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A Novel Transformation of Alcohols to Thiols

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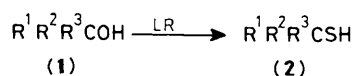
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Treatment of alcohols with 2,4-bis(*p*-methoxyphenyl)-1,3-dithiaphosphetane-2,4-disulphide (Lawesson reagent) gave the corresponding thiols.

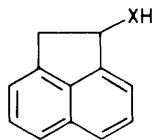
2,4-Bis(*p*-methoxyphenyl)-1,3-dithiaphosphetane-2,4-disulphide (Lawesson reagent: LR) is known to be a superior reagent for conversion of a wide variety of carbonyls to thiocarbonyl compounds.¹ In our exploration of the reactivity of the cyclic-conjugated thioamide systems,² we employed LR for thiation of amides to thioamide compounds. We report now that LR reacts with alcohols to produce the thiols.

Triphenylmethanol (**1a**) was treated with 0.55 mol. equiv. of LR in dimethoxyethane (DME) at room temperature under argon for 15 h to give triphenylmethanethiol (**2a**) in quantita-

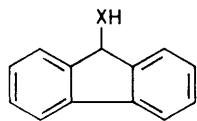
tive yield. At a higher temperature (reflux in toluene), this reaction proceeded more smoothly and was completed in a short period (*ca.* 10 min) (Table 1). Similarly, the alcohols (**1b–c**, **f–g**, **i–n**) were converted to corresponding thiols in moderate to high yields when they were heated with LR under reflux in toluene. However, treatment of tertiary alcohols (**1d,e,h**), which possess an alkyl group at the α -position, with LR gave the corresponding thiols (**2d,e,h**) and dehydration products, alkenes (**3**)–(**7**). At a lower temperature, the thiols were produced predominantly. Treatment of 1,1-diphenylethanol (**1d**) with LR at room temperature yielded 1,1-diphenylethanethiol (**2d**) and 1,1-diphenylethylene (**3**) in 77 and 13% yields, respectively, while at higher temperature (reflux in toluene) (**1d**) yielded (**2d**) and (**3**) in 7 and 91% yields, respectively. The thiol (**2d**) thus obtained was refluxed in toluene in the presence of LR and gave the dehydration



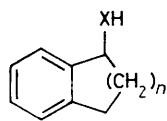
R^1	R^2	R^3	R^1	R^2	R^3
a ; Ph	Ph	Ph	f ; Ph	Me	H
b ; Ph	Ph	H	g ; Ph	Et	H
c ; Ph	H	H	h ; PhCH ₂	Me	Me
d ; Ph	Ph	Me	i ; PhCH=CH	H	H
e ; Ph	Me	Me			



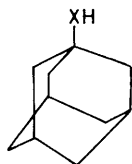
(**1j**); X = O
(**2j**); X = S



(**1k**); X = O
(**2k**); X = S



(**1l**); $n = 1$, X = O
(**2l**); $n = 1$, X = S
(**1m**); $n = 2$, X = O
(**2m**); $n = 2$, X = S

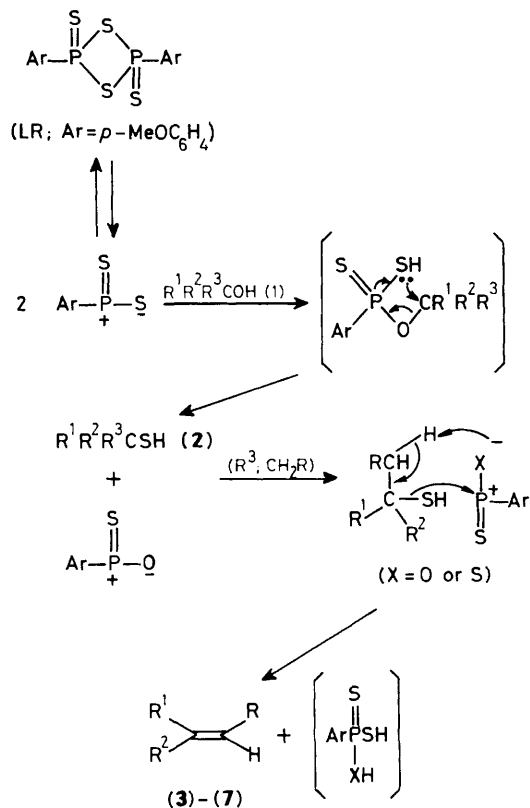


(**1n**); X = O
(**2n**); X = S

Table 1. Yield of the thiols (**2**).

	Solvent	Time/ h	% Yield ^a	
			(2)	Other products
(1a)	DME ^{b,c}	15	100	
	Toluene ^d	0.2	100	
(1b)	Toluene ^d	0.5	94	
(1c)	Toluene ^d	48	55	
(1d)	DME ^c	3	77	Ph ₂ C=CH ₂ (3) 13
	Toluene ^d	0.5	7	(3) 91
(1e)	Toluene ^d	3	39	PhC(Me)=CH ₂ (4) tr.
(1f)	Toluene ^d	0.5	25	
(1g)	Toluene ^d	6	45	
(1h)	DME ^c	15	— ^c	
	Toluene ^d	0.5	9	PhCH=CMe ₂ (5) 17 PhCH ₂ C(Me)=CH ₂ (6) 11
(1i)	Toluene ^d	2	73	
(1j)	Toluene ^d	0.5	72	Acenaphthylene (7) 13
(1k)	Toluene ^d	0.5	18	
(1l)	Toluene ^d	0.5	67	
(1m)	Toluene ^d	0.5	65	
(1n)	Toluene ^d	3	23	

^a Isolated yield. ^b Dimethoxyethane. ^c Room temperature. ^d Reflux temperature. ^e No reaction.



Scheme 1

product, 1,1-diphenylethylene (3), in 86% yield. On the other hand, (3) was not formed when (2d) was refluxed in toluene in the absence of LR under the same conditions. Allylic alcohol

(1i) also gave the corresponding thiol (2i) by treatment of (1i) with LR. As shown in Scheme 1, a possible mechanism for the formation of the thiols (2) and dehydration products (3)—(7) may be envisaged involving a thiophosphoric acid intermediate.³ The nucleophilic reaction of the alcohol (1) to a dipolar species of LR, which may be present in solution,⁴ gives a thiophosphoric acid intermediate in the first step. Subsequent P-SH addition to the O-CR₃ carbon atom, followed by O-CR₃ bond cleavage gives the final product, thiol (2). Elimination of hydrogen sulphide from the thiols (2) by the mixed O,S-phosphine ylide (X = O) thus formed or thiophosphine ylide (X = S), then affords the dehydration products (3)—(7). The former ylide might be more appropriate for the elimination reaction since only half an equivalent of LR was used in these reactions. The reaction described here thus provides a facile method for the synthesis of thiols⁵ from alcohols.

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