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Use of Lawesson's Reagent in Organic Syntheses

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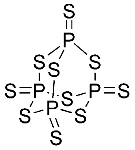
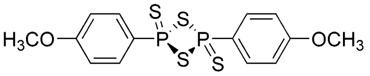
1. Introduction

Transformation of a carbonyl functional group into thiocarbonyl has been an important interest to synthetic organic chemists for many years. Two reagents, phosphorus pentasulfide (P_4S_{10}) **1** and Lawesson's reagent (LR) **2** are the most widely used agents for such a transformation as well as for the synthesis of wide range of heterocyclic compounds having sulfur atoms. On the other hand, LR has been the most widely used reagent since the beginning of the last quarter of the 20th Century, and due to its important applications in synthetic organic chemistry, it has regularly been reviewed.[1−6]

From the second half of the 19th Century until the initiation of systematic study of the use of LR in 1978 by Lawesson and co-workers,[7−10] P_4S_{10} remained the main reagent for such a transformation.[11−13] Although various reagents including the analogues of LR and hydrogen sulfide have been used, in general with limited success, LR has remained the most important reagent in thionation chemistry, and was followed by P_4S_{10}. Generally it is claimed that LR has advantages over P_4S_{10} in terms of requirements for excess P_4S_{10} and longer reaction time. It could even be true when the number of publications appeared each year that both reagents are considered. On the other hand, depending on our experience of many years on both reagents, it is also correct to say that each reagent can have its own advantages and disadvantages over particular reactions, that is both reagents deserve to be tried.

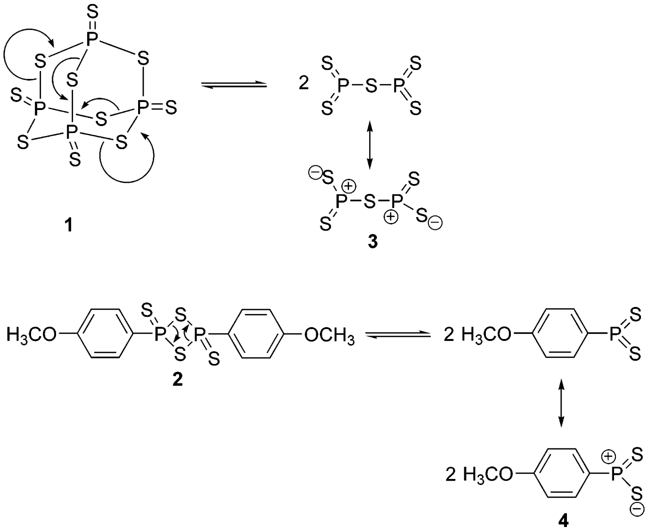

1



2

The usual method of thionation is performed in refluxing benzene, toluene, or xylene, in which the possible mechanisms of both reagents were suggested to involve dissociation equilibriums, which yield **3** and **4** (Scheme 1).[2,14,15] These decomposition products can then react with carbonyl functional groups to form four-membered rings **5**, which decompose to the corresponding thioketones **7** (Scheme 2). Initially, Lawesson and co-workers and then some other research

Scheme 1. Dissociation Mechanisms of P_4S_{10} and LR



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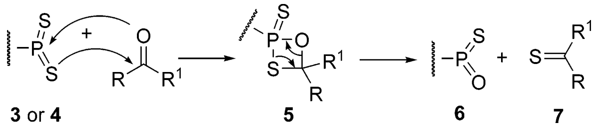
Turan Ozturk was born in Kizilcaoren in Divrigi, Turkey. He received his Ph.D. degree from the University of East Anglia, England, on the synthesis of amphimedine alkaloid. He was then moved to the University of Kent at Canterbury, England, as a postdoctoral fellow, where he worked on the synthesis of new BEDT-TTF type organic superconductors and developed a new method for the synthesis of fused 1,4-dithiin and thiophene rings from 1,8-diketones using Lawesson's reagent and P_4S_{10}. He took up a position at Tubitak MRC, Turkey, then Middle East Technical University, Turkey, and joined Istanbul Technical University as a full professor. He has previously been British Council Research Fellow, NATO Research Fellow and Honorary Lecturer at the University of Kent at Canterbury and Senior Research Fellow at University of Waterloo, Canada. His research interests concentrate on the development of new organic materials having electronic and optical properties, as well as development of new organic reactions, particularly the new reactions of Lawesson's reagent and P_4S_{10}.

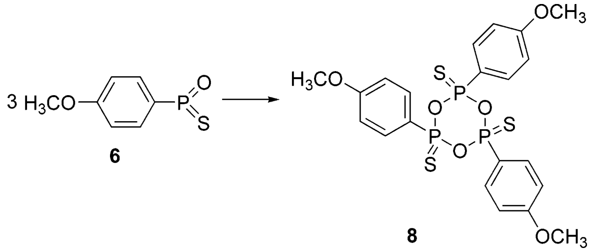
Erdal Ertas was born in Erzincan, Turkey. He graduated from the University of Trakya in 1997 and completed his M.Sc. and Ph.D. studies in the University of Marmara under the direction of Prof. Turan Ozturk in 2002 and 2005, respectively. His research focused on the development of new methodologies on the synthesis of new bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) and dithienothiophene (DTT) derivatives. He has been working at Tubitak Marmara Research Centre as a researcher since 1997. His current research interests include the synthesis of new potential organic superconductors and conductors based on tetrathiafulvalene (TTF) and dithienothiophene (DTT) as well as development of new analysis and formulation methods for food chemistry such as toxics, additives, and aroma formulation.

Olcay Mert was born in Saray, Tekirdag, Turkey. He graduated from Kocaeli University in 2002. He is currently a Ph.D. student in the Polymer Science and Technology Program under the direction of Professor Turan Ozturk and Professor Ayhan S. Demir at Middle East Technical University. His Ph.D. research involves the synthesis of dithienothiophene (DTT) and ethenedithiothiophene (EDTT) type compounds and their electrochemical polymerizations. His other research area includes controlled release of anticancer drugs in biodegradable polymers.

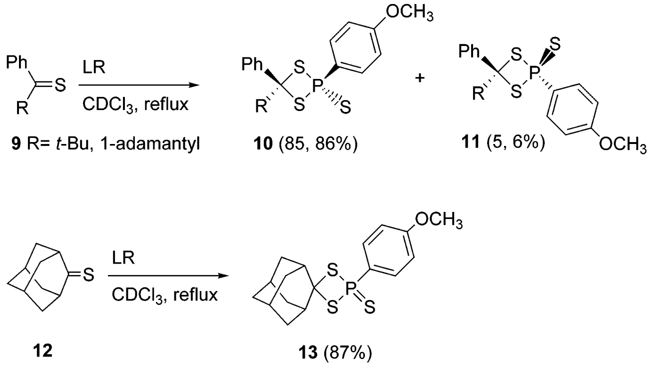
Scheme 2. Thionation Mechanism of 3 and 4



Scheme 3. Formation of the Side Product 8



Scheme 4. Synthesis of 1,3,2-Dithiaphosphetane 2-Sulfides



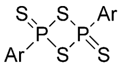
groups, including us, isolated the trimer *p*-methoxyphenylmetathiophosphonate **8** of LR, which is a side product of **6** (Scheme 3).[7,16] It could be evidence for such a mechanism. Obviously, the P−O bond is much stronger than the P−S bond, which results in the thermodynamically more stable product **6**. This could be concluded as one of the important driving forces behind the mechanisms of both reagents.[2,6]

Recently, during an in-depth study of the mechanism of LR, the analogues, 1,3,2-dithiaphosphetane 2-sulfides **10**, **11**, and **13**, of the intermediate 1,3,2-oxathiaphosphetane **5** (Scheme 2) were isolated as a result of the reaction of the ketones **9** and **12** with LR in refluxing $CDCl_3$ (Scheme 4). This is an important indication that the thionation reaction of LR goes through such a Witting-type intermediate.[17]

In this review, considering the more widespread use of LR in organic syntheses, LR has been reviewed in depth starting from 1985 as some reviews appeared in that year.

2. Lawesson's Reagent (LR)

First synthesis of LR **2** appeared in 1956 along with a number of aryl thionophosphinesulfides **14** which were the products of the reactions between P_4S_{10} and some aromatic groups.[14,18]



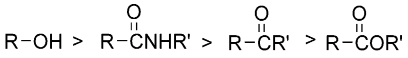
14

Ar= Ph, 4-EtOC$_6$H$_4$, 3,4-diMeC$_6$H$_3$,
1-napthyl, 2-*i*-Pr-napthyl

In the following decade, the chemistry of these compounds did not receive much attention. In 1967, a report appeared that LR could convert benzophenone to thiobenzophenone in acetonitrile.[19] However, it remained unexplored for a further 10 years. In 1978, Lawesson and co-workers systematically studied the use of **2** (now commonly called Lawesson's reagent) in organic syntheses, particularly for the conversion of carbonyl groups to thiocarbonyls.[7−10]

LR is now commercially available and widely used in organic synthesis. It can easily be synthesized with the reaction of anisole and P_4S_{10} (150 °C, 6 h, ~70%).[2,3,8] Also, the reaction of anisole with elemental sulfur and red phosphorus (150−155 °C, 6 h, 76%) produces LR.[20] It was indicated that LR is not stable in solution at temperatures over 110 °C, and it decomposes or polymerizes slowly.[14,15] Single-crystal structures, obtained from 1,2-dichloroethane and toluene, were disclosed to be monoclinic $P12_1/c1$ and $P\bar{1}$,[21,22] respectively, along with its solid-state NMR studies.[22]

Nishio et al. reported the reactivity order of LR toward hydroxyl and carboxyl groups.[23] The authors indicated that hydroxyl groups are the most and esters are the least reactive functional groups among hydroxyl, amide, ketone, and esters. Amides come second and the ketones third. Their order is as follows:

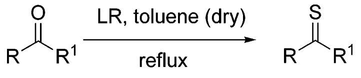


$$R{-}OH > R{-}\overset{O}{\overset{\|}{C}}NHR' > R{-}\overset{O}{\overset{\|}{C}}R' > R{-}\overset{O}{\overset{\|}{C}}OR'$$

2.1. Ketones

LR **2** effectively converts the oxo groups of ketones **15** to thiones **16** even in the presence of various functional groups such as aromatic and heterocyclic rings, halogen, nitro, nitrile, alkyl, alkylamine, and ester functional groups (Scheme 5 and Table 1).

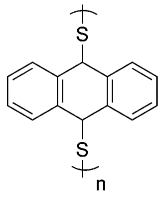
Scheme 5. General Reaction of LR with Ketones



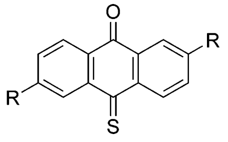
15 **16**

Although toluene (dry) is the most widely used solvent, there are examples where other solvents such as benzene, pyridine, THF, dimethoxyethane, CH_2Cl_2, and CS_2 are used. The reaction is generally conducted at the refluxing temperature of the solvents under inert atmosphere. On the other hand, there are examples where the reaction was performed at room temperature, open to atmosphere, (Table 1, entries 8, 9, 12, 22, 25).

The use of LR to convert ketone functional groups to thione sometimes results in unexpected products. Attempts to convert anthraquinone to dithioanthraquinone yielded the polymeric material **17**,[50] which demonstrated that, in contrast to its monothioquinone analogue **18**,[51] dithioquinone is too reactive and polymerizes to the polydisulfide. On the other hand, it was reported by a separate group that 9,10-anthraquinone **19** was transformed to 9,10-dithioanthraquinone **20** by reacting with LR in refluxing toluene, although it gave low yield, 13%, along with **21** (Scheme 6).[52]



17



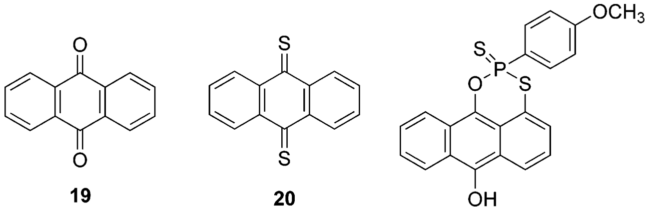
18 R= H, MeO

The same group reported that the reaction of 1,8-dihydroxyanthraquinone **22** with LR in refluxing toluene produced the dimer **23** in 30% yield, probably through an initial thionation reaction (Scheme 7).[53]

The reaction of 9-benzanthrone oxime **24** with LR in refluxing benzene yielded 9-benzanthronethione **25** in 36% yield, along with polymeric materials (Scheme 8).[54]

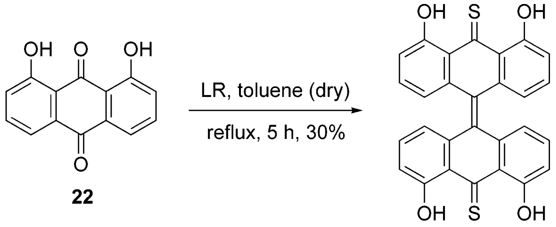
Treatment of indanone **26** with LR in refluxing toluene gave **27** in 95% yield, the structure of which was determined after a single-crystal X-ray analysis (Scheme 9).[55]

