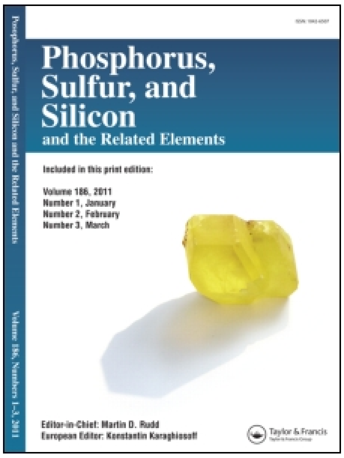

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

NONCONVENTIONAL FRIEDEL-CRAFTS CHEMISTRY II. ON THE CATALYTIC ACTION OF TRIFLIC ACID AND ALUMINIUM CHLORIDE ON SELECTED ARYL THIOESTERS

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To cite this Article El-zohry, M. F. , El-khawaga, A. M. , Ismail, M. T. and Abdel-wahab, A. A.(1991) 'NONCONVENTIONAL FRIEDEL-CRAFTS CHEMISTRY II. ON THE CATALYTIC ACTION OF TRIFLIC ACID AND ALUMINIUM CHLORIDE ON SELECTED ARYL THIOESTERS', Phosphorus, Sulfur, and Silicon and the Related Elements, 61: 3, 373 — 380

To link to this Article: DOI: 10.1080/10426509108036820

URL: http://dx.doi.org/10.1080/10426509108036820

Phosphorus, Sulfur, and Silicon, 1991, Vol. 61, pp. 373–380
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Communication

NONCONVENTIONAL FRIEDEL-CRAFTS CHEMISTRY II. ON THE CATALYTIC ACTION OF TRIFLIC ACID AND ALUMINIUM CHLORIDE ON SELECTED ARYL THIOESTERS†

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(Received February 14, 1991)

The catalytic action of triflic acid and/or aluminium chloride on seven selected aryl thioesters (**1–7**) gave in all cases aryl thiols, diaryl sulfides, diaryl disulfide, and thianthrene derivatives in addition to the corresponding aryl carboxylic acids. Thioester **5** gave thiochromanone derivatives in good yield under the same conditions. Plausible mechanisms were suggested to rationalize the obtained results.

Key words: Aryl thioesters; Friedel-Crafts reactions; triflic acid; aluminium chloride.

INTRODUCTION

Continuation to our previous studies on thermal decomposition,[1] electrochemical oxidation[2] and electrochemical reduction[3] of aryl thioesters in addition to the utilization of Friedel-Crafts reactions in the synthesis of sulfur containing compounds[4–12] and to our interest in Friedel-Crafts and sulfur chemistry,[13–19] the present work deals with the action of triflic acid and/or aluminium chloride on selected aryl thioesters aiming to find analogous reactions of fries rearrangements.[20–23]

RESULTS AND DISCUSSIONS

The seven investigated thioesters were phenyl thiobenzoate (**1**), benzyl thiobenzoate (**2**), phenyl thiophenylacetate (**3**), benzyl thiophenylacetate (**4**), phenyl thiocinnamate (**5**), benzyl thiocinnamate (**6**) and phenyl thioacetate (**7**) were prepared according to the literature procedures[1] and their purity was checked by comparison with the reported melting or boiling points and GC/MS.

Compounts **1–7** were treated with triflic and/or $AlCl_3$ in methylene chloride

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† Accepted and presented at 3rd IBN SINA Symposium on Heterocyclic Chemistry Jan. 28–31, 1991 Aswan, Egypt.

