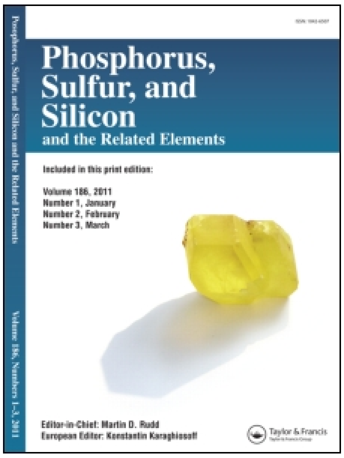

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ELIMINATION OF THIOPHENOL FROM PHENYL ORTHOTHIOESTERS IN THE MASS SPECTROMETER AND NOVEL REARRANGEMENT OF KETENE THIOACETALS UPON ELECTRON IMPACT

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The mass spectra of four selected phenyl orthothioesters (**1–4**) have been measured. The obtained spectra revealed the conversion of the compounds (**1–4**) into ketene thioacetals (**5–8**) via the elimination of thiophenol in the mass spectrometer. The thermal nature of the process was confirmed and the mass spectra of ketene thioacetals (**5–8**) have been discussed. A novel fragmentation path for ketene thioacetals was suggested.

INTRODUCTION

In recent years ketene thioacetals have become of interest to organic chemists for theoretical[1–6] and preparative[7] purposes. Today more than ten different routes give access to a variety of ketene thioacetals under diverse reaction conditions. As a consequence it has been possible to develop and exploit the wide spectrum of chemical transformations which ketene thioacetals undergo. These compounds allow the protection of functionalities in molecules so efficiently that they have become accepted as useful tools in natural product chemistry.

Most chemical transformations achieved on, or with the help of ketene thioacetals are based on the specific properties of the bisulfur substituted double bond. The stabilizing effect of sulfur on neighbouring positive and negative charges makes this double bond reactive to both electrophiles and nucleophiles. For this reason there are no limits in the imaginative use of ketene thioacetals and versatility for organic synthesis purposes.[8–11]

During our investigation on the effect of Lewis acids on thiol esters we obtained phenyl orthothioesters as crystalline solid products. The identities of these solids were confirmed by ^{13}C, ^{1}H, ^{13}C coupled with ^{1}H NMR. Here we present our results about the production of ketene thioacetals from phenylorthothioesters in the mass spectrometer, and the rearrangement accompanying the electron impact of these ketene thioacetals.

RESULTS AND DISCUSSION

We synthesized four phenyl orthothioesters $R_1R_2CH(SPh)_3$, namely, 1,1,1-tris(phenylthio)ethane (**1**), 1,1,1-tris(phenylthio)propane (**2**), 1,1,1-tris(phenylthio)-

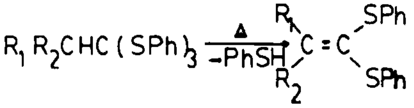
2-methylpropane (**3**), and 1,1,1-tris(phenylthio)-2-phenylethane (**4**). The mass spectra of the compounds (**1–4**) were measured and discussed.

Examination of the mass spectral data of compounds (**1–4**) revealed that contrary to our expectation, we obtained the mass spectra of products resulting from the elimination of thiophenol from phenyl orthothioesters.

Since ^{1}H NMR and ^{13}C NMR spectra of compounds (**1–4**) indicated that they have the right structure, we concluded that such behaviour of phenyl orthothioesters is either thermal elimination prior to electron impact or it is electron impact induced fragmentation.

The thermal nature of the elimination process was secured in two ways, first by performing GC/MS analysis whereby we observed two peaks in the chromatogram corresponding to thiophenol and the elimination products respectively, and second by obtaining the mass spectra of these compounds by direct sample insertion into the ion source. Spectra obtained in this manner were characterized by a low intensity peak corresponding to the molecular ion.

In an attempt to support our suggestion about the thermal elimination of thiophenol from phenyl orthothioesters (**1–4**), each of these compounds was subjected to pyrolysis in a sealed tube at 120°C for one hour. This condition was found to be optimal for the pyrolysis of 1,1,1-tris(phenylthio)methane (**1**), and was used for the rest of this series. It is apparent from the results obtained by GC/MS analysis, that upon pyrolysis, phenyl orthothioesters loose thiophenol and give rise to the corresponding ketene thioacetals (**5–8**) as follows (Scheme 1):



$$R_1R_2CHC(SPh)_3 \xrightarrow[-PhSH]{\Delta} R_1R_2C{=}C(SPh)_2$$

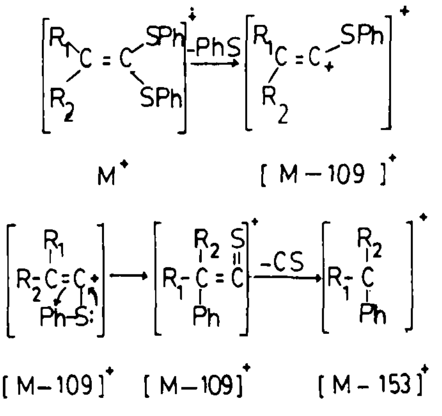
(1-4) (5-8)