Scheme 6. Synthesis of 9,10-Dithioanthraquinone



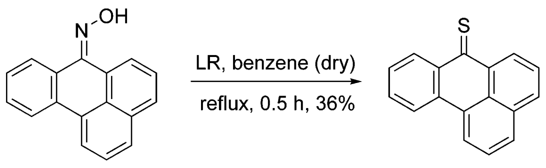
19 **20** **21**

Scheme 7. Formation of the Dimer of 1,8-Hydroxyanthraquinone



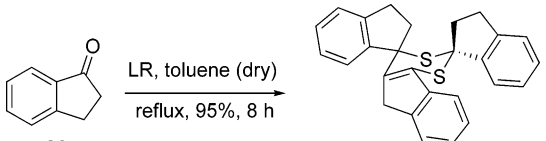
22 **23**

Scheme 8. Thionation of 9-Benzanthone Oxime



24 **25**

Scheme 9. Dimerization of Indanone 26



26 **27**

Table 1. Products of the Corresponding Ketones with LR

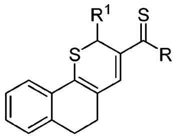
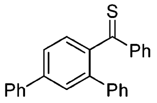
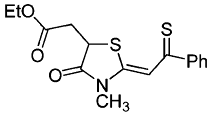
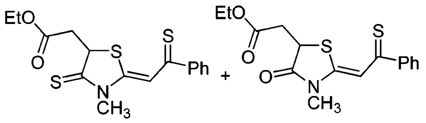
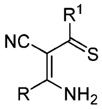
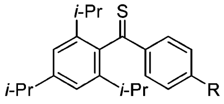
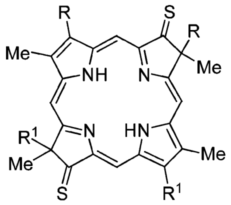
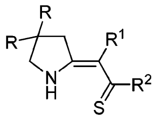
Entry	Product	Conditions	Yield (%)	ref
1	 R= Ph, 4-ClC$_6$H$_4$, 4-MeOC$_6$H$_4$, 2-Thienyl, 2-furyl R^1= Ph, Me, H	CS$_2$, Δ, N$_2$, ~ 5 h	48-88	24, 25
2		CS$_2$, Δ, N$_2$, ~ 5 h	60	24
3		toluene, Δ, 10 min	64	26
4	 A B	toluene, Δ, 2 h	A= 48, B= 52	26
5	 R= Me, Ph, 4-MeOC$_6$H$_4$ R^1= Me, 4-MeOC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$, 2-furyl, 2-thienyl, (CH=CH)$_2$-Ph, C≡C-C$_6$H$_4$	benzene, Δ, N$_2$	45-78	27
6	 R= H, OMe	-	~65	28
7	 R= Et, CH$_2$CH$_2$CO$_2$Me R^1= CH$_2$CH$_2$CO$_2$Me	toluene, N$_2$, 1 h	65-70	29
8	 R= H, Me, R^1= H, Ph, 4-ClC$_6$H$_4$, 4-FC$_6$H$_4$ R^2= *t*-C$_4$H$_9$, *i*-C$_3$H$_7$, PhCH$_2$, 4-ClC$_6$H$_4$, 3-Py, 4-Py	dimethoxyethane, rt, 1.5 h	70-90	30

Table 1 (Continued)

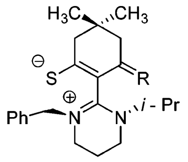
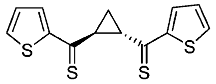
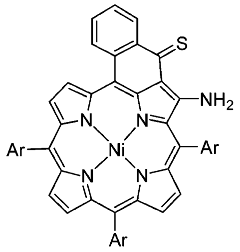
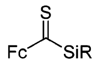
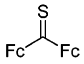
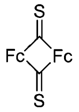
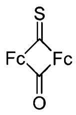
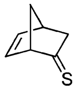
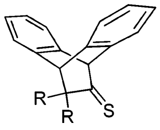
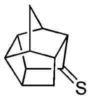
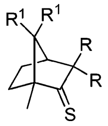
Entry	Product	Conditions	Yield (%)	ref
9	 R= O, S	toluene, rt, 21 h	R = O, 18 R = S, 78	31
10		toluene, reflux, 1 h	-	32
11		benzene, reflux, 2 h	97	33
12	 Fc= Ferrocenyl R= Me_3, Me_2Ph, Ph_3	THF, rt, 5-30 min	60-80	34
13		benzene, reflux, 3 h, N_2	71	35
14	 + 	toluene, reflux, 2 h, N_2	13-46	35
15		toluene, reflux, 2 h	25	36
16	 R = H, Me	toluene, reflux, 5 h	R = H, 20 R = Me, 16	36
17		THF	85	37
18	 R= Me, R^1= H R= H, R^1= Me R= R= - $(CH_2)_4$ - , R^1= Me R= R= - $CH_2(o\text{-}C_6H_4)CH_2$ -, R^1= Me	toluene, reflux xylene	82-98, quantitative	38, 39

Table 1 (Continued)

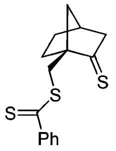
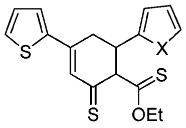
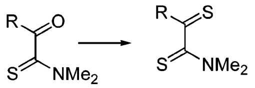
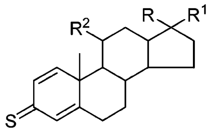
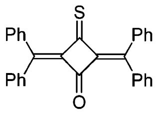
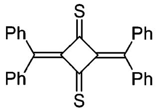
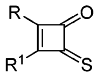
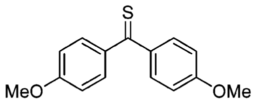
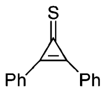
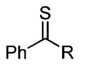
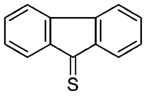
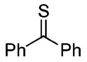
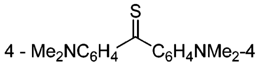
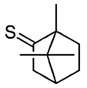
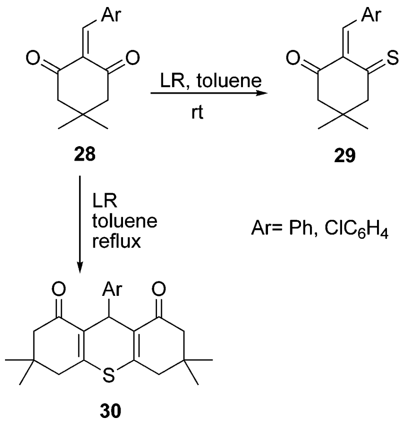
Entry	Product	Conditions	Yield (%)	ref
19		toluene, reflux, N_2, 2.5 h	84	40
20	 X= S, O	benzene, reflux, 4 h	S: 40 , O: 40	41
21	 R= *t*-Bu, Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$NO_2C_6H_4$, 2-thienyl	toluene / DME, reflux, 2 -16 h	63-87	42
22	 R= O, = $CHCO_2Et$, $CH(Me)CH_2OAc$, $CH(Me)CO_2Me$, OAc, C≡CH R^1= H, OAc, OH R^2= H, OCH_2OMe	THF, rt, 1 h	32-96	43
23		toluene, reflux, 1 h	58	44
24		toluene, reflux, 3-4 h	37	44
25	 R= O - *i*-Pr, NEt_2, NBr_2, $N(CH_2)O$ R^1= Ph, Bu, 4-MeC_6H_4, 4-$Me_2NC_6H_4$, Ph, OEt	CH_2Cl_2, rt, overnight	33-76	45
26		toluene, reflux, 1 h	quant.	46
27		toluene, reflux, 3 min	74	47
28	 R= Ph, 4-BrC_6H_4	mw, 3 min	97	48
29		mw, 3 min	86	48

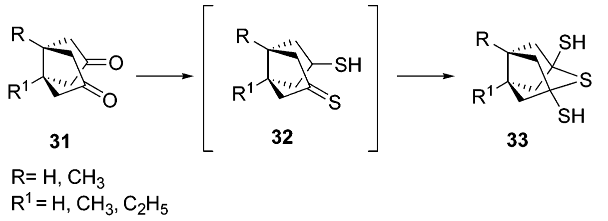
Table 1 (Continued)

Entry	Product	Conditions	Yield (%)	ref
30		toluene, reflux, 15 min	94 (HPLC)	49
31		xylene, 110 °C, 1.5 h	96 (HPLC)	49
32		toluene, reflux, 7 h	95 (HPLC)	49

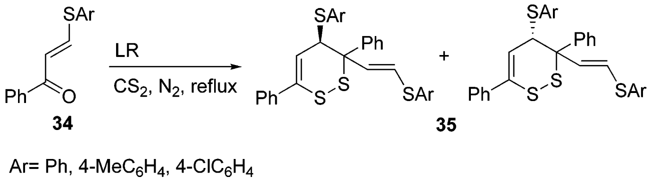
Scheme 10. Reaction of 1,3-Cyclohexadione 28 with LR



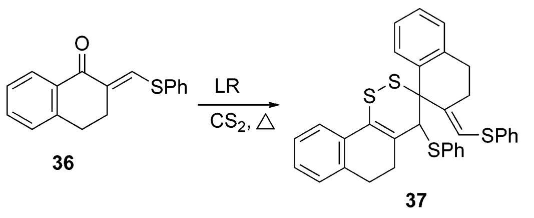
Scheme 11. Reaction of Bicyclodione 31 with LR



Scheme 12. Reaction of α,*β*-Unsaturated Ketone 34 with LR



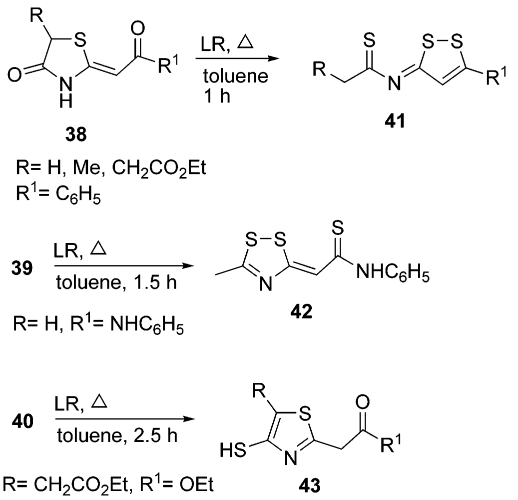
Scheme 13. Dimerization of α,*β*-Unsaturated Ketone 36



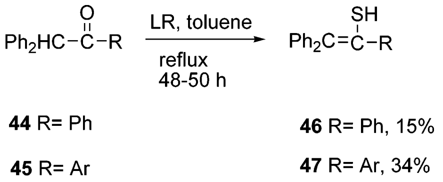
When 1,3-cyclohexadione **28** was treated with LR at room temperature in toluene, its thione derivative **29** was obtained (Scheme 10).[56,57] On the other hand, when the same reaction was performed in refluxing toluene, a dimerized product **30** was reported to be isolated.

The reaction of bicyclic dione **31** with LR yielded **33**, having a cage-like structure, the reaction path of which is likely to involve the thiol intermediate **32** (Scheme 11).[58]

Scheme 14. Reaction of α,*β*-Unsaturated Ketones Having 4-Oxothiazolidine Rings



Scheme 15. Synthesis of Ethenethiols



Treatment of α,*β*-unsaturated ketone **34** with LR in refluxing CS_2 under N_2 resulted in dimerization to produce 3,4-dihydro-1,2-dithiins **35** (Scheme 12).[59]

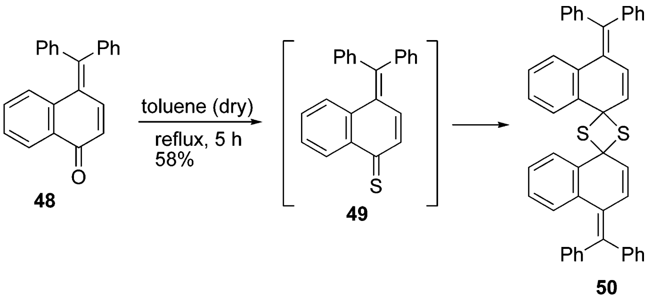
Similarly, α,*β*-unsaturated ketone, 2-(phenylthio)methylene-1-tetralone **36**, following the same reaction path gave the analogue of 3,4-dihydro-1,2-dithiins **37** (Scheme 13).[24,25]

Recently, formation of interesting products from the reactions of α,*β*-unsaturated ketones **38**−**40** (each having a 4-oxothiazolidine ring) with LR was reported.[26,60] Production of the new 1,2-dithiole **41**, dithiazole **42**, and thiazole **43** rings could be attributed to the presence of different functional groups next to the carbonyl group (Scheme 14). Amide or ester characters of the groups led to the formation of dithiazole **42** or thiazole **43** heterocycles, respectively.

An attempt to synthesize ethenethiols **46** and **47**, from ketones **44** and **45**, respectively, resulted in the production of expected products (Scheme 15).[61]

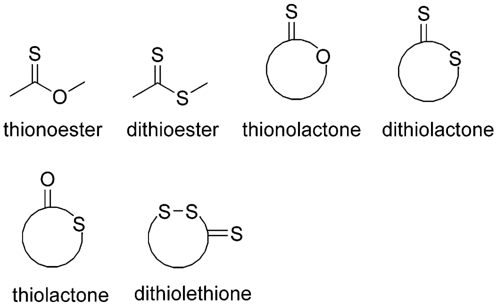
Treatment of the naphthalenone **48** with LR in refluxing toluene gave the dimeric adduct **50**, the mechanism of which possibly went thought a thione intermediate **49** (Scheme 16).[62]

Scheme 16. Dimerization of Naphthalenone 48



2.2. Thionoesters, Dithioesters, Thionolactones, Dithiolactone, Thiolactones, and Dithiolethiones

Exchange of one or more oxygen atoms of esters and lactones with a sulfur atom using LR has been demonstrated by various examples, although such conversions are reported to be the most difficult ones due to the generally low reactivity of the ester functional group toward thionation reagents.[23]



The reaction may require prolonged reaction time, generally refluxing in usual LR solvents such as toluene and xylene (Table 2). On the other hand, employment of microwave shortened the reaction time to a few minutes (Table 2, entries 2, 18−21, 44).[48,96,97] Not only were conversions of carbonyl groups of the esters to thiones (entries 1−8, 21, 22) reported, but synthesis of dithioesters (entries 9−12) was reported to be successful as well.

Replacement of the carbonyl oxygen of lactones, having various ring sizes (entries 13−21, 23−45) was disclosed. Ring sizes varied from five (entry 13) to seventeen (entry 26) some of which included conversion of two (entry 23), three and five (entry 28) carbonyl groups of lactones at the same time.

Installment of sulfurs in place of carbonyl and the ring oxygens to synthesize dithiolactones (entries 46, 47) was also reported.

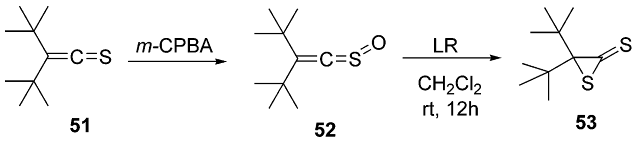
Oxidation of thioketene **51** with *m*-CPBA to form thioketene *S*-oxide **52** and then treatment with LR at room temperature in CH_2Cl_2 for 12 h led to the formation of dithiolactone **53** having a three-membered ring (Scheme 17).[100]

An interesting reaction of α-methylene-*β*-lactone **54** with LR yielded thiolactone **55**, the possible mechanism of which was reported to include ring opening and formation of a new ring (Scheme 18).[101,102]

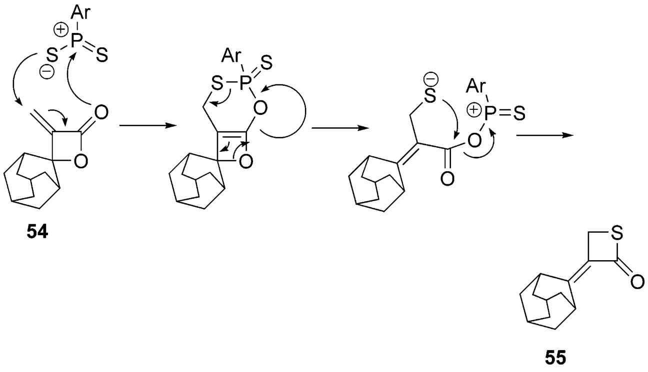
It was reported that treatment of 1,3-diesters[103−105] **56**−**58** with LR could yield dithiolethiones **59**−**61**, respectively (Scheme 19).

