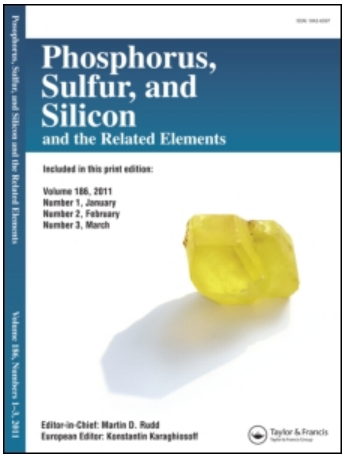

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2, 4-bis(4-methoxyphenyl)-1, 3, 2, 4-dithiadiphosphetane 2, 4-disulfide, lr, as a new activation reagent in preparation of peptides, amides and esters

U. Pedersen[a]; B. Yde[a]; T. Andersen[a]; M. Thorsen[a]; K. Clausen[a]; S. -O. Lawesson[a]
[a] Department of Organic Chemistry, Chemical Institute, University of Aarhus, Aarhus C, Denmark

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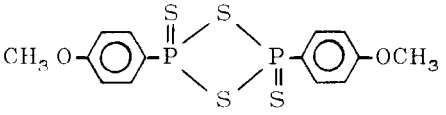
2,4-BIS(4-METHOXYPHENYL)-1,3,2,4-DITHIADIPHOSPHETANE 2,4-DISULFIDE, LR, AS A NEW ACTIVATION REAGENT IN PREPARATION OF PEPTIDES, AMIDES AND ESTERS

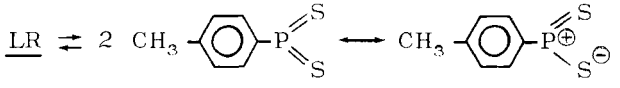
U.PEDERSEN, B.YDE, T.ANDERSEN, M.THORSEN, K. CLAUSEN, and S.-O.LAWESSON
Department of Organic Chemistry, Chemical Institute, University of Aarhus, DK-8000 Aarhus C, Denmark

2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, LR, is easily prepared by refluxing P_4S_{10} in anisole for two hours produces the title compound in high yield.



(LR)

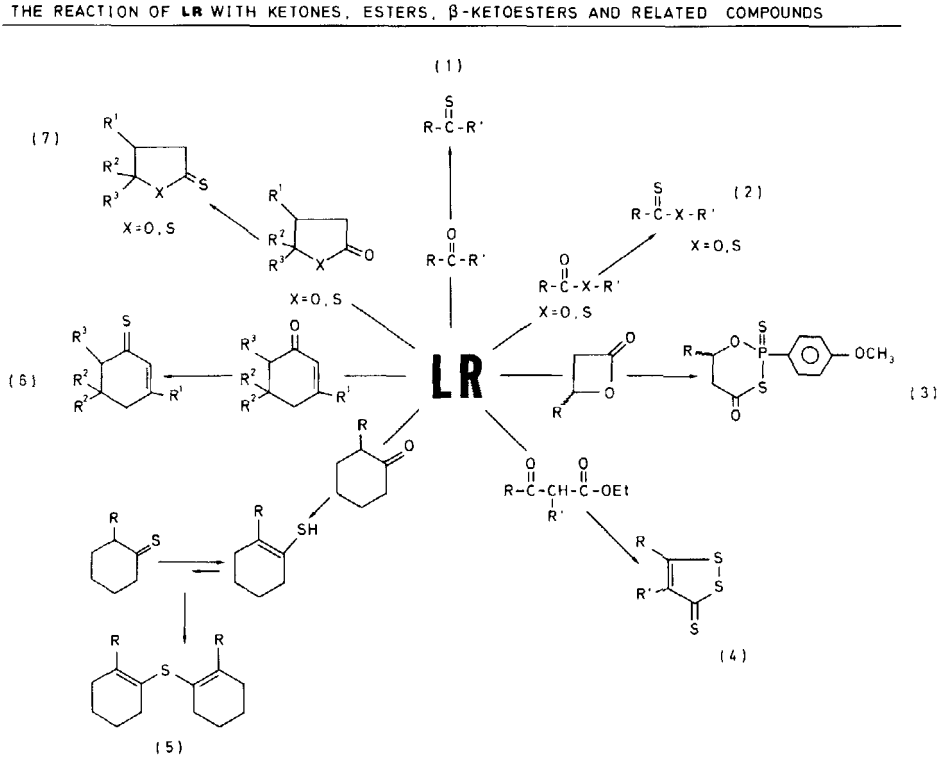
In the solid state LR exists in the E-form but in solution it is also assumed to exist in monomeric forms.



