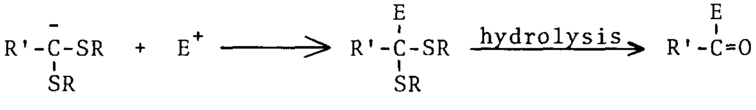
Tetrahedron Letters No. 7, pp 675 - 678, 1978. Pergamon Press. Printed in Great Britain.

SILVER(I) ASSISTED HYDROLYSIS OF PHENYLORTHOTHIOESTERS. A SYNTHESIS OF PHENYLTHIOESTERS.

Robin A.J. Smith* and Gan S. Keng
Chemistry Department, University of Otago,
Dunedin, New Zealand.

(Received in UK 19 December 1977; accepted for publication 29 December 1977)

Carbanions bonded directly to two or three sulphur atoms (**1**; R' = H, alkyl, aryl or SR) have found wide applicability as masked acyl anion equivalents ($R'-\overset{O}{\overset{\|}{C}}{}^{-}$) resulting in the umpolung of the normal reactivity of carbonyl compounds:[1]

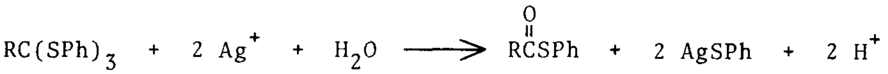


$$R'-\overset{-}{\underset{SR}{C}}-SR \;+\; E^{+} \longrightarrow R'-\overset{E}{\underset{SR}{C}}-SR \xrightarrow{\text{hydrolysis}} R'-\overset{E}{C}=O$$

(**1**) (**2**) (**3**)

Inherent in this type of synthetic methodology is the requirement to hydrolyse a thioacetal or related group to a carbonyl system. Many methods for effecting the hydrolysis reaction have been reported (cf. ref. 1) but this step can still present a major difficulty in using sulphur-stabilized carbanions as efficient synthetic reagents. We report a convenient and odourless hydrolysis procedure for phenylorthothioesters (**2**; R = Ph, E = SPh) which extends the previously reported[2,3] synthetic utility of the tris(phenylthio)methyl anion (**1**; R = Ph, R' = SPh) and provides ready access to phenylthioesters which are useful synthetic intermediates.[4]

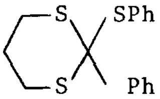
During experiments designed to increase the applicability of the 1,4-addition reactions of **1** (R = Ph, R' = SPh) with α,β-unsaturated ketone systems it was noted[5] that the addition of copper(I) salts did not increase the yield of 1,4-addition product[6] but gave instead a complex mixture resulting from carbon-sulphur bond cleavage processes. Reports[7] have appeared of copper(I) induced carbon-sulphur bond cleavages in phenylthioacetals to give phenylthio-substituted alkenes and ketones. Subsequent experiments showed that silver(I) also induced carbon-sulphur bond cleavage and hydrolysis gave the corresponding thioester[8] in good yield (Table) according to the stoichiometry:



$$RC(SPh)_3 \;+\; 2\,Ag^{+} \;+\; H_2O \longrightarrow R\overset{O}{\overset{\|}{C}}SPh \;+\; 2\,AgSPh \;+\; 2\,H^{+}$$

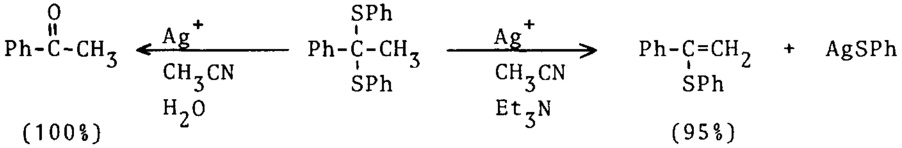
Addition of one mole equivalent of silver(I) salt resulted in 1:1 ($\pm$ 5% by ^{1}H nmr) mixture of orthothioester and thioester, and the formation of silver thiophenoxide[9] (AgSPh) was shown by isolation of the compound from the reaction medium by simple filtration. The solution became acidic during the course of the reaction but, if necessary, the pH change could be attenuated by the addition of a tertiary amine. Competitive elimination to a phenylthioketene acetal was observed in one example (c.f. Table). A mechanism involving Ag^+ induced carbon sulphur bond cleavage as the initial and rate determining step followed by rapid formation of thioester utilizing another equivalent Ag^+ seems appropriate for these reactions.

Silver tetrafluoroborate and silver trifluoromethanesulphonate were found to be satisfactory reagents, being easily handled and giving comparable yields (Table). It is noteworthy that the mixed orthothioester (4) was unreactive under the Ag^+ hydrolysis conditions hence the procedure would appear to be specific for phenyl substituted orthothioesters.[10,11]



(4)

Hydrolysis of bis(phenylthio)acetals (2; R = Ph; R',E = alkyl or aryl) also proceeded in good yield to give the corresponding ketones, while operation under anhydrous conditions in the presence of a tertiary amine gave phenylthioenol ethers[12] in suitable cases:[13]

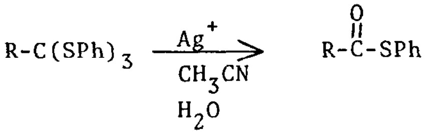


Typical Experiment:

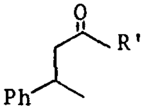
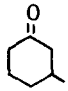
A solution of $AgBF_4$ (0.39 g) in CH_3CN (10 ml) was poured into a stirred solution of phenyl orthothiobenzoate[14] (0.42 g, 1.00 mmole) in CH_3CN (50 ml) and water (5 ml) contained in a 100 ml beaker at room temperature. A transient yellow colour of the solution was followed by rapid precipitation (~30 sec) of AgSPh as a photosensitive white solid.[9] Filtration and dilution of the filtrate with water followed by ether extraction gave pure phenyl thiobenzoate (0.21 g, 0.98 mmole).