Moderate to high yields (61−87%) of α,*β*-unsaturated dithioesters **63** were obtained from α-hydroxyketene dithioacetals **62** upon treatment with LR in refluxing benzene (Scheme 20).[106]

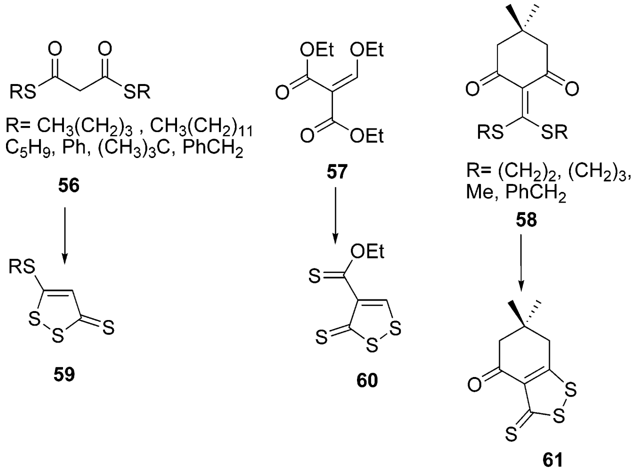
Scheme 17. Reaction of Ketene *S*-Oxide 52 with LR



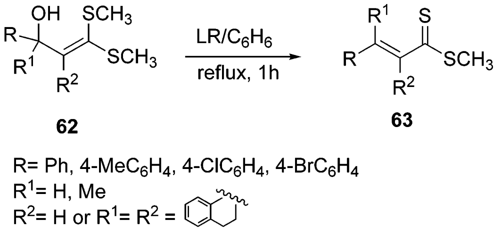
Scheme 18. Possible Mechanism of the Formation of 55



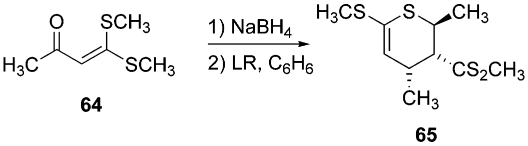
Scheme 19. Formation of Dithiolethiones 59−61 from 1,3-Diesters 56, 57, and 1,3-Diketone 58



Scheme 20. Reaction of α,*β*-Unsaturated Dithoesters with LR



Scheme 21. Reaction of Acylketene Dithioacetal with LR



Contrary to the result obtained with **62**, the reaction of acylketene dithioacetal **64** initially with $NaBH_4$, which yields the corresponding α,*β*-unsaturated alcohol, and then with LR

Table 2. Products of the Corresponding Esters and Lactones

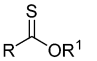
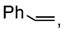
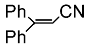
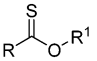
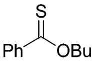
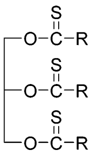
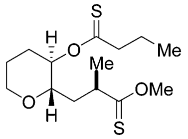
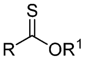
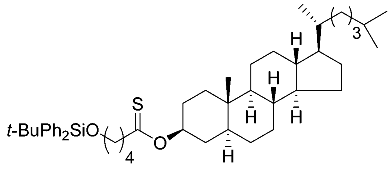
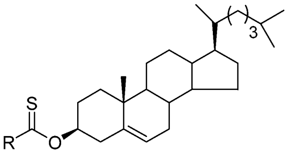
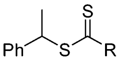
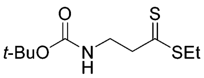
Entry	Product	Reaction conditions	Yield (%)	ref
1	 R= Ph, 4-$NO_2C_6H_4$, 1-naphthyl n-C_6H_{13}, ,[a] CH_3,[b]  R^1= Me, Et, i-Pr, t-Bu, 2-naphthyl	xylene, toluene,[a] ethylbenzene,[b] reflux	4-95 (HPLC)	49
2	 R= Ph, 4-i-PrC_6H_4, $PhCH_2$,  2-furyl, 2-thienyl R^1= Me, Et	MW, 3-4 min	76-96	48
3		toluene, 30 min	23	46
4		neat, N_2, 150 °C	99	63
5		xylene/tetramethylthiourea, 160 °C, ~2 h	47	64, 65
6	 R= n-C_7H_{15}, cyclohexyl, 1-adamantyl, PhCHCH, Me, α-benzyl-γ-butyrolactone R^1= Me, Et, CH_2SiMe_3, 2-naphthyl, α-benzyl-γ-butyrolactone	toluene, 110 °C, 12-36 h	29-88	66
7		xylene, reflux	-	67
8	 R= Ph, Me	glyme	35-48	46
9	 R= Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-BrC_6H_4	toluene, reflux, 4 h	82-91	68
10		toluene, 80-100 °C, Ar, 7-12 h	12-23	69

Table 2 (Continued)

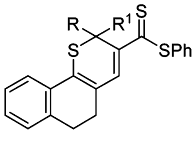
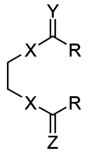
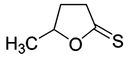
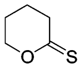
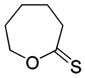
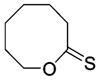
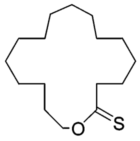
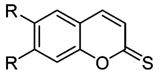
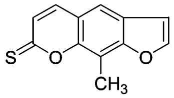
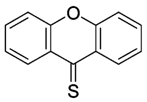
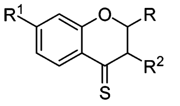
Entry	Product	Reaction conditions	Yield (%)	ref
11	 R= H, Me, Ph R^1= H, Me	toluene, N_2, reflux, 7-10 h	50-72	70
12	 X= Y= O, Z= S X= O, Y=Z= S X= Y= Z= S R = Me, Ph	toluene, reflux, N_2	4-72	71
13		toluene, reflux, 3 h	85 (HPLC)	49
14		MeCN, reflux, 4 h	71 (HPLC)	49
15		toluene, reflux, 1h	73 (HPLC)	49
16		toluene, reflux, 1 h	58 (HPLC) 60 (HPLC)	49 46
17		xylene, reflux, 5 h	84 (HPLC)	49
18	 R= H, OMe	neat, MW, 3 min	94-98	48
19		neat, MW, 3 min	92	48
20		neat, MW, 4 min	96	48
21	 R= H, Ph, 4-$MeOC_6H_4$ R^1= H, OMe, OAc R^2= H, Ph, 4-$MeOC_6H_4$	neat, MW, 3 min	92-95	48

Table 2 (Continued)

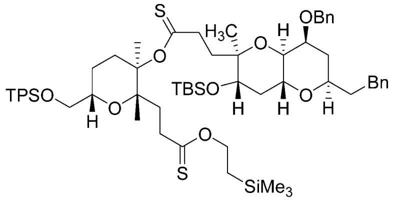
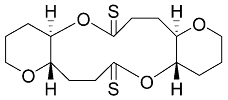
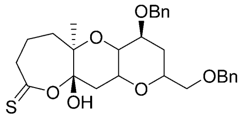
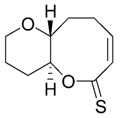
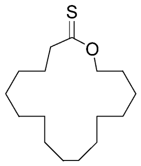
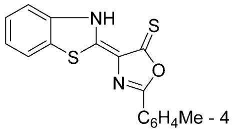
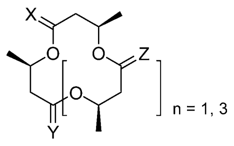
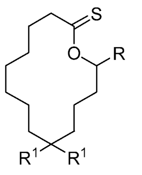
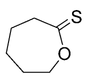
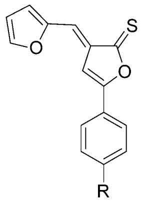
Entry	Product	Reaction conditions	Yield (%)	ref
22		xylene, 175 °C, 1.5 h, 4 eq. $S=C(NMe_2)_2$	49	65
23		toluene, reflux, 16 h	78	72
24		toluene, 110 °C, 3 h	82	65
25		toluene, reflux, 3.5 h	60	73
26		toluene, reflux, 14 h	60	73
27		dioxane, reflux, 48 h	~70	74
28	 for n = 1 A= X= S, Y= O, Z= O B= X= Y= S, Z= O C= X= Y= Z= S	xylene, reflux, ~17 h	for *n* = 1 A = 25-42 B = 13-29 C = 2-29	75
29	 R= H, Me, R^1= H, Me	toluene, reflux	47-77	76
30		toluene, reflux	10	77
31	 R= H, Me, OMe, Cl	toluene, reflux, 2 h	55-60	78

Table 2 (Continued)

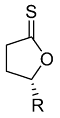
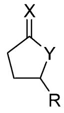
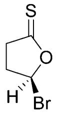
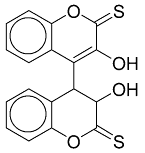
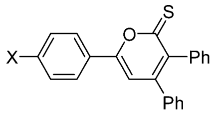
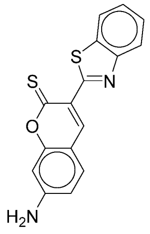
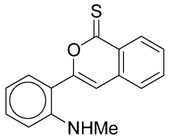
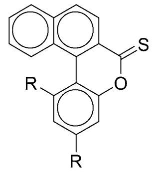
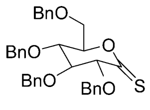
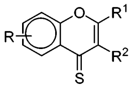
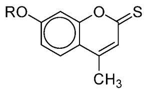
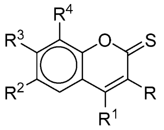
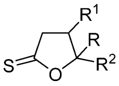
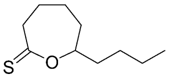
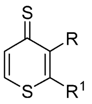
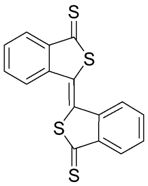
Entry	Product	Reaction conditions	Yield (%)	ref
32	 R= Me, Et, *n*-Pr, *n*-Bu, *n*-pent, *n*-Hex	toluene, reflux, N_2, 4 h	65-91	79
33	 R = Ph, 4-BrC_6H_4, 4-MeOC_6H_4 A= X= S, X= O B= X= O, Y= S	benzene, reflux, 24 h	A = 12-37 B = 1-10	80
34		toluene, reflux, 3 h	75.5	81
35		toluene, reflux, 2 h	80	82
36	 X= OH, Cl, OMe, CN, NEt_2	toluene, reflux, 3 h	-	83
37		toluene, reflux, 15 h	-	84
38		benzene, reflux, 24 h	50	85
39	 R = H, Me, OMe, *t*-Bu	toluene, reflux, 20 h	~75	86-88
40		toluene, reflux, crushed mol. sieves, 4 h	62	89

Table 2 (Continued)

Entry	Product	Reaction conditions	Yield (%)	ref
41	 R= H, 7-MeO, 7-AcO R^1= H, Me, Ph R^2= 2,4-$(MeO)_2$-C_6H_3, 3,4-$(MeO)_2C_6H_3$, 4-$NO_2C_6H_4$, Ph, 4-$MeOC_6H_4$, 2-$ClPhCH_2$, 3-$ClPhCH_2$, 4-$ClPhCH_2$, 2-$BrPhCH_2$, 3-$BrPhCH_2$, 4-$BrPhCH_2$, 4-NO_2PhCH_2, 4-$CNPhCH_2$	toluene, reflux, 3 h	67-91	90-93
42	 R= $PhCH_2$, 2-$MePhCH_2$, 3-$MePhCH_2$, 4-$MePhCH_2$, 2-$FPhCH_2$, 3-$FPhCH_2$, 4-$FPhCH_2$, 2-$ClPhCH_2$, 4-$ClPhCH_2$, 4-NO_2PhCH_2, $PhSO_2^-$, 4-$MeSO_2^-$	toluene (dry), reflux, 3 h	75-91	94
43	 R= H R^1= Me, H, $CH_2CO_2CH_3$ R^2= H, OH R^3= OH R^4= $COCH_3$, CH_2-CH=CH_2, H, $CSCH_3$, $CSCH_3$	toluene, reflux, N_2	61-70	95
44	 R= H R^1= H, Me R^2= Me, C_2H_5, C_4H_9, C_6H_{13}, C_7H_{15}, C_8H_{17}	hexamethyldisiloxane, N_2, Schlenk tube, MW	73-96	96, 97
45		toluene, reflux, N_2, 5 h	65	96, 97
46	 R= OH R^1= Me, Et	dioxane, reflux, ~1 h	39	98
47		chlorobenzene, reflux, 3 h	-	99

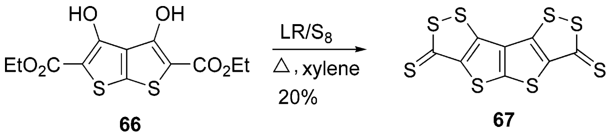
resulted in the production of a dimerized product **65** in 57% (Scheme 21).