LR has mainly been investigated as thiation reagent and it has been shown that LR smoothly transforms ketones into thioketones, esters into O-substituted thioesters, S-substituted thioesters into dithioesters, lactones into thiolactones, thiolactones into dithiolactones, amides into thioamides, lactams into thiolactams, and fully protected dipeptides into fully protected thiodipeptides.

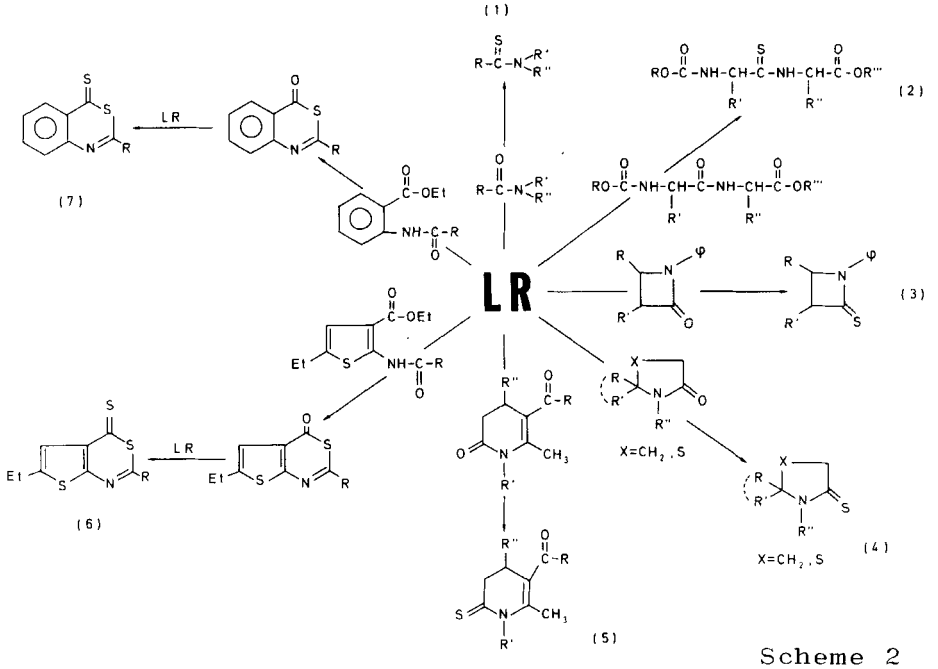
Nucleophiles have been reacted with LR and different types of P-heterocycles are formed. Carboxylates produce the salt of a mixed anhydride ((1) in Scheme 3) which has been S-methylated and reacted with alcoholates and amines under formation of the corresponding esters and amides in high yields (Scheme 4).

The mixed anhydride has been used as coupling reagent in preparation of peptides (Scheme 5).