Table

Silver(I) Induced Hydrolysis of Phenylorthothioesters



$$\text{R-C(SPh)}_3 \xrightarrow[\substack{CH_3CN \\ H_2O}]{Ag^+} \text{R-}\overset{\overset{O}{\|}}{C}\text{-SPh}$$

R		Method^a	Yield^{8,b} (%)
H-		A	80^c
CH_3-		A	92
C_2H_5-		A	50^d
Ph –		A	98
	R' = CH_3	A	100^e
		B	100^e
	R' = Ph	A	100^e
		B	100^e
		A	100^e
		B	100^e

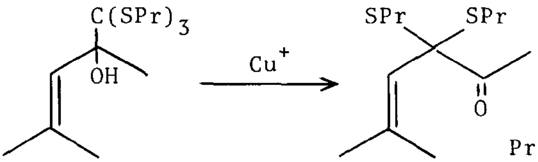
[a] A: $AgBF_4$; B: $AgCF_3SO_3$. [b] Isolated yield. [c] 20% Unreacted orthothioester recovered. [d] Also 50% 1,1-bis(phenylthio)propene .

[e] The crude reaction product was pure thioester from ^{1}H nmr.

References and Notes:

1. For a recent review see: B.T. Grôbel and D. Seebach, Synthesis, 357 (1977).
2. A. Fröling and J.F. Arens, Rec.Trav.Chim.Pays-Bas, 81, 1009 (1962); D. Seebach, Angew.Chem.Int.Ed., 6, 442 (1967).
3. A.R. Manas and R.A.J. Smith, J.C.S.Chem.Comm., 216 (1975).
4. (a) Ketone synthesis with organocuprates: R.J. Anderson, C.A. Henrick and L.D. Rosenblum, J.Amer.Chem.Soc., 96, 3654 (1974); L. Rosenblum, R. Anderson and C. Henrick, Tetrahedron Letters, 419 (1976); (b) α-Enolate anion formation and alkylation: R.A. Gorski, G.T. Walker and J. Wemple, Tetrahedron Letters, 2577 (1976); (c) Aldol condensation of derived enolates: J. Wemple, Tetrahedron Letters, 3255 (1975).
5. A.R. Manas, M. Sc.Thesis, University of Otago (1975).
6. For examples of thiophenoxy substituted cuprates see: T. Mukaiyama, K. Narasaka and M. Furusato, J.Amer.Chem.Soc., 94, 8641 (1972).
7. (a) T. Cohen, G. Herman, J.R. Falck and A.J. Mura, J.Org.Chem., 40, 812 (1975); (b) T. Cohen, D. Kuhn and J.R. Falck, J.Amer.Chem.Soc., 97, 4749 (1975); (c) T. Cohen, A.J. Mura, D.W. Shull, E.R. Fogel, R.J. Ruffner and J.R. Falck, J.Org.Chem., 41, 3218 (1976).
8. All new compounds were characterized by standard spectral and analytical techniques.

9. Silver thiophenoxide was characterized by (a) elemental analysis (Found: C, 33.5; H, 2.3; S, 15.2. C_6H_5SAg requires: C, 33.2; H, 2.3; S, 14.8%). (b) independent synthesis from $AgBF_4$ and thiophenol (1 equivalent) in CH_3CN and (c) reaction with 2,4-dinitrochlorobenzene in pyridine to give 2,4-dinitrodiphenyl sulphide.
10. However, alkylorthothioesters react with $CuCF_3SO_3$ in CH_3CN in a reaction similar to phenylthioacetals:[7b]



[A. Lal, M.Sc. Thesis, University of Otago (1977)]

Pr = C_3H_7

11. Phenylthioesters are reported to be unreactive towards $AgBF_4$ and $AgCF_3SO_3$: S. Masamune, Y. Hayase, W. Schilling, W.K. Chan and G.S. Bates, J.Amer. Chem.Soc., 99, 6756 (1977).
12. For an analogous reaction utilizing $CuCF_3SO_3$ c.f. ref.7a.
13. For other reports of silver salt induced hydrolysis of thioacetals c.f. (a) [$AgNO_3$] C.A.Reece, J.O. Rodin, R.G. Brownlee, W.G. Duncan and R.M. Silverstein, Tetrahedron, 24, 4249 (1968); (b) [Ag_2O] D. Gravel, C. Vaziri and S. Rahal, J.C.S.Chem.Comm., 1323 (1972); (c) [$AgClO_4$] T. Mukaiyama, S. Kobayashi, K. Kamio and H. Takei, Chemistry Letters, 237 (1972).
14. Prepared by reacting **1** (R, R' = Ph) [W.E. Truce and F.E. Roberts, J.Org.Chem., 28, 961 (1963)] with PhSSPh.