Formation of two dithiolethione rings fused to thienothiophene **67** was accomplished by treatment of **66** with LR in boiling xylene in the presence of S_8 (Scheme 22).[107]

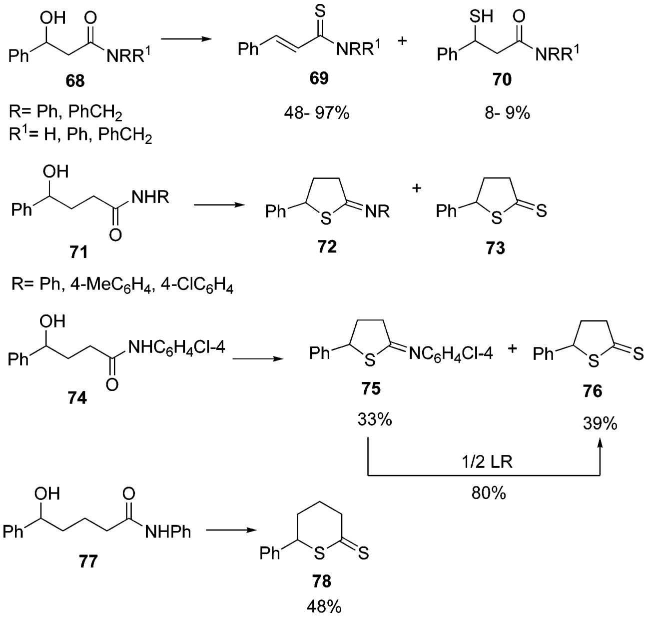
2.3. Amides

Conversion of the oxo group of amides into the corresponding thio derivatives is a well-established and selective process in the presence of ketone, ester, and lactone groups due to its high reactivity (Table 3).[23] Moreover, in the

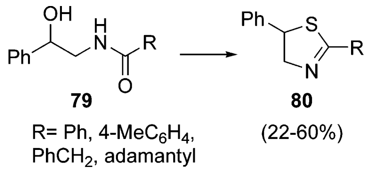
Scheme 22. Formation of Bisdithiolethione Rings



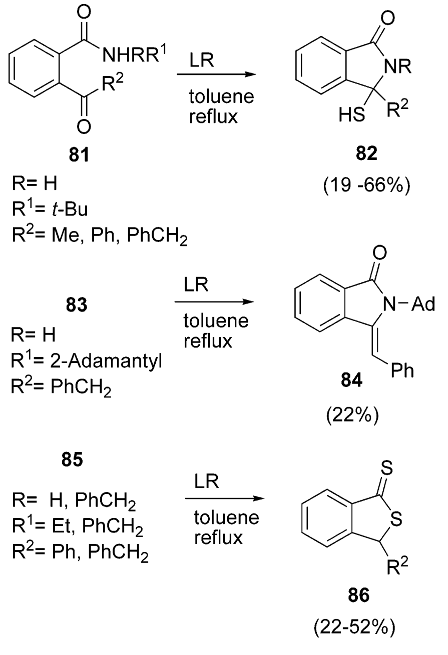
Scheme 23. Reaction of β,γ- and κ-Hydroxy Amides with LR



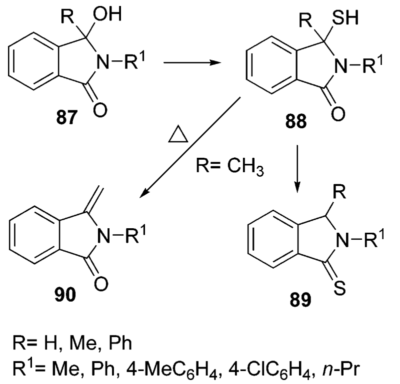
Scheme 24. Formation of Thiazole from β-Hydroxy Amide



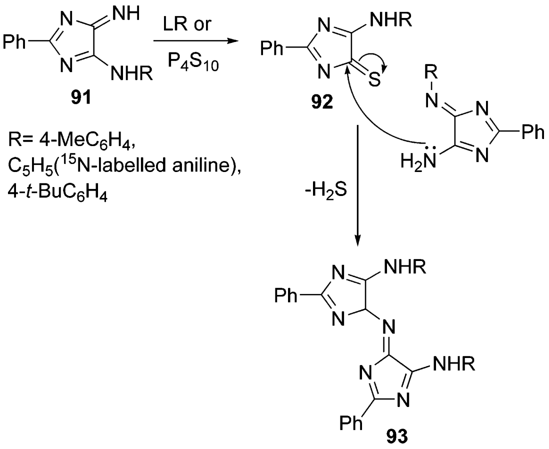
Scheme 25. Reactions of 2-Acylbenzamides with LR



Scheme 26. Reactions of 3-Hydroxyisoindolin-1-one with LR



Scheme 27. Reaction of Imidazole 91 with LR or P_4S_{10}



presence of a carbamate group, without affecting it, the oxo group of the amide was successfully converted to the thio derivative in relatively high yield.[69] Similar selectivities were demonstrated in various examples (Table 3). Reactions were, in general, performed in refluxing dry toluene or benzene under inert atmosphere. On the other hand, there are reactions where THF, HMPA, DME, dioxane, xylene, etc. were used as solvent, and also some reactions were conducted at room temperature.

Nishio et al. investigated the thionation reactions of β-, γ- and κ-hydroxy amides **68**, **71**, **74**, **77**, which resulted in the formation of various products such as α,β-unsaturated thioamide **69**, mercaptoamide **70**, thiopheneimine **72**, **75**, and thiones **73**, **76**, **78** (Scheme 23).[151,153,154]

On the other hand, when the position of the nitrogen of the amide was changed, a different product, thiazole, was obtained (Scheme 24). That is, treatment of the amide **79** with LR gave the thiazole **80** in moderate yield.

2.4. Lactams

Lactams, like amides, react readily with LR, giving corresponding thiolactams, even in the presence of various functional groups (Table 4).

It was reported that the reaction of 2-acylbenzamides **81**, **83**, **85** with LR yielded various products **82**, **84**, and **86**, depending on the groups attached to the starting material (Scheme 25).[135]

The same group reported the result of the reaction of 3-hydroxyisoindolin-1-one **87** with LR (Scheme 26).[199] The reaction was performed with 0.5 equiv of LR in refluxing toluene yielding 3-mercaptoisoindolinone **88**, further reaction of which with 0.5 equiv of LR gave isoindolinethione **89**. In the case of R = CH_3, an elimination product, methylideneisoindolinone **90**, was obtained.

Table 3. Thionation Products of the Corresponding Amides

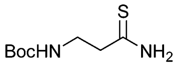
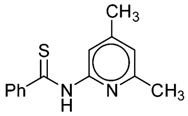
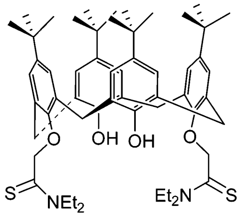
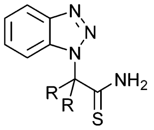
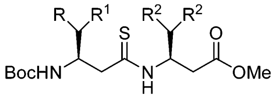
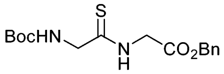
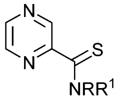
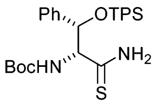
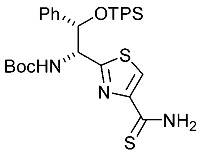
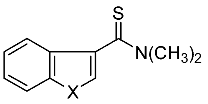
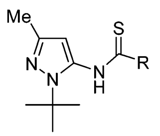
Entry	Product	Reaction conditions	Yield (%)	ref
1		THF, 20 °C, Ar, 24 h	70	69
2		HMPA, 90-95 °C, 10 min	19	108
3		toluene, 60 °C, 4 h	~ 7	109
4	 R= H, Me	THF, rt, 2 h	83-86	110
5	 R= R^1= Me, R^2= H R= *i*-Pr, R^1= H, R^2 = Me	THF, rt, 2.5-4 h	93-95	111
6		THF, reflux	-	112
7	 R = H, *i*-Pr, R^1 = Me, *t*-Bu, *i*-Pr	toluene, 3-40 h, reflux	44-98	113
8	 TPS: *tert*-butyldiphenylsilyl	DME, overnight, rt	quantitative	114
9		dioxane, 3 h, 70 °C	92	114
10	 X= O, S	xylene, HMPA, several hours, 100 °C	75-93	115
11	 R= H, Et, *n*-Pr, 4-BrC$_6$H$_4$, 4-ClC$_6$H$_4$	toluene (dry), 5 h, 80 °C	60-77	116

Table 3 (Continued)

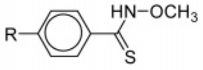
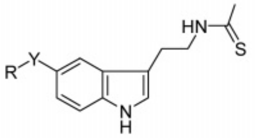
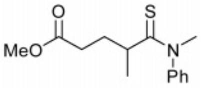
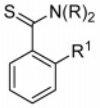
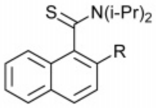
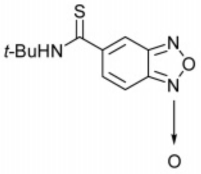
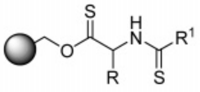
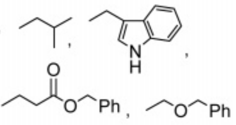
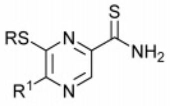
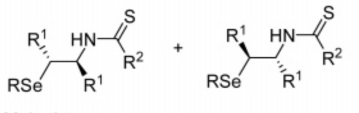
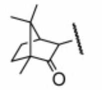
Entry	Product	Reaction conditions	Yield (%)	ref
12	 R= H, OMe, NO_2	benzene, N_2, 12 h, reflux	-	117
13	 R= Me, Et, Y= O, S	toluene, reflux	23-69	118
14		toluene, reflux	93	119
15	 R= Me, *i*-Pr, R^1= Me, Et	R= Me, THF, rt R= *i*-Pr, 1,2,4,-$Cl_3C_6H_2$, 165°C , 19 h -24 h	90-98	120
16	 R = Me, Et	1,2,4,-$Cl_3C_6H_2$, 100 - 144 h, 165 °C	40-48	120
17		MW, 3x2 min	88	121
18	 R=H, Bn, Me,  R^1= Ph, 2-furyl, 2-thiophenyl, 4-*t*-BuC_6H_4	toluene, 5 h, 75°C	~ 68 (HPLC)	122, 123
19	 R= Me, C_2H_5, C_3H_7, C_4H_9, Ph R^1= C_3H_7, C_4H_9, $C(CH_3)_3$	toluene (dry), 4 h, reflux	20-94	124
20	 R=  R^1= C_2H_5, C_3H_7, C_4H_8, Ph, H R^2= Me, *n*-Pr, Ph	THF, 1.5-6 h, reflux	17-72	125

Table 3 (Continued)

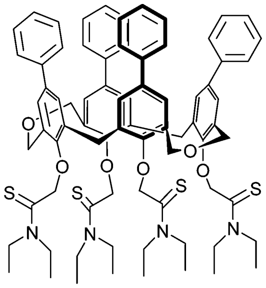
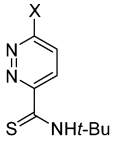
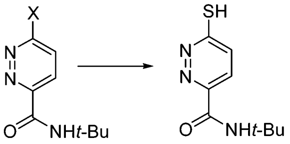
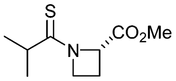
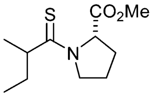
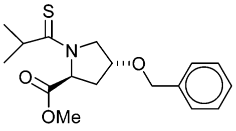
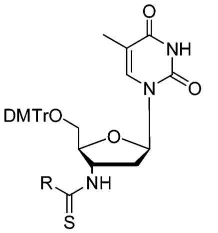
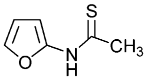
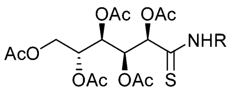
Entry	Product	Reaction conditions	Yield (%)	ref
21		toluene (dry), 2 h, 90 °C	94.5	126, 127
22	 X= Cl, H, SMe	toluene, 8- 46 h, reflux	16-97	128
23	 X= Cl, OMe	toluene, 5-24 h, reflux	23-76	128
24		toluene, reflux	93	129
25		toluene, reflux	70	129
26		toluene, 25 min, reflux	81	130
27	 R= *i*-Pr, FmocNH(CH_2)$_5$	R = *i*-Pr; THF 30 min, rt R = FmocNH(CH_2)$_5$: THF/ Pyr, 30 min, rt	22 50	131, 132
28		THF (dry), rt, 21 h	56	133
29	 R = Me, C_2H_5, *n*-C_3H_7, *i*-C_3H_7, C_6H_{11}, C_6H_5, 4-MeOC_6H_4, 4-BrC_6H_4	benzene, reflux, ~48 h	60-97	134

Table 3 (Continued)

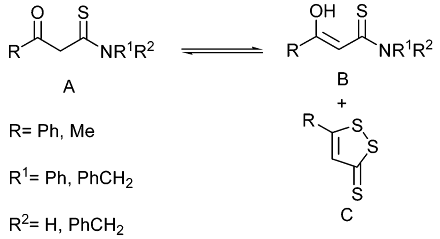
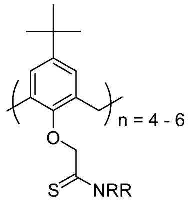
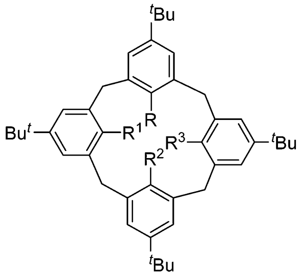
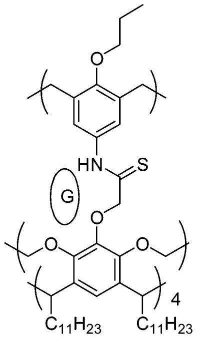
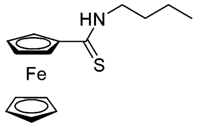
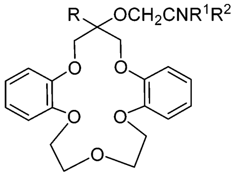
Entry	Product	Reaction conditions	Yield (%)	ref
30	 R= Ph, Me R^1= Ph, $PhCH_2$ R^2= H, $PhCH_2$	toluene, Ar, reflux, 30 min	A + B = 33- 65 C = 3-51	135
31	 R= Et, $(CH_2)_4$, $CH_3CH_2CH_2$	HMPA (dry), 100 °C, N_2, 5 h	38-69	136
32	 R= R^2= $OCH_2C(S)N(CH_3)_2$, R^1= R^3= OH R= R^1= $OCH_2C(S)N(CH_3)$, R^2= R^3= OH R= R^1= R^2= R^3= $OCH_2CH_2OCH_2C(S)N(CH_3)_2$ R= R^1= $OCH_2C(S)N(CH_3)_2$, R^2= R^3= OH	toluene, 85-90 °C, overnight	48-90	137
33	 G= DMF, DMA, NMP Ethyl methyl sulfoxide, 2-Butanone	xylene (dry), 140 °C, 2 h	> 95	138
34		toluene(dry), 4 h, reflux	66	139
35	 R= H; C_3H_7 R^1= H, $C_{1\text{-}6}H_{3\text{-}13}$ R^2= H, $C_{1\text{-}6}H_{3\text{-}13}$	toluene, ~10 h, reflux	32-85	140

Table 3 (Continued)