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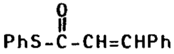
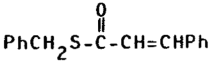
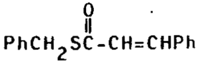
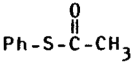
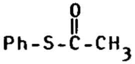
TABLE I

Reactions of aryl thioesters with triflic acid and aluminium chloride catalyst

Entry	Thioester	Reaction Conditions[a]		Observed Products[b] (%)
		Catalyst	Time (hrs)	
1	$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}S{-}Ph}$	CF_3SO_2H	9	Thiophenol(6), diphenylsulfide(8), diphenyldisulfide(4), benzoylthiophenol(6), benzoyldiphenylsulfide(9), thiophenoxybenzoicacid(5), thianthrene(4), thioxanthone(3), benzoic acid(15).
2	$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}S{-}Ph}$	$AlCl_3$	9	Thiophenol(8), diphenylsulfide(17), diphenyldisulfide(9), benzoylthiophenol(3), benzoic acid(20), thianthrene(5), thioxanthone(5).
3	$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}S{-}CH_2Ph}$	CF_3SO_2H	9	Benzylthiol(5), benzoic acid(22), thiobenzoic(4), stilbene(7), dibenzylsulfide(5), 2,3:6,7-dibenzo-1,5-dithiaocane(8), thiobenzyloxybenzylthiol(10).
4	$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}S{-}CH_2Ph}$	$AlCl_3$	24	Benzylthiol(5), benzoic acid(20), dibenzylsulfide(9), dibenzyldisulfide(5), 2,3:6,7-dibenzo-1,5-dithiaocane(10), benzoylbenzylmercaptane(5), 4-methylbenzophenone(8), stilbene(6).

5	$Ph\text{-}CH_2\overset{O}{\overset{\|}{C}}\text{-}S\text{-}Ph$	CF_3SO_2H	9	Thiophenol(5), phenylacetic acid(17), thianthrene(10), benzylthianthrene(8), diphenylsulfide(5), diphenyldisulfide(5), phenylacetylthianthrene(7).
6	$Ph\text{-}CH_2\overset{O}{\overset{\|}{C}}\text{-}S\text{-}Ph$	$AlCl_3$	24	Thiophenol(6), phenylacetic(7), thianthrene(19), benzylthianthrene(8), diphenylsulfide(4), diphenyldisulfide(6), phenylacetylthianthrene(5).
7	$Ph\text{-}CH_2\overset{O}{\overset{\|}{C}}\text{-}SCH_2Ph$	CF_3SO_3H	9	Benzylthiol(7), phenylacetic acid(10), diphenylmethane(3), dibenzylsulfide(7), dibenzyldisulfide(8), benzylmercaptophenylacetic acid(10)[c], 2,3:6,7-dibenzo-1,5-dithiaocane(9).
8	$Ph\text{-}CH_2\overset{O}{\overset{\|}{C}}\text{-}SCH_2Ph$	$AlCl_3$	24	Benzylmercaptane(9), phenylacetic(17), diphenylmethane(3), dibenzylsulfide(7), dibenyldisulfide(5), benzylmercaptophenylacetic acid(3), 2,3:6,7-dibenzo-1,5-dithiaocane(10), dibenzyl(3).
9	$Ph{-}S{-}\overset{O}{\overset{\|}{C}}\text{-}CH{=}CHPh$	CF_3SO_3H	9	Thiophenol(17), cinnamic acid(5), 2-phenylthiochromanone(55), mercaptobenzalacetophenone(4), 2-phenylthiochrom-2-en-4-one(9), diphenylsulfide(5), diphenyldisulfide(2).
10	$Ph{-}S{-}\overset{O}{\overset{\|}{C}}\text{-}CH{=}CHPh$	$AlCl_3$	24	Thiophenol(2), cinnamic acid(5), 2-phenylthiochromanone(13), 2-phenylthiochrom-2-en-4-one(8), thiochrom-2-en-4-one(70).

TABLE I (*Continued*)