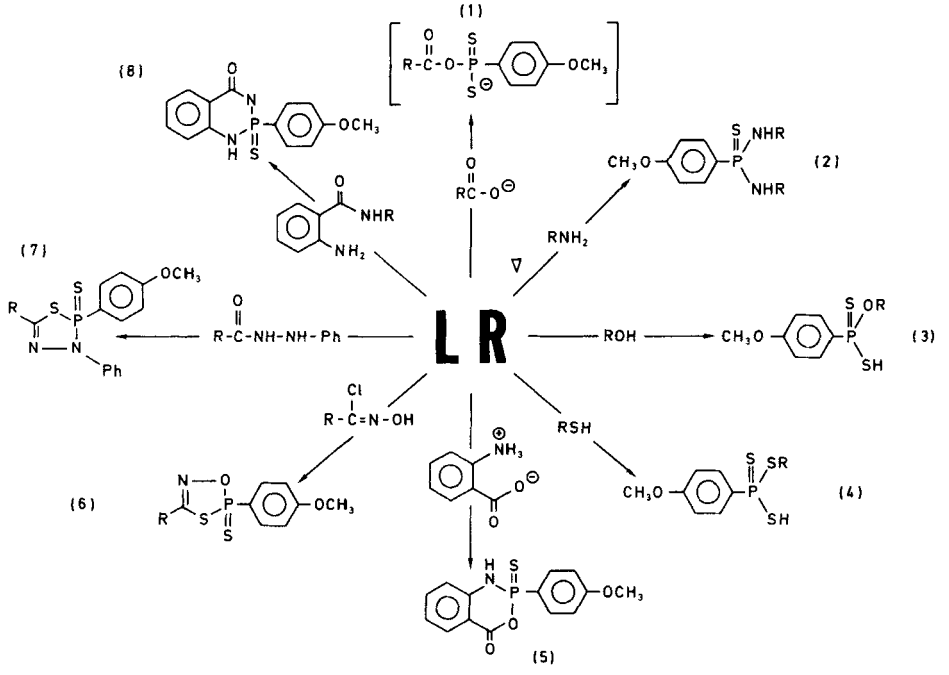


Scheme 1

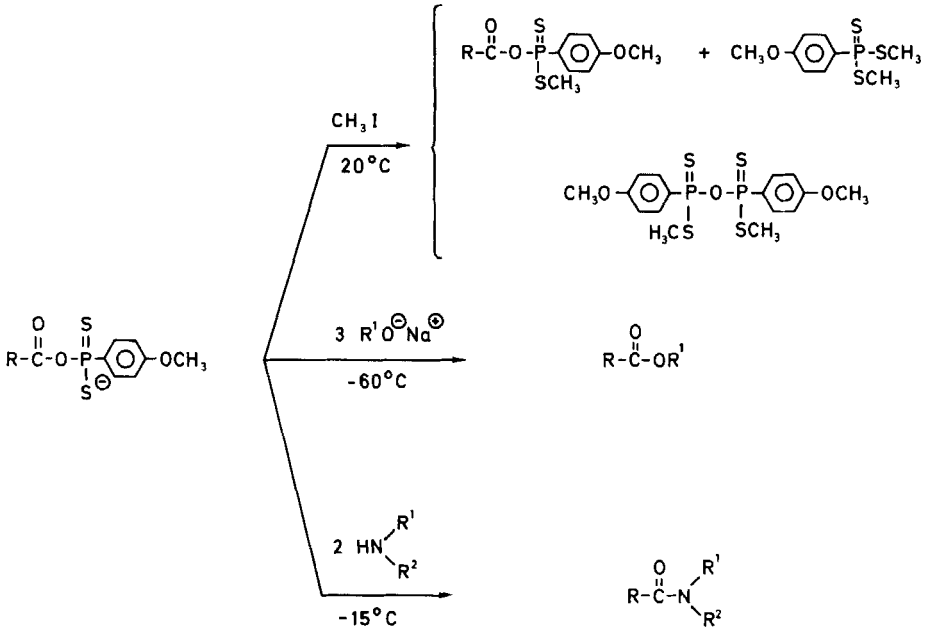
THE REACTION OF LR WITH AMIDES AND RELATED COMPOUNDS



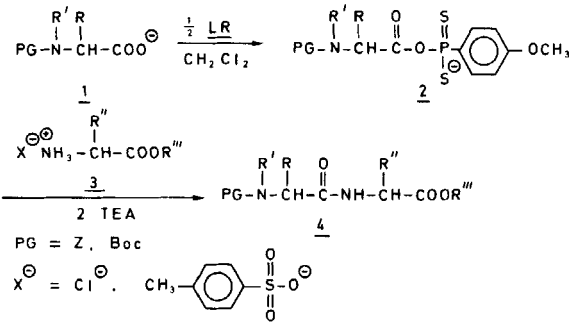
Scheme 2



Scheme 3



Scheme 4



Starting materials		Reaction time/hr	Yields (%)	Mp (°C)	$[\alpha]_D$
Boc-Gly-OH	HCl·H-Gly-OBzl	4	93	84(84-5)	
Boc-S-Ser(Bzl)-OH	HCl·H-Gly-OBzl	4	83	52(52-4)	-7.1(-7.1)
Boc-S-Tyr(Bel)-OH	TosOH·H-Gly-OBzl	4	83	103-4(103-5)	-3.4(-3.4)
Z-S-Arg(Z$_2$)-OH	HCl·H-Gly-OBzl	16	47	136-8(136-7)	+16.3(+16.6)
Z-S-Pro-OH	HCl·H-S-Phe-OtBu	16	92	72-3(74-5)	-27.5(-27.4)
Z-S-Pro-OH	HCl·H-Gly-OEt	16	95	oil	-60.4

Scheme 5