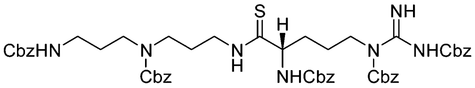
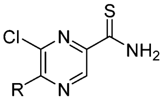
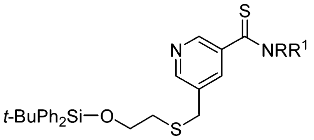
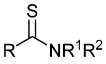
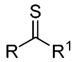
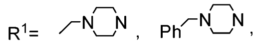
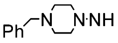
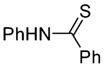
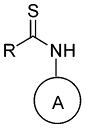
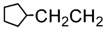
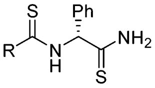
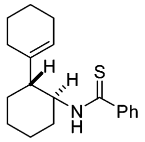
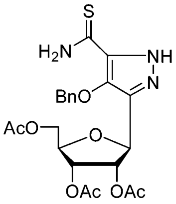
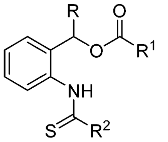
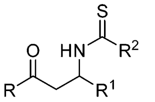
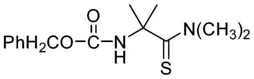
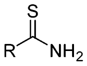
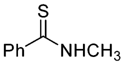
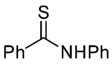
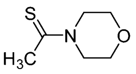
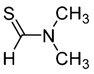
Entry	Product	Reaction conditions	Yield (%)	ref
36		toluene, 80 °C, 1.5 h	63	141
37	 R= $CH_3(CH_2)_{2,3,}$ $(H_3)_2CH$, $(CH_3)_2CHCH_2$, $(CH_3)_3C$	toluene (dry), reflux, 4 h	69-86	142
38	 R= R^1= H; R= H, R^1= Me; R= R^1= Me	toluene, 80-100 °C, 2 h	55-85	143, 144
39	 R= H, Me, Ph R^1= H, Me R^2= H, Me, Ph	MW, 2 min	87-97	48
40	 R= Ph, 2-MeC_6H_4, 3-MeC_6H_4 2-Thiophene, 4-$FC_6H_4CH_2$  $(CH_3)_2N(CH_2)_2NH$, $(i\text{-}Pr)_2N(CH_2)_2NH$, 	MW, 8 min	35-100	145
41		petroleum ether/toluene (8/2) heat, 90 min	14	46
42	 A= Rink resin R= Et, 4-t-BuC_6H_4, 4-ClC_6H_4 2-$MeOC_6H_4CH_2$, 	THF, reflux, 4 h	-	146
43	 R= Ph, 4-$MeOC_6H_4$, 2-thienyl, cyclohexyl, i-propyl	toluene, 100°C, N_2, 40 min	-	147
44		toluene (dry), 100°C, Ar, 2 h	quant.	148

Table 3 (Continued)

Entry	Product	Reaction conditions	Yield (%)	ref
45		dioxane (dry), reflux, 2 h	Unstable product	149
46	 R= H, Ph R^1= 4-MeC_6H_4, Me, *t*-Bu, 2-Furyl 2-Thienyl R^2= 4-MeC_6H_4, *t*-Bu, 2-Furyl, 2-Thienyl	toluene, reflux, Ar, 15 min.	39-98	150
47	 R= EtO, Ph, 4-MeC_6H_4 R^1= Ph, 4-MeC_6H_4, Me R^2= Me, Ph, 4-MeC_6H_4, Bu, 4-ClC_6H_4	toluene, Ar, reflux, 15 min-5 h	4-95	151
48		toluene, reflux, 14 h	52	152
49	 R= Ph, 3-Pyr	CH_2Cl_2, reflux, 1 h	96 (HPLC)	49
50		CH_2Cl_2, rt, 9 h	98(HPLC)	49
51		benzene, reflux, 1 h	96 (HPLC)	49
52		CH_2Cl_2, rt, 6 h	100 (HPLC)	49
53		CH_2Cl_2, rt, 0.5 h	100 (HPLC)	49

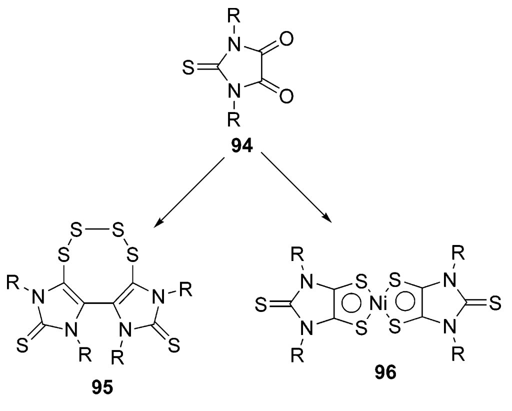
Treatment of the imidazole **91** with LR or P_4S_{10} to obtain its thioxo derivative resulted in dimerization (Scheme 27).[200] Its possible mechanism involved formation of thiolactam moiety **92**, which was subsequently reacted with the amine group of the imidazole **91** to yield the dimer **93**.

Tetrathiacino derivatives **95** were reported to be isolated upon treatment of imidazolidine-2-thione **94** with LR in refluxing toluene (Scheme 28).[201] On the other hand, addition of $NiCl_2 \cdot 6H_2O$ to the reaction mixture resulted in the formation of Ni-complexes **96**.

A surprising epimerization was observed in an attempt to convert the lactam carbonyl to a thiolactam group (Scheme 29).[202] It was assumed that treatment of **97** with LR caused a ring opening on the fused pyrrolidine ring. The final closure yielded the epimerized product **98**.

The reaction of *N*-methyl barbituric acid **99a**, with LR in refluxing toluene (dry) yielded enethiole **100** in 20% along with the dimer **101** in 62% yield, which is a result of the loss of H_2S from **100** (Scheme 30).[54] On the other hand, when unsubstituted barbituric acid **99b** was subjected to the

Scheme 28. Reaction of 94 with LR and Its Ni-Complex

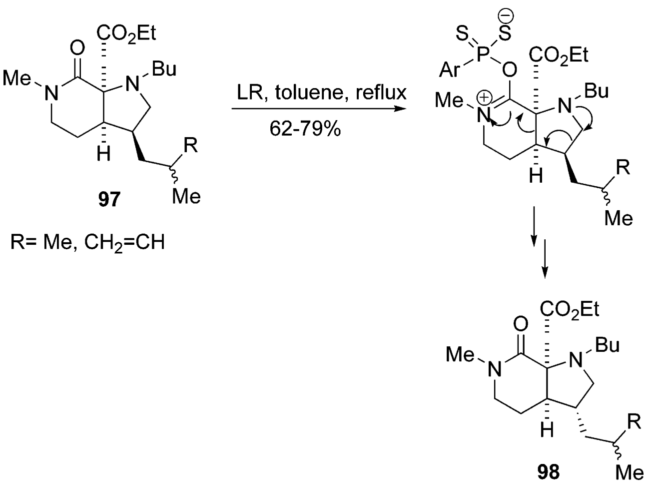

94

95

96

R= Et, *i*-Pr, Bu

Scheme 29. Epimerization of 97 using LR

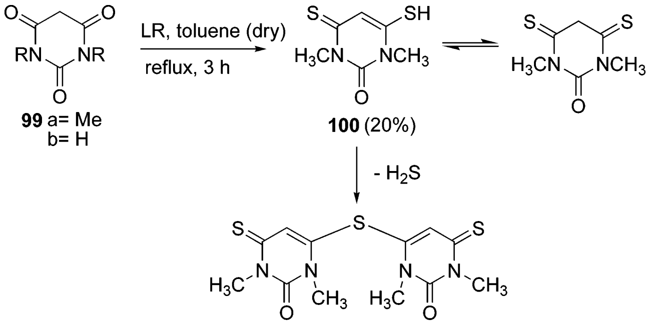


97

98

R= Me, CH_2=CH

Scheme 30. Reaction of Barbituric Acid with LR

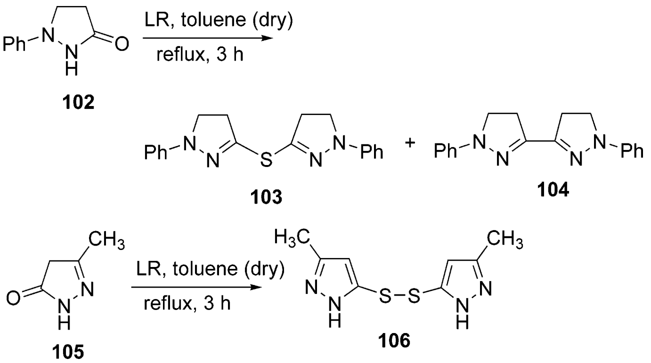


99 a= Me
b= H

100 (20%)

101 (62%)

Scheme 31. Reactions of Pyrazolones 102 and 105 with LR



102

103

104

105

106

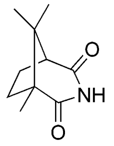
similar reaction with LR, starting material was recovered partially unchanged.

Similarly, the reaction of pyrazolone **102** and 3-methylpyrazole-5-one **105** with LR under the same conditions, i.e., refluxing toluene (dry), 3 h, produced the dimers **103** (75%), **104** (20%), and **106** (60%) respectively (Scheme 31).

2.5. Imides

Conversion of the oxo group of imides to the corresponding thio group has been performed successfully. Its high reactivity led the conversion to be achieved even in the presence of various functional groups such as ketones, esters, SO_2, CN, and amines (Table 5).

Thionation of the imide **107** produced thionation on the less hindered side (Table 5, entry 15). On the other hand treatment of the amide **108** with LR yielded thionation on the other side **109** (Scheme 32).[210] Similar ring closure to give the imide **111** was observed with the corresponding amide **110**.

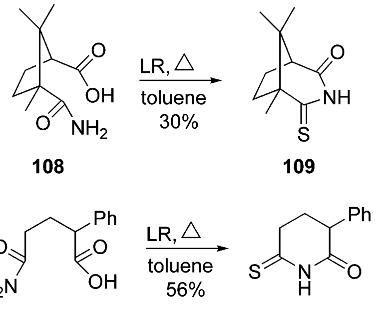

107

Treatment of the thioimide **94** with LR led to the dimerization to give **95**, the structure of which was explained by X-ray crystallography (Scheme 33).[217−219]

2.6. Thiophenes

Synthesis of thiophenes, particularly from 1,4-diketones, is now a well-established strategy. Its possible mechanism

Scheme 32. Formation of Thioimide from 1-Amide-6-carboxylic Acid



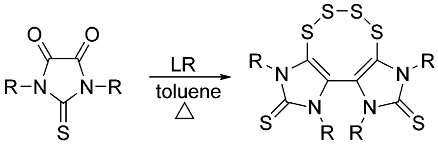
108

109

110

111

Scheme 33. Dimerization of the Imide 94 with LR

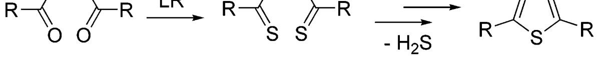


94

95

R= Me, Et, *i*-Pr, *n*-Bu

Scheme 34. General Scheme for the Synthesis of Thiophene Ring



112

113

114

Table 4. Thionation Products of the Corresponding Lactams

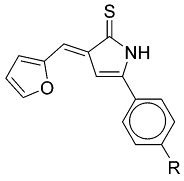
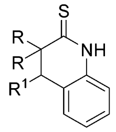
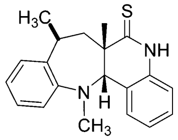
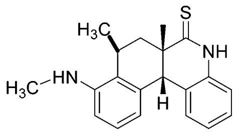
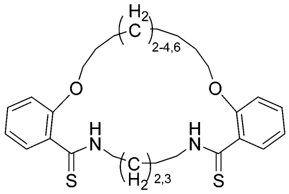
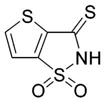
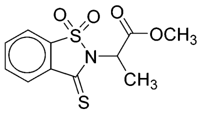
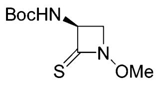
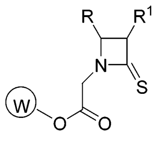
Entry	Product	Reaction conditions	Yield (%)	ref
1	 R = H, Me, OMe, Cl	benzene, reflux, N_2, 2 h	55-70	78
2	 R = H, Me R^1 = H, C_6H_4-NMe, 4-MeNHC$_6$H$_4$	toluene (dry) or dioxane (dry), 6 h	46-77	155
3		toluene (dry) or dioxane (dry), 6 h	46-87	155
4		toluene (dry) or dioxane (dry), 6 h	46-87	155
5		Method A: Silica gel, MW, 15 min Method B: toluene, reflux, 2-3 h	A: 84-89 B: 83-90	156
6		toluene (dry), 24 h, N_2, reflux	73	157
7		toluene (dry), 2 h, N_2, reflux	88	157
8		dioxane, reflux, 2 h	90	158
9		toluene, 80 °C, 50 min	17	159
10	 W= Wang resin R= 4-ClC$_6$H$_4$, 4-MeC$_6$H$_4$, Ph, 4-BrC$_6$H$_4$, 2-BrC$_6$H$_4$ R^1=PhO, MeO, Me, Ph(CH$_2$)$_3$	toluene (dry), N_2, 95 °C, 2 h	-	160

Table 4 (Continued)

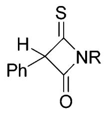
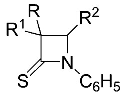
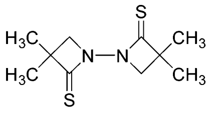
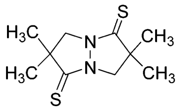
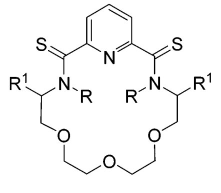
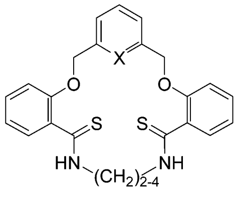
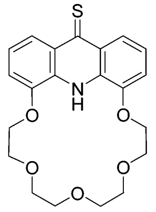
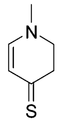
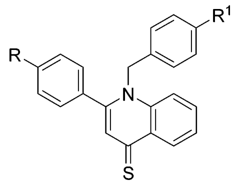
Entry	Product	Reaction conditions	Yield (%)	ref
11	 R= Me, CHMe$_2$, CH$_2$Ph	toluene, reflux, 6-8 h	43-50	161
12	 R= R^1= Me or H R^2= H, C$_6$H$_5$	toluene, reflux, 2 h	47-62	162
13		toluene, reflux, 2 h	53	162
14		toluene, reflux, 2 h	61	162
15	 R= H, Me R^1= PhCH$_2$, Ph	toluene (dry), reflux, Ar, 9 h	88-90	163
16	 X = N, CH	toluene, reflux, 3 h	50-72	164
17		benzene (dry), reflux, 8 h	64	165
18		DME, 20 °C, 30 min	85	166
19	 R = H, OMe, CF$_3$ R^1= H, OMe	toluene, reflux, 16 h	41-71	167

Table 4 (Continued)