11	 $\mathrm{PhS{-}\overset{O}{\overset{\parallel}{C}}{-}CH{=}CHPh}$	$AlCl_3$	72	Thiophenol(3), cinnamic acid(4), thiochom-2-en-4-one(90).
12	 $\mathrm{PhCH_2S{-}\overset{O}{\overset{\parallel}{C}}{-}CH{=}CHPh}$	CF_3SO_3H	9	Benzylthiol(6), 1-indanone(3), cinnamic acid(20), dibenzylsulfide(6), dibenzyldisulfide(5), 2,3:6,7-dibenzo-1,5-dithiaocane(6).
13	 $\mathrm{PhCH_2S\overset{O}{\overset{\parallel}{C}}{-}CH{=}CHPh}$	$AlCl_3$	24	Benzylthiol (15), cinnamic acid (15), dibenzylsulfide (8), dibenzyldisulfide (7), dibenzyl (3), 2,3:6,7-dibenzo-1,5-dithiaocane (7), 1-indanone (3).
14	 $\mathrm{Ph{-}S{-}\overset{O}{\overset{\parallel}{C}}{-}CH_3}$	CF_3SO_3H	9	Thiophenol(12), diphenylsulfide(8), diphenyldisulfide(5), thianthrene(6), 1,1,1-tris(phenylthio)ethane(30).
15	 $\mathrm{Ph{-}S{-}\overset{O}{\overset{\parallel}{C}}{-}CH_3}$	$AlCl_3$	24	Thiophenol(8), diphenylsulfide(8), diphenyldisulfide(8), thianthrene(5), 1,1,1-tris(phenylthio)ethane(20).

a, All experiments has been carried out in CH_2Cl_2 at reflux temperature.

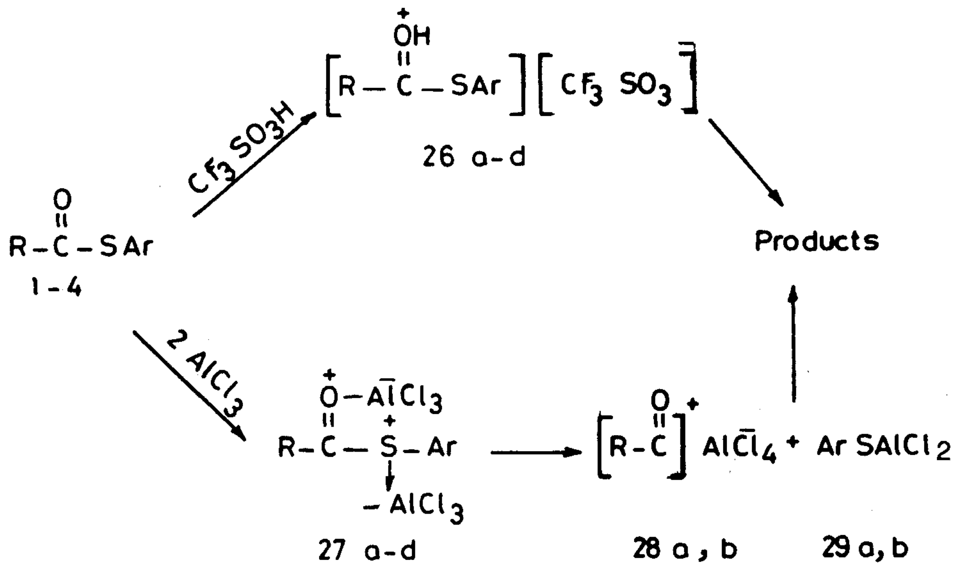
b, Estimates by GC/MS.

c, Two isomers observed.

under different reactions conditions. Examination of the results depicted in Table I revealed that when **1** was subjected to the action of Friedel-Crafts catalysts (e.g. CF_3SO_3H, $AlCl_3$) gave thiophenol (8,6%), diphenylsulfide[18] (9,8%), diphenyldisulfide (10,4%), benzoylthiophenol (11,6%), benzoyldiphenylsulfide (12,9%), thiophenoxybenzoic acid (13,5%), thianthrene (14,4%), thioxanthone (15,3%) and benzoic acid (16,15%). The thioester **2** afforded benzyl thiol (17,5%), benzoic acid (16,22%), thiobenzoic acid (18,4%), stilbene (19,7%), dibenzylsulfide (20,5%), 2,3:6,7-dibenzo-1,5-dithiaocane (21,8%) and thiobenzyloxybenzylthiol (22,10%) upon treatment with triflic acid and/or $AlCl_3$. In a typical run phenyl thiophenylacetate (**3**) (Table I, entries 5 & 6) yielded compounds **8**, **9**, **10**, **14**, benzylthianthrene (23,8%), and phenylacetylthianthrene (24,7%). Also when benzyl thiophenylacetate (**4**) was treated with triflic acid and/or $AlCl_3$ catalyst (Table I, entries 7,8) gave compounds **17**, **20**, **21** and thiobenzyloxy acetic acid (**25**).

