14	**4d**	66
5	4-Methylbenzal-4`-methylacetophenone	12	**4e**	74
6	2-Benzal-2-acetylthiophene	11	**4f**	61
7	2-(4`-Methylbenzal)-1-tetralone	15	**5**	54
8	Dibenzalacetone	17	**-**	-

The structure of disulphide **4** was supported by analytical and spectral data. First, in the IR spectra of **4**, the absorption at 1670-1680 cm^{-1} attributed for carbonyl stretching of saturated system showed a clear shift than that corresponding to starting α,β-unsaturated ketones. The ^{1}H-NMR spectra of **4f** for example showed two doublets at 3.46 and 3.29 as well as two triplets at 4.42 and 4.16 ppm. These were assigned to the C-2 and C-3 protons respectively.

A plausible mechanism for the present reaction may proceed as depicted in Scheme 3 through 1,2- and 1,4- addition of stoichiometric thiosilane generated in situ from the reaction of TCS and Na_2S in 2:1 molar ratio (proposed hexachlorodisilathiane **A**.; HCDST) to the carbonyl group of the aldehydes as well as to the α,β-unsaturated ketones respectively.



Scheme 3

CONCLUSION

We have developed a new thiosilane reagent generated in situ from the readily available and inexpensive tetrachlorosilane and sodium sulphide which acts as a mild and potent thionating reagent for aromatic aldehydes in acetonitrile at room temperature without catalysis giving the corresponding trithioaldehydes in good yields. Under these mild conditions, α,β-unsaturated ketones react with $SiCl_4$-Na_2S using a catalytic amount of $CoCl_2.6H_2O$ to give the respective β-mercaptoketones which isolated as disulfides via a well known auto-oxidative dimerisation step exploring the synthetic value of tetrachlorosilane in synthetic organic chemistry.

EXPERIMENTAL

Note: Sodium sulphide nonahydrated ($Na_2S.9H_2O$) was dried by refluxing under dry benzene with Dean & Stark for 3 days.

General procedure for thionating of carbonyl compounds:

A mixture of anhydrous Na_2S (10 mmol) and $SiCl_4$ (20 mmol) in MeCN (15 ml) was stirred for 15 min at ambient temperature. To this mixture, a solution of carbonyl compound (5 mmol) in MeCN was added as well as a catalytic amount of $CoCl_2.6H_2O$ (in case of a,β-unsaturated ketones) and the reaction mixture was allowed to be stirred at room temperature. On completion (the reaction was monitored by TLC), the mixture was quenched with cold water, extracted with ethyl acetate (for aldehydes) or with $CHCl_3$ (for a,β-unsaturated ketones), dried over anhydrous $MgSO_4$ and the solvent was vaporized under vacuum and the residue was recrystalized in to give compounds **2** or chromatographed in most cases to give pure **4,5.** All prepared trithioaldehydes **2** are known[5] but most of disulfides **4,5** are unknown[6]. Data for **4f** as representative example are showed below:

Bis- [1-phenyl)-3-oxo-3-thienylpropyl]disulphide 4f. Yield 61%; Purification by column chromatography using pet. ether-ethyl acetate (20:1) as eluent system; mp 97 °C; IR (KBr plate, cm^{-1}) ν 3094, 3027, 2920, 1659 ($COCH_2$), 1599 (C=C), 1515, 1451, 1413, 1357, 1329, 1237, 1063, 856, 753, 726, 699**;** ^{1}H-NMR ($CDCl_3$) δ 7.6-7.54 (m, 2H, Ar-H), 7.27-7.15 (m, 10H, Ar-H), 7.1-7.05 (m, 4H, Ar-H), 4.42 (t, 1H, *J* = 6.6 Hz), 4.16 (t, 1H, *J* = 7 Hz), 3.46 (d, 2H, *J* = 7 Hz), 3.29 (d, 2H, *J* = 7.4 Hz)**;** Anal. Calcd. For $C_{26}H_{22}O_2S_4$ (494.704): C, 63.12; H, 4.48. Found: C, 63.02; H, 4.29

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