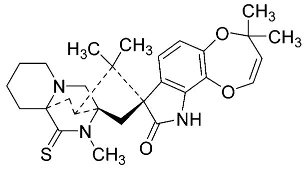
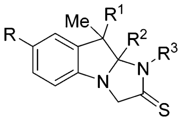
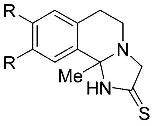
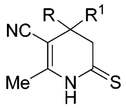
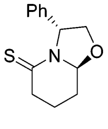
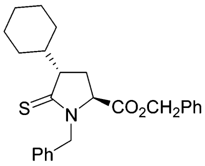
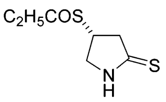
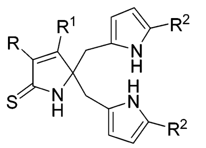
Entry	Product	Reaction conditions	Yield (%)	ref
20		toluene, reflux, 3 h	50-60	168
21	 R= H, Me $R^1 + R^2 = CH_2CH_2CH_2CH_2$ R^3= H, Et	toluene, reflux, 2 h	50-60	169
22	 R = H, OMe	toluene, reflux, 1.5 h	32	169
23	 R= Ph, Me, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$ 4-MeC_6H_4, 4-$NO_2C_6H_4$, $Me(CH_2)_4$, 2-Furyl, 4-ClC_6H_4 R^1= H, Me	benzene (dry), reflux, N_2	75-94	170
24		benzene (dry), reflux, 1 h	81	171
25		toluene (dry), 100 °C, 5 h	69	172
26		toluene , 95 °C, 20 min	87	173
27	 R= $CH_2CH_2CO_2Me$ R^1= CH_2CO_2Me R^2= CO_2Bn, CH_2CBr_3, CN	benzene, reflux, Ar	67-81	174

Table 4 (Continued)

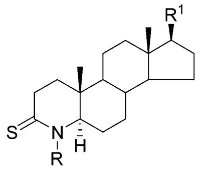
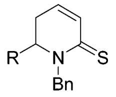
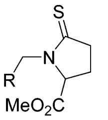
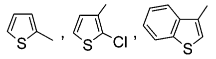
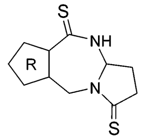
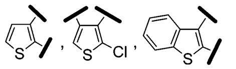
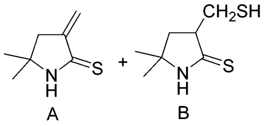
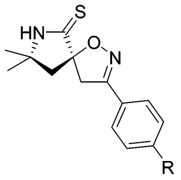
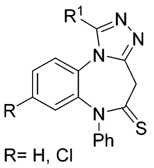
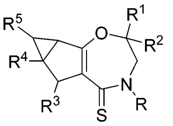
Entry	Product	Reaction conditions	Yield (%)	ref
28	 R= H, Me R^1= CONH*t*-Bu, $COCH_3$, OH, =O, $COOCH_3$ $CONHCH(CH_2CH(CH_3)_2)CSNHCH_3$	CH_2Cl_2, rt, 8-10 h	80-90 except R = OH, 30	175
29	 R = Me, Ph	THF (dry), reflux, 10 min	48, 52	176
30	 R= 	THF (dry), reflux, 24 h	82-87	177
31	 X= Y= S X= O, Y= S R= 	THF (dry), reflux, 24 h	75-91	177
32		THF (dry), rt, 24 h	A = 85 B = 5	178
33	 R = H, Me, Cl, NO_2	THF (dry), rt, 24 h	40-62	176
34	 R= H, Cl R^1= H, Me, Ph	Dowtherm A, 150 °C, 30-60 min	75-87	179, 180
35	 R = Me, C_2H_5, $(CH_2)_3CH_3$, CH_2Ph, H R^1 = R^2 = Me; R_1 = H, R^2 = Ph R^2 = H, Me R^4 = H, Me R^5 = MeO, $C_6H_4CH_2O$, 2-$ClC_6H_4CH_2O$, 4-$ClC_6H_4CH_2O$	toluene(dry), reflux, 4 h	56-84	181, 182

Table 4 (Continued)

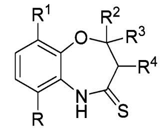
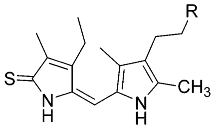
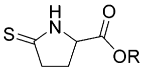
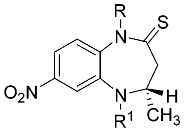
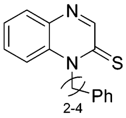
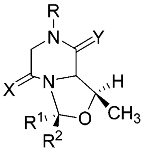
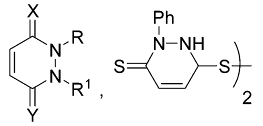
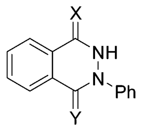
Entry	Product	Reaction conditions	Yield (%)	ref
36	 R= H, Me R^1= H, MeO, $PhCH_2O$, 2-$ClC_6H_4CH_2O$ 4-$NO_2C_6H_4CH_2O$ R^2= H, Me, Ph, 4-$MeOC_6H_4$, 3,4-$(CH_3O)_2C_6H_3$, 3,4,5-$(CH_3)_3C_6H_2$, 2-naphthyl, 2-furyl, 2-thienyl R^3= H, Me R^4= H	toluene(dry), reflux, 4 h	63-89	182, 183
37	 R = H, CO_2CH_3	THF(dry), N_2, reflux, 12 h	82, 83	184
38	 R= H, Me, *t*-Bu	DME (dry), rt or toluene (dry), 80 °C	46 -94	185
39	 R= H, Me R^1= H, Me	toluene, 70-115 °C, 2-6 h	72-95	186
40		toluene, reflux, 2 h	56-85	187
41	 A= X= Y= S B= X= S, Y= O R= CH_2Ph, Ph R^1= H, Ph, CH_2Ph R^2= H, Ph	THF (abs), reflux, 24 h	A = 27-58 B = 38-60	188
42	 X= Y= S; R= Me, R^1= Ph X= O, Y= O; R= Me, R^1= Ph X= S, Y= O; R= Me, R^1= Ph X= Y= S; R= H, R^1= Ph	toluene (dry), reflux,~ 30 min	-	189
43	 X= Y= S X= S, Y= O	toluene (dry), reflux, ~ 30 min	-	189

Table 4 (Continued)

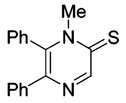
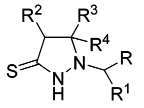
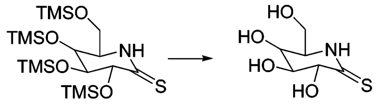
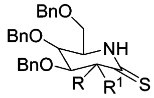
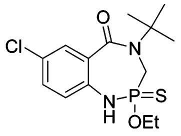
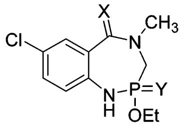
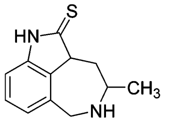
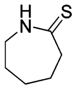
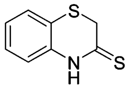
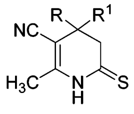
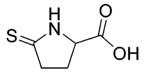
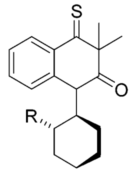
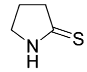
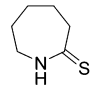
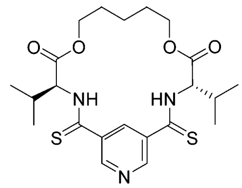
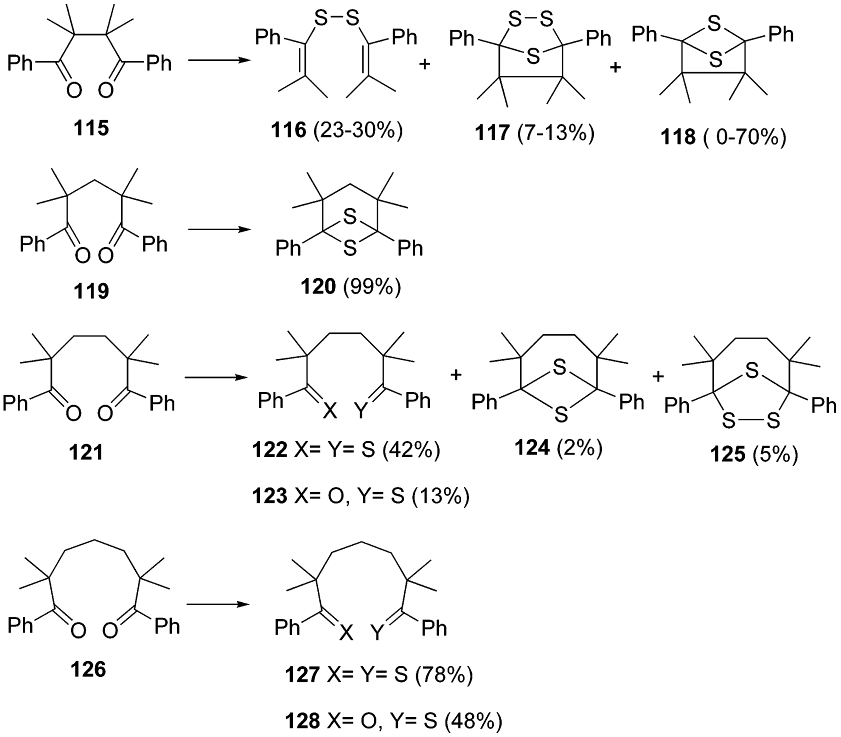
Entry	Product	Reaction conditions	Yield (%)	ref
44		toluene (dry), reflux, 4 h	57	190
45	 R= H, Fluorenylidene -(9) R^1= Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$, 4-*i*-PrC_6H_4, fluorenylidene-(9) R^2= H, Me R^3= H, Me R^4= H, Me	CH_2Cl_2 (dry) or benzene, 20-40 °C	-	191
46		-	-	192
47	 R= OBn, R^1= H R=H, R^1= OBn	benzene (dry), reflux, 6 h	99	193
48		toluene, reflux, 5 h	93	194
49	 A= X= Y= S B= X= O, Y= S	toluene, reflux, 3.5 h	A (45 %) B (16 %)	194
50		toluene, BHT, reflux, 2 h	24	195
51		MW, 2 min	88	45
52		MW, 3 min	MW, 3 min	45
53	 R= Ph, Me, 4-$MeOC_6H_4$, 2-$MeOC_6H_4$, 4-MeC_6H_4, 4-$NO_2C_6H_4$, $Me(CH_2)_4$, 4-Furyl, 4-ClC_6H_4 R^1 = H, Me	benzene (dry), N_2, reflux, 4 -10 h	75- 94	196

Table 4 (Continued)

Entry	Product	Reaction conditions	Yield (%)	ref
54		DME(dry), rt, 2.5 h	63	197
55	 R= MeO, Me	toluene, reflux, 2 h	24, 43	198
56		CH_2Cl_2, rt. 1 h	100 (HPLC)	49
57		CH_2Cl_2, rt. 1 h	100 (HPLC)	49
58		benzene, N_2, reflux, 3 h	Quant.	203

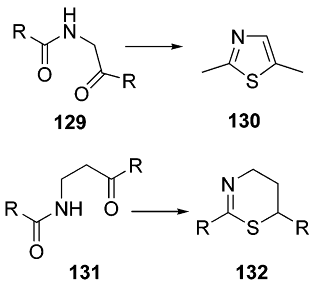
Scheme 35. Reaction of 1,4-, 1,5-, 1,6-, 1,7-Diketones with LR



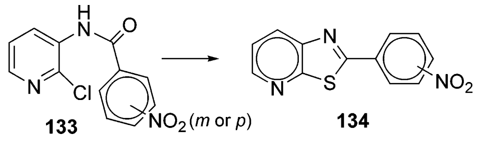
was proposed to involve initial conversion of the 1,4-oxo groups **112** to 1,4-thiones **113**, which is a known replacement of carbonyl by thione (Scheme 34). It subsequently undergoes in situ cyclization and elimination of H_2S to give thiophene **114**.

1,4-Dicarbonyls with different functional groups including carboxylic acid, aldehyde, ester, hydroxyl, amide, epoxide, and thioester led to the formation of a thiophene ring (Table 6). Oxygen atoms of polycyclic cage compounds were successfully replaced with sulfur (entry 37).[249] Polymerization of the 1,4-ketone array to obtain polythiophene systems was reported (entries 8 and 25). Diketone systems such as 1,4- **115**, 1,5- **119**, 1,6- **121**, and 1,7- **126**, having fully alkylated α-positions, produced various compounds including disulfide

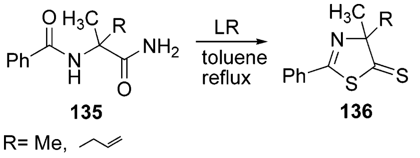
Scheme 36. General Reactions of Thiazole and Thiazine Formations



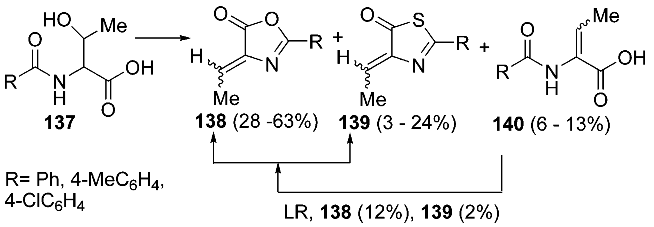
Scheme 37. Reaction of 1-Chloro-4-oxo Compound 133 with LR



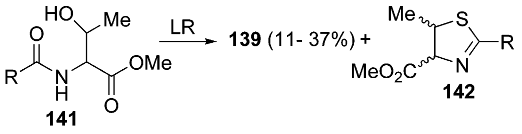
Scheme 38. Reaction of 1,4-Diamides 135 with LR



Scheme 39. Reaction of *N*-Acrylthreonines 137 with LR



Scheme 40. Reaction of Methylester of *N*-Acrylthreonine 141 with LR



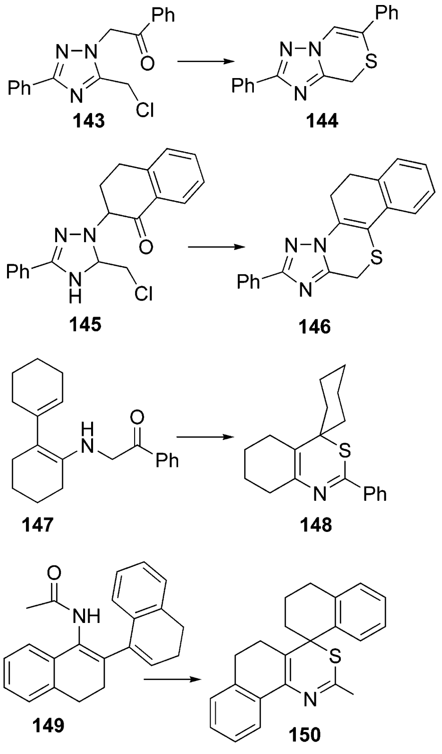
116, trithiolane **117**, **125**, and 1,3-dithietane **118**, **120**, **124** (Scheme 35).[252–255] It appears that ring formation decreased with the increase of conversion of oxo groups to thiones, **122**, **123**, **127**, **128**.