The behaviour of thioesters (**1–4**) towards the catalytic action of triflic acid and/or $AlCl_3$ catalyst could be explained as shown in Scheme I.

The formation of thiophenol (**8**), benzylthiol (**17**) may directly from **26a** or **26b** or by the hydrolysis of **29a** or **29b** respectively. The intermediates **29a** and **29b** can be reacted under the reaction conditons to afford **9** and **20** which subsequently gave diphenyldisulfide and dibenzyldisulfide. The formation of thioanthrene (**14**)



	R	Ar
1	Ph	Ph
2	Ph	$PhCH_2$
3	$PhCH_2$	Ph
4	$PhCH_2$	$PhCH_2$

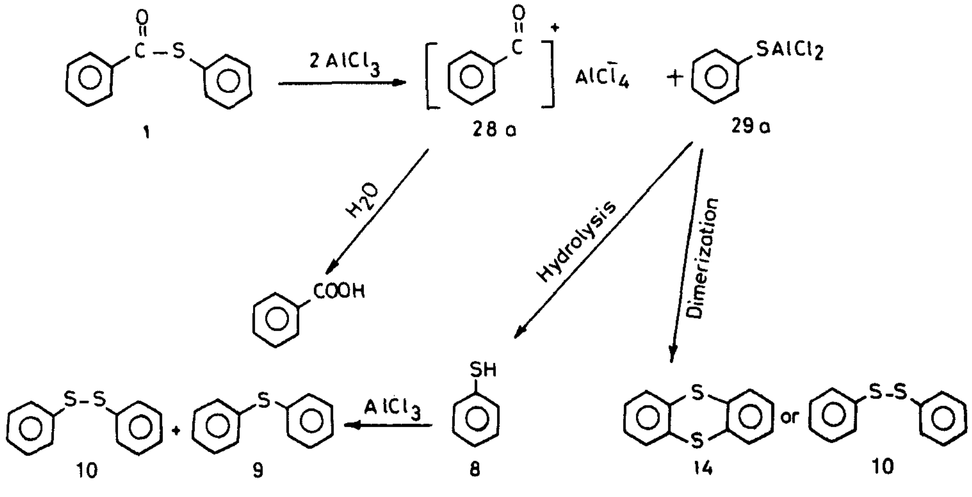
Scheme I

(Table I entries 1 & 2) and 2,3:6,7-dibenzo-1,5-dithiaocane (**21**) (Table I, entries 3 & 4 and 8) may be attributed to the cyclization of **29a,b** under Friedel-Crafts reaction conditions (Scheme II).

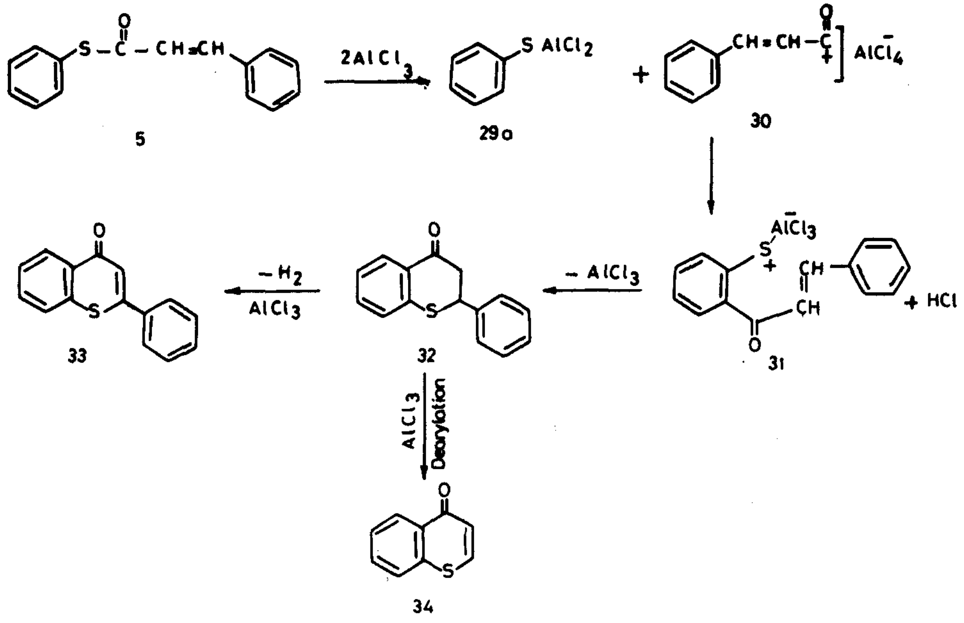
The reaction of **28a** with **8** and **9** yielded compounds **11** and **12** whereas the ortho cyclization of **28a** on the substrate **29a** afforded thioxanthone (**15**). The desulfurization of **20** under the reaction conditions[1] gave dibenzyl which dehydrogenated under the mentioned reaction conditions to afford stilbene (**19**).[19] Treatment of phenylthiocinnamate (**5**) with triflic acid and/or $AlCl_3$ catalyst (Table I, entries 9, 10 and 11) yielded 2-phenylthiochromanone (**32**), 2-phenylthiochrom-2-en-4-one (**33**) and thiochrom-2-en-4-one (**34**) Scheme III.

