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A Novel Transformation of Alcohols to Thiols

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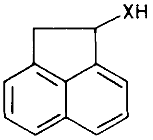
Treatment of alcohols with 2,4-bis(*p*-methoxyphenyl)-1,3-dithiaphosphetane-2,4-disulphide (Lawesson reagent) gave the corresponding thiols.

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.

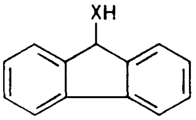
Triphenylmethanol (**1a**) was treated with 0.55 mol. equiv. of LR in dimethoxyethane (DME) at room temperature under argon for 15 h to give triphenylmethanethiol (**2a**) in quantitative yield. At a higher temperature (reflux in toluene), this reaction proceeded more smoothly and was completed in a 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

$$\underset{(\mathbf{1})}{R^1R^2R^3COH} \xrightarrow{LR} \underset{(\mathbf{2})}{R^1R^2R^3CSH}$$

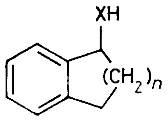
	R^1	R^2	R^3		R^1	R^2	R^3
a;	Ph	Ph	Ph	**f**;	Ph	Me	H
b;	Ph	Ph	H	**g**;	Ph	Et	H
c;	Ph	H	H	**h**;	$PhCH_2$	Me	Me
d;	Ph	Ph	Me	**i**;	PhCH=CH	H	H
e;	Ph	Me	Me				



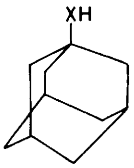
(**1j**); X = O
(**2j**); X = S



(**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

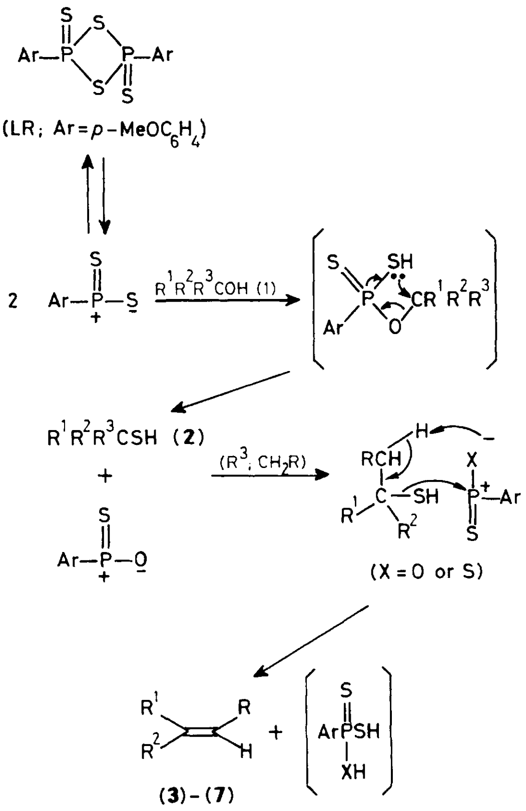


(**1n**); X = O
(**2n**); X = S

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	$Ph_2C=CH_2$ (**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	—[e]	
	Toluene[d]	0.5	9	PhCH=CMe_2 (**5**) 17 $PhCH_2C(Me)=CH_2$ (**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–CR_3 carbon atom, followed by O–CR_3 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 thiols[5] from alcohols.

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