2.7. Thiazoles and Thiazines

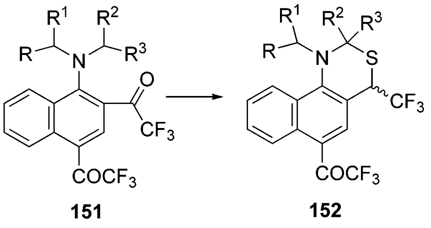
Treatment of the 1,4-dicarboxyl **129** system having amide functionality successfully gave the thiazole **130** heterocycle (Scheme 36, Table 7).

When the system was extended to 1,5-dicarbonyl compound **131**, a six-membered heterocycle thiazine **132** was obtained. The presence of a hydroxyl group in place of the carbonyl at either the 4- or 5- position did not alter the reaction product. Having a cyanide group next to the amide nitrogen in the 1,4-dicarbonyl system, gave cyclization through cyanide carbon rather than the carbonyl group, producing 2-aminothiazole (Table 7, entry 16).[269,270]

Scheme 41. Reactions of 1-Carbonyl-5-chlorides with LR



Scheme 42. Reaction of System Having 1-Dialkylamino-4-carbonyl with LR



R= H, Me
R^1= H, R_1= R_2= -(CH_2)- , -$(CH_2)_3$-
R^2= H, Me
R^3= H, Me

Treatment of 3- or 4-nitrobenzamide **133**, having a 2-chloro-3-pyridyl group on amide nitrogen, with LR in the presence of hexamethylphosphoric-triamide gave successful cyclization to thiazoles **134** in around 70% (Scheme 37).[271]

1,4-Diamides **135** were reported to give thiazolethiones **136** upon reacting with LR in refluxing toluene (Scheme 38).[272–274]

Reactions of LR with *N*-acrylthreonines **137** in refluxing toluene resulted in isolation of a mixture of products, oxazolones **138**, thiazolones **139**, and olefins **140**, reaction of which with LR yielded **138** and **139** (Scheme 39).[275]

On the other hand treatment of methyl ester of *N*-acrylthreonine **141** with LR in refluxing toluene gave thiazolone **139** and 4-methoxycarbonyl thiazoline **142** (Scheme 40).

1-Carbonyl-5-chlorines **143**, **145** and 1-amide-5-unsaturated **147**, **149** systems produced six-membered thiazine heterocycles **144**, **146**[276] and **148**, **150**,[277] respectively (Scheme 41). The yields of the latter two spiro products were reported to be 63 and 93%, respectively.

Table 5. Synthesis of Thioimides from Corresponding Imides Using LR

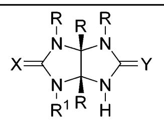
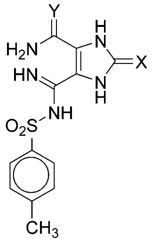
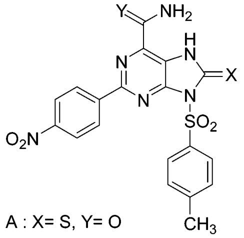
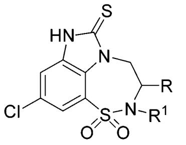
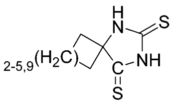
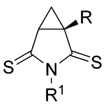
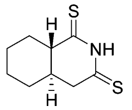
Entry	Product	Reaction conditions	Yield (%)	ref
1	 A: X= Y=S, R= Me, R^1= H B: X= S, Y= O, R= Me, R^1= H C: X= O, Y= S, R= Me, R^1= CH_3O D: X= O, Y= S, R= Me, R^1= CH_3CS E: X= O, Y= S, R= Me, R^1= $CH_3(CH_2)_2CO$	A= 3 eq LR; B= 1 eq LR C= 1.3 eq LR, 60 °C, D= 1.3 eq LR, reflux E= 1.2 eq LR, 60 °C 16h	A = 60 B = 83 C = 47 D = 22 E = 74	204
2	 A: X= S, Y= O B: X= Y= S C: X= O, Y= S	THF, N_2, reflux, 12 h	A(45) + B (10) + C (15)	205
3	 A : X= S, Y= O B : X= Y= S C : X= O, Y= S	THF, N_2, reflux, 5-7 h	A(15) + B(12) + C (32)	205
4	 R= H, Me R^1= H, CH_2CH_3, $CH_2CHC(CH_3)_2$	dioxane (dry), 100 °C, 10-22 h	29-93	206
5		toluene, reflux, 6 h	82-96	207
6	 R= Me, Ph, *i*-Pr R^1= H, Me	toluene, reflux, 2 h	62	208
7		toluene, reflux, 2 h	-	208

Table 5 (Continued)

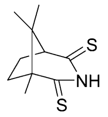
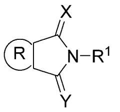
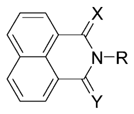
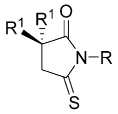
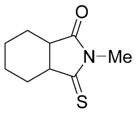
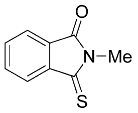
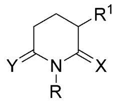
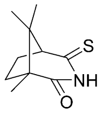
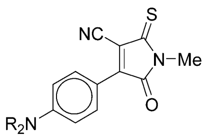
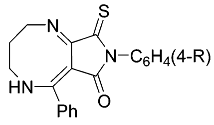
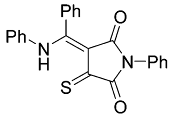
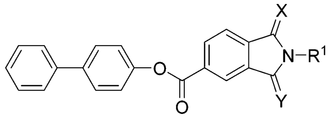
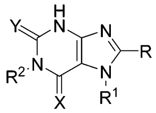
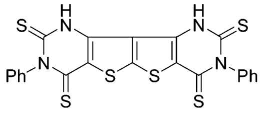
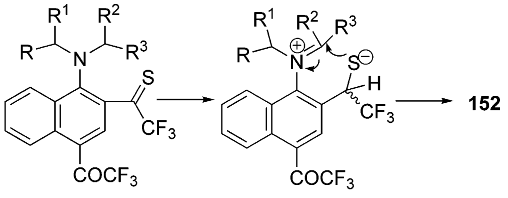
Entry	Product	Reaction conditions	Yield (%)	ref
8		toluene, reflux, 2 h	-	208
9	 R= H, Ph, 1,4-$Cl_2C_6H_3$, 4,5-$Cl_2C_6H_3$ R^1= H, CH_3, Ph, *t*-Bu, 1-adamantyl A= X= Y= S B= X= S, Y= O	toluene (dry), reflux, 1 h	A(0-98) + B(0-53)	209
10	 R= H, Me A= X= Y= S B= X= S, Y= O	toluene (dry), reflux, 1 h	A(88-98) + B(0-10)	209
11	 R= H, Ph R^1= H, Me	toluene, reflux, 0.5-1 h	51, 57	210
12		toluene, reflux, 1 h	80	210
13		toluene, reflux, 0.5 h	58	210
14	 R= Ph, R^1= H, X= O, Y= S R= H, R^1= Ph, X= O, Y= S R= H, R^1= Ph, X= S, Y= O	toluene, reflux, 0.5-3 h	56-65	210
15		toluene, reflux, 3 h	30, 64	210
16	 R= Me, Et	toluene, reflux	50, 72	211

Table 5 (Continued)

Entry	Product	Reaction conditions	Yield (%)	ref
17	 R = H, Me	toluene	-	212
18		toluene	-	212
19	 R= H, CN, $C_{10}H_{21}O$, $C_{11}H_{23}O$ R^1= $CH(CH_3)C_2H_5$, $CH_2CH(CH_3)C_2H_5$, C_6H_{13} A= X= O, Y= S B= X= S, Y= O C= X= S, Y= S	toluene (dry), reflux, 1 h	A(10 - 30) +B(10 - 35) +C(10 - 25)	213, 214
20	 R= H, Me R^1= H, Me R^2= H, Me A : X= S, Y= O B : X= Y= S	MW, 5-10 min	90-99	215
21		toluene (dry), reflux, 4 h	93	216

Scheme 43. Suggested Reaction Mechanism of 1-Dialkylamino-4-carbonyl System with LR

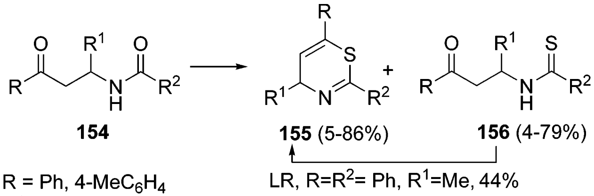


153

Different from the systems above, the 1-dialkylamino-4-carbonyl system **151** yielded the similar thiazine heterocycle **152** in refluxing toluene in 30−81% yields (Scheme 42).[278] Its possible mechanism was suggested to involve initially the usual conversion of the oxo group to thione **153**, which was followed by a hydride migration from the carbon next to the nitrogen atom to the thione carbon (Scheme 43). The ring closure then forms the thiazine ring **152**.

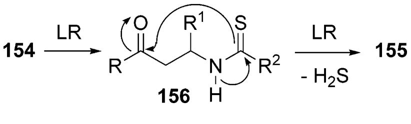
Treatment of 3-*N*-acylamino ketones **154** with LR in refluxing toluene produced thiazine **155** and thiacrylaminoketones **156**; following the reaction of which with LR converted it to thiazine **155** (Scheme 44).[261]

Scheme 44. Reaction of *N*-Acylamino Ketones with LR



R = Ph, 4-MeC_6H_4
R^1= Ph, 4-MeC_6H_4, Me
R^2= Ph, 4-MeC_6H_4, *t*-Bu, 4-ClC_6H_4

Scheme 45. Suggested Reaction Mechanism of *N*-Acrylamino Ketones with LR



The reaction mechanism of thiazine **155** was suggested to involve the initial thionation of the amide group **156**

Table 6. Synthesis of Thiophene Rings from the Corresponding Diketones unless Otherwise Stated

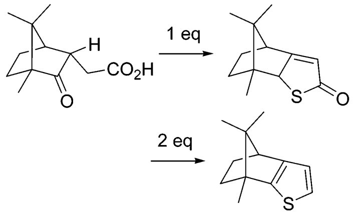
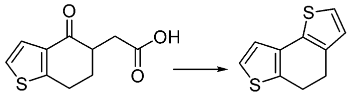
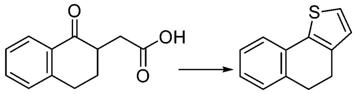
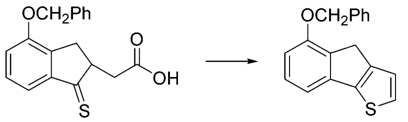
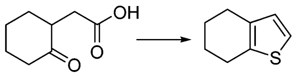
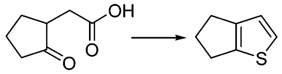
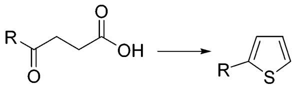
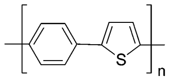
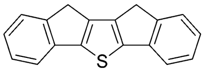
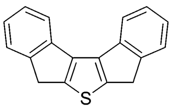
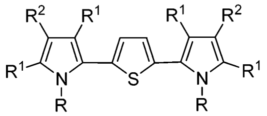
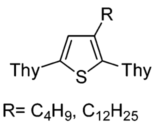
Entry	Product	Reaction conditions	Yield (%)	ref
1		toluene, N_2, reflux	61	220
2		toluene, N_2, reflux	56	220
3		toluene, N_2, reflux	44	220
4		toluene, N_2, reflux	34	220
5		toluene, N_2, reflux	8	220
6		toluene, N_2, reflux	10	220
7	 R = Ph, 2-thienyl	toluene, Ar, reflux, 30 min	11-13	220
8		dichlorobenzene, 190 °C, 48 h	-	221
9		toluene, reflux, 2.5 h	90	222
10		toluene, reflux, 2.5 h	94	222
11	 R= H, $PhSO_2$, $MeSO_2$ R^1= R^2= H R^1= EtO_2C, R^2= Me	toluene (dry), reflux, 4 -6 h	65-76	223
12	 R= C_4H_9, $C_{12}H_{25}$ Thy= 2-thienyl	toluene, reflux	58-77	224

Table 6 (Continued)

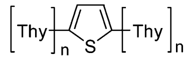
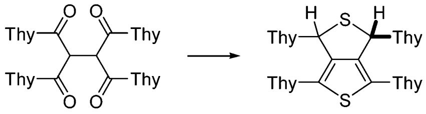
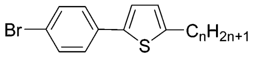
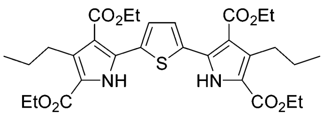
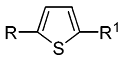
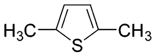
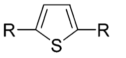
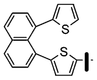
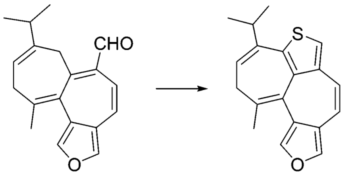
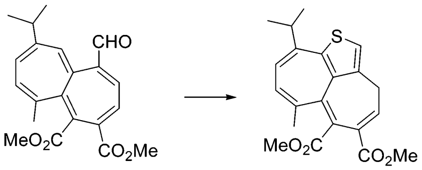
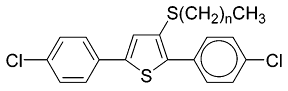
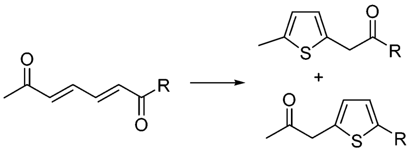
Entry	Product	Reaction conditions	Yield (%)	ref
13	 n = 1, 2 Thy= 2-thienyl	toluene (dry), reflux, 2 h	87-90	225
14	 Thy= 2-thienyl	xylene (dry), reflux, 3 h	60	226
15	 n = 3 - 11	-	76- 87	227
16		toluene, N_2, reflux, 4 h	55	228
17	 A : R= R^1= 2-Furyl B : R= 2-Thienyl, R^1= 2-Furyl	toluene, reflux, overnight	A = 70 B = 75	229
18		chlorobenzene (dry), N_2, 135 °C	65	230
19	 R = 	toluene, reflux	64	231
20		toluene (dry), N_2, 110 °C, 30 min	61	232
21		toluene (dry), N_2, 110 °C, 30 min	68	232
22	 n = 3, 9, 17	toluene (dry), reflux, 2 h	65-73	233
23	 R= Me, Ph, EtO, 4-$MeO_2CC_6H_4$, 4-$MeOC_6H_4$	EtOH or BF_3 / CH_2Cl_2	2-93	234