From Scheme III it is clear that the formed intermediate **29a** was attacked by the most stable cinnamoyl cation to afford **31** which was cyclized to **32** under the mentioned reaction conditions. Compound **32** gave **33** via the dehydrogenation reactions whereas the dephenylation reactions afforded **34**. The catalytic action of triflic acid and/or $AlCl_3$ on benzyl thiocinnamate (**6**) yielded the same products of 2 and 4 whose formed through the reactions of **29b**, in addition to cinnamic acid (Table I, entries 12 and 13). Thioester **7** afforded thiophenol (**8**), diphenylsulfide (**9**), diphenyldisulfide (**10**), thianthrene (**14**) and 1,1,1-tris(phenylthio)ethane (**35**) upon treatment with triflic acid and/or $AlCl_3$ catalyst. The formation of **8**, **9**, **10** and **14** could be explained as mentioned before in the cases of compounds **1–4** whereas the formation of **35** can be attributed to the addition of **29a** to the starting thioester **7** in the presence of acidic catalysts.[16] The identities of the formed products were based namely on GC/MS analysis, ^1H NMR spectroscopy, IR spectroscopy and elemental analysis.

It is clear that the stability of the formed acylonium ion plays an important rule in the way of rearrangement of the thioesters, for example, in the case of thioester **5** the easily formed cinnamoyl cation acylates the ortho position of **29a** to afford **31** which gave **32** under the reaction conditions (Scheme III). Moreover, thioester



Scheme II



Scheme III

6 deviates from this route because of the high reactivity of **29b** which easily dimerized to dibenzylsulfide (**20**) and/or cyclized to **21** prior the acylation with cinnamoyl cation.

EXPERIMENTAL

Melting points are uncorrected. ^1H NMR were measured on 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. Infrared spectra were recorded on a Pye-Unicam SP 200-G spectrophotometer. Elemental analyses were obtained on a Perkin-Elmer 240 microanalyser.

Reaction of Aryl thioesters with Triflic Acid and/or $AlCl_3$ Catalyst

General Procedure. A 100 ml 3-necked flask equipped with thermometer, dropping funnel, reflux condenser capped with calcium chloride tube and magnetic stirrer was charged with 0.022 mole of triflic acid and/or anhydrous $AlCl_3$, 50 ml of dichloromethane as solvent. To this mixture was added dropwise 0.01 mole of the thioester to be investigated (**1–7**). The reaction mixture was stirred for the required time at the reflux temperature, cooled to room temperature and decomposed with cold 10% hydrochloric acid solution. The organic layer was separated, washed with water, dried over anhydrous magnesium sulfate and filtered. The solvent was removed using rotatory evaporator and residue was subjected for analysis. Results are found in Table I.

ACKNOWLEDGEMENT

The authors are grateful for the great help offered by the Department of Chemistry, the University of Texas at Ausin for performing GC/MS analysis, ^1H-NMR and Mass spectroscopic analyses.

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