	R_1	R_2		R_1	R_2
1,	H	H	**5**,	H	H
2,	CH_3	H	**6**,	CH_3	H
3,	CH_3	CH_3	**7**,	CH_3	CH_3
4,	Ph	H	**8**,	Ph	CH_3

SCHEME 1

Examination of the mass spectra of compounds (**5–8**) revealed that the spectra of these compounds are characterized by a prominent molecular ion $(M)^+$ and a base peak at m/z equal to $[M\text{-}109]^+$. Most remarkable, and perhaps not expected is the peak at m/z of $[M\text{-}153]^+$. The peak at m/z of $[M\text{-}109]^+$ is most probably due to the loss of PhS from the molecular ion. However, the characteristic peak in all the spectra of compounds (**5–8**) at m/z equal to $[M\text{-}153]^+$ showed the occurrence of a $1 \sim 3$ phenyl migration during the fragmentation of the ion $[M\text{-}109]^+$. The following scheme is suggested to account for the formation of the ions $[M\text{-}109]^+$, and $[M\text{-}153]^+$ during the fragmentation of ketene thioacetals

(Scheme 2):



Principal peaks in the mass spectra of ketene thioacetals $R_1R_2C{=}C(SPh)_2$

R_1	R_2	M^+	$[M\text{-}109]^+$	$[M\text{-}153]^+$
H	H	244 (67.46)	135 (100)	91 (64.70)
CH_3	H	258 (70.16)	149 (100)	105 (62.29)
CH_3	CH_3	272 (75.80)	163 (100)	119 (53.13)
Ph	H	320 (84.70)	211 (100)	167 (28.23)

SCHEME 2

CONCLUSION

Phenyl orthothioesters of the formula $R_1R_2CHC(SPh)_3$ are thermally unstable. They eliminate thiophenol during their evaporation in the mass spectrometer and produce the corresponding ketene thioacetals. Upon electron impact ketene thioacetals show a general trend, first they loose PhS to give ion of $[M\text{-}109]^+$. The latter ion undergo 1→3 phenyl migration prior to loss of CS to show a characteristic peak at *m/z* of $[M\text{-}153]^+$.

EXPERIMENTAL

Melting points are uncorrected, NMR spectra were obtained with NT-200 instrument. They were recorded in $CDCl_3$ solutions containing Me_4Si as internal standard and are reported in δ-units. GC/MS analyses were performed on a Finnigan 4023 quadrupole system equipped with Model 4500 source upgrade, using a 50 m DB-1 fused silica WCOT capillary column with a film thickness of 0.25 mμ. Mass spectra were determined on Dupont 21-49 mass spectrometer equipped with data system. All preparations of phenyl orthothioesters and ketene thioacetals were performed in analogy with literature procedures.

1. General Procedure for the Preparation of Phenyl orthothioesters[12]

a. Preparation of Lithiotris(phenylthio)methane. The preparation was carried out in a three-necked flask equipped with a mechanical stirrer, gas inlet, pressure-equalizing dropping funnel, and a drying tube. The apparatus was flame dried and cooled by passing nitrogen through. A solution of 13.6 g (0.04 mol) of phenyl orthothioformate in 100 ml dry THF was introduced into the flask. The contents were cooled to −60°C while stirring in a nitrogen atmosphere and a solution of 0.045 mol of commercial *n*-butyllithium in dry ether was added dropwise. The straw-yellow reaction mixture was stirred for 30 min after addition was completed.

b. Alkylation of the lithiotris(phenylthio)methane. To the above reaction mixture, there was added 0.05 mol of different alkyl halides (CH_3X, CH_3CH_2X, $(CH_3)_2CHX$, and $PhCH_2X$) over a period of 30 minutes. The cooling bath was removed and the temperature was allowed to rise gradually but not to exceed 45°C within 15 minutes. Water (100 ml) was added and the solvent was distilled under reduced pressure. The reaction mixture was extracted with benzene and the benzene solution was dried over anhydrous magnesium sulfate. Concentration of the benzene solution and cooling left a solid crystalline product. Recrystallization from CCl_4:pentane gave the following phenyl orthothioester:

1) 1,1,1-tris(phenylthio)ethane: m.p. 146–148°C (lit.[14] m.p. 146–148°C). ^1H NMR 1.29 (s, 3H), 7.4–7.7 (m, 15 ArH).

2) 1,1,1-tris(phenylthio)propane: m.p. 65–67°C (lit[12] m.p. 65.0–67.5°C) ^1H NMR ($CDCl_3$), δ 1.18 (t, 3H), δ 1.78 (q, 2H), δ 7.4–7.7 (m, 15 Ar · H).

3) 1,1,1-tris(phenylthio)-2-methylpropane: m.p. 119–120°C lit[13] m.p. 119–120.5°C); ^1H NMR ($CDCl_3$), δ 1.21 (d, 6H), δ 1.74 (h, 1H), δ 7.4–7.7 (m, 15 Ar · H)

4) 1,1,1-tris(phenylthio)-2-phenylethane: m.p. 80–82°C, ^1H NMR, δ 1.90 (s, 2H), δ 7.4–7.7 (m, 15 Ar · H). Anal. Calcd. for $C_{26}H_{22}S_3$: C, 72.55; H, 5.11; S, 22.32. Found: C, 72.44; H, 5.02; S, 22.21.

2. Pyrolysis of Phenyl orthothioesters (General Procedure):

A sample of 0.005 mol of phenyl orthothioesters (**1–4**), was placed in a thick-wall glass tube which was flushed with nitrogen and sealed. The tube was heated in an oven at 120°C for one hour, then cooled in dry ice down to −10°C before opening. The crude product was extracted with cold 5% NaOH to remove the produced thiophenol. The residue was passed through a silica gel column and eluted with ether.

The physical data of the ketene bis(phenylthio)acetals (**5–8**) from these pyrolytic experiments are in agreement with the literature[11] values. Most important is that, the mass spectral data of ketene thioacetals (**5–8**) produced either by pyrolysis of (**1–4**) in a sealed tube or in the mass spectrometer are almost identical.

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