Table 6 (Continued)

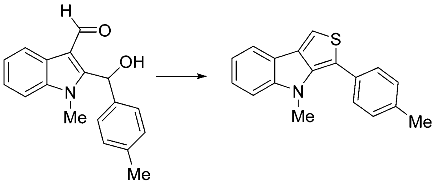
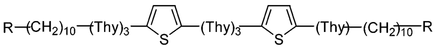
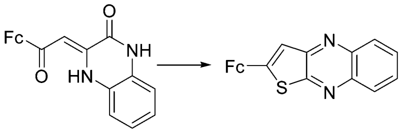
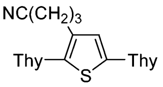
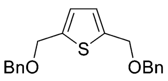
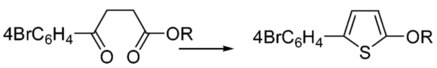
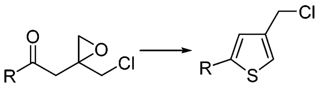
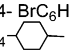
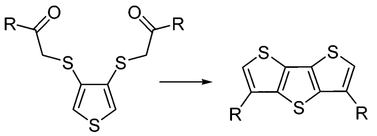
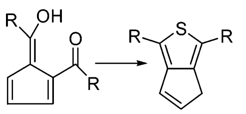
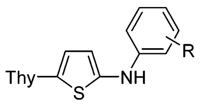
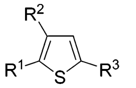
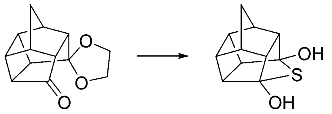
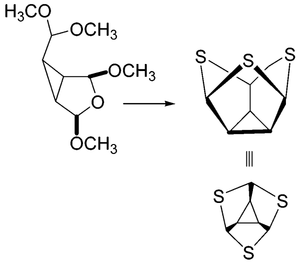
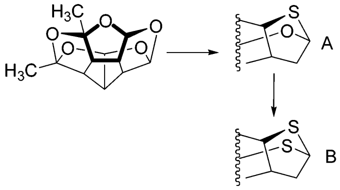
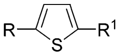
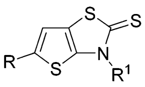
Entry	Product	Reaction conditions	Yield (%)	ref
24		dioxane, reflux, 4 h	63	235
25	 R= polystyrene Thy= 2,5-thienyl	toluene, Ar, 80 °C, 5 h	30	236
26	 Fc= ferrocenyl	toluene, Ar, reflux, 2 h	81	237
27	 Thy= 2-thienyl	toluene(dry), reflux, 6 h	82	238
28		toluene, 3 h, rt → 1 h reflux	74	239
29	 R= $C_{2-12}H_{25}$, $CH(CH_3)C_6H_{13}$, $4\text{-}MeOC_6H_4$, 6-Br-2-naphthyl	toluene (dry), Ar, reflux, 1.5-48 h	35-94	240
30	 R= $4\text{-}FC_6H_4$, $3,4\text{-}ClC_6H_4$, 4- BrC_6H_4, $4\text{-}FC_6H_4CH_2CH_2$, 4 $\text{-}FC_6H_4$- 	benzene, p-TSA, reflux, ~1.5 h	20-32	241, 242
31	 R= Ph, $4\text{-}MeOC_6H_4$, $4\text{-}BrC_6H_4$, $4\text{-}NO_2C_6H_4$	toluene, N_2, LR or P_4S_{10}, reflux, ~3 h	50-58	243
32	 R= Ph, 2-thienyl, 5-Me-2-thienyl	toluene, reflux	8-22	244
33	 R= H, 2-MeO, 4-MeO, 2,4-diMeO, 2-Me, 2-F, 4-F, 2-Cl, 3-Cl, 4-Cl, 2-Br, 4-Br, 2,4-diBr, 2-I, $3\text{-}NO_2$, $4\text{-}CO_2Me$, 4-CN Thy= 2-Thienyl	toluene, reflux, 15 -30 min	7-55	245

Table 6 (Continued)

Entry	Product	Reaction conditions	Yield (%)	ref
34	 R^1= furyl, hexyl, heptyl R^2= Ph, 2-thienyl R^3= Ph, 3-hydroxyphenyl	$Bi(OTf)_3$/[bmim]BF_4, 90°C, 4.5- 5 h	80-87	246
35		THF (dry), N_2	-	247
36		toluene, sonication, rt, 12h	25	248
37		$CHCl_3$, sonication, reflux, 12 h	A = 46 B = 26	249
38	 R= Ph, 4- BrC_6H_5, 4- $MeOC_6H_4$ R^1= $PhOC_2H_5$, OC_4H_9, OC_6H_{13}, OC_8H_{17}, $OCH(CH_3)C_6H_{13}$, $OC_{10}H_{21}$, $OC_{12}H_{25}$, 4- BrC_6H_4O	MW, 3,4 min	65 - 94	250
39	 R= Ph, 4- MeC_6H_4, 2- thienyl, 4- BrPh, 4- MeC_6H_4 R^1= Ph, 4- MeC_6H_4, 4- ClC_6H_4, $PhCH_2$	xylene, reflux, 4 h	89-95	251

followed by thionation of the ketone functionality; subsequent attack from the amide thione to the thioketone finally gave **155** after a H_2S elimination (Scheme 45).

2.8. Thiadiazoles and Thiadiazines

Similar to thiophenes, thiadiazoles **158**, were successfully synthesized upon treatment of 1,4- diamide **157** systems with LR (Scheme 46).

Cyclization was achieved in the presence of various functional groups such as ester, pyridyl, and nitro (Table 8). Use of MW, in place of a high-boiling-point solvent such as toluene, resulted in a high yield of the product. Polymers incorporating thiadiazole groups were successfully obtained by treatment of 1,4-diamide systems in the polymer chain with LR.

1,2,4-Thiadiazoles **160**, **162** having various functional groups were reported to be obtained from acyl or aroylaminooxazoles **159**, **161** (Scheme 47).[291] Its possible mechanism involved initial conversion of amide oxo to thione, and then the attack from the nitrogen next to the ring oxygen resulted in the rearrangement of the system to thiadiazole.

Synthesis of 1,2,3-thiadiazoles **164** from α-diazo *β*-ketoesters **163** after treatment with LR in refluxing benzene was reported (Scheme 48).[292] Its possible mechanism involves initial conversion of the oxo group to thione **165**, the

Table 7. Synthesis of Thiazole and Thiazine Rings from the Corresponding 1,4-Dicarboxyl 129 and 1,5- Dicarboxyl 131 Systems or from the Compounds Stated in the Table

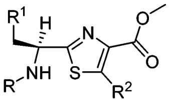
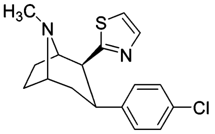
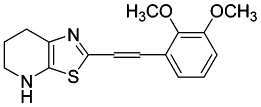
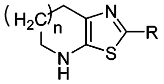
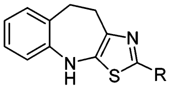
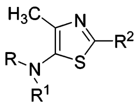
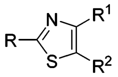
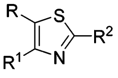
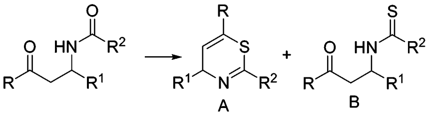
Entry	Product	Reaction conditions	Yield (%)	ref
1	 R= CBz, BOC R^1= 3-indolyl, Ph R^2= Ph, 2-naphthyl, 3-pyridyl, isopropyl, Me	THF, N_2, reflux, 6 h	66-76	256
2		toluene, N_2, reflux, 5 h	30	257
3		pyridine, 100°C, 4 h	53	258
4	 n = 1-8 R= Me, Ph, 4- $MeOC_6H_4$	pyridine, 100°C, 4 h	23, 39	258
5	 R = 4-$MeOC_6H_4$, PhCH=CH	pyridine, 100°C, 4 h	66, 69	258
6	 R= Ph, Et, 4-Picolyl R^1= H, Et R^2= Me, Ph	pyridine, 100°C, 5 h	35-86	258, 259
7	 R= H, C_5H_{11}, Ph, 2-thienyl, 2-BnO-5-MeO-C_6H_3, *N*-Boc-piperidin-4-yl, 5-(4-Cl-C_6H_4)oxazol-4-yl R^1= Ph, CO_2Me R^2= Me, Ph, 4-Cl-C_6H_4, 4-$MeO_2CC_6H_4$	THF (dry), reflux, 4-6 h	34-89	260
8	 R= Ph, Me R^1= H, Me, $PhCH_2$ R^2= Ph, *t*-Bu, 2-adamantyl, 2-furyl, 2-thienyl	toluene, Ar, reflux, 15 h	12-92	261
9	 R= Ph, 4-MeC_6H_4 R^1= Me, Ph, 4-MeC_6H_4 R^2= Ph, 4-MeC_6H_4, 4-ClC_6H_4, *t*-Bu	toluene, Ar, reflux, 15 min	A (trace-86) B (trace-79)	261

Table 7 (Continued)

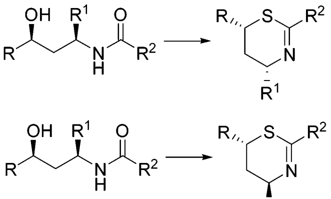
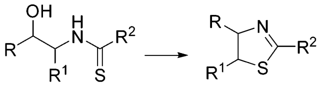
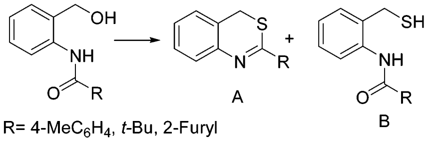
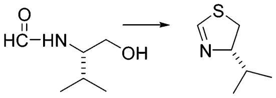
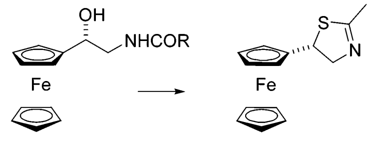
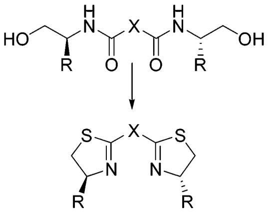
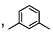
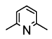
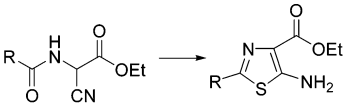
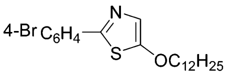
Entry	Product	Reaction conditions	Yield (%)	ref
10	 R= Ph, 4-MeC$_6$H$_4$ R^1= Me, Ph, 4-MeC$_6$H$_4$ R^2= 4-MeC$_6$H$_4$, 4-ClC$_6$H$_4$	1 mol LR, toluene, Ar, reflux, 15 min	40-88	262
11	 R= Ph, Me R$_1$= H, Me, PhCH$_2$ R^2= Ph, 2-furyl, 1-adamantyl, 4-MeC$_6$H$_4$, α-naphthyl, PhCH$_2$	toluene, Ar, 15-30 min	34-91	263, 264
12	 R= 4-MeC$_6$H$_4$, *t*-Bu, 2-Furyl	toluene, Ar, 15 min	A (trace-31) B (13-54)	263
13		Mineral oil, 110-120°C, 45 min	30	265
14	 R= Ph, ferrocenyl	THF (dry), reflux, N$_2$	65, 84	266, 267
15	 X= C(Me)$_2$, CH$_2$CH$_2$, ,  R= Ph, PhCH$_2$, *i*-Pr	toluene, reflux	Quantitative	268
16	 R= H, Me, Ph	benzene (dry), reflux, 24 h	10-70	269, 270
17		MW, 5-8 min. 1-9.3 mol LR	83-90	250

Table 8. Synthesis of Thiadiazoles from the Corresponding 1,4-Diamides

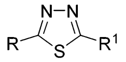
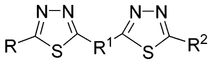
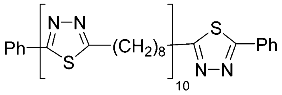
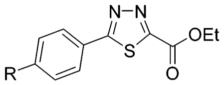
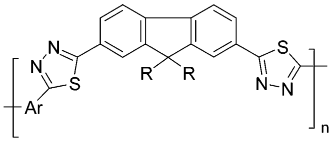
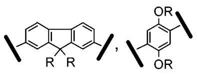
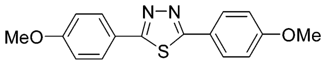
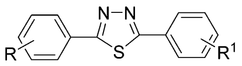
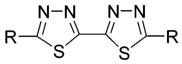
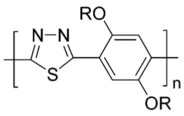
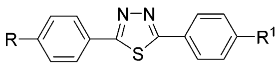
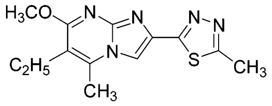
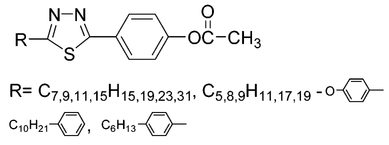
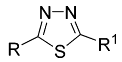
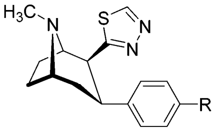
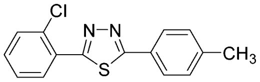
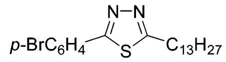
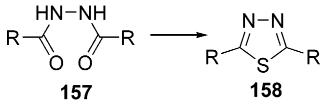
Entry	Product	Reaction conditions	Yield (%)	ref
1	 R= Ph, 4-$MeOC_6H_4$, 4-$NO_2C_6H_4$, 2-Pyr, 3-Pyr, 4-Pyr, pentyl R^1= Ph, 4-$NO_2C_6H_4$, 2-Pyr, 3-Pyr, 4-Pyr, pentyl, F_3C, Ph-NH-, PhCHCH-	toluene (dry), reflux, 1-5 h	54- 96	279
2	 R= Ph, 2-Pyr R^1= 1,4-Ph, -$(CH_2)_8$-, 1,6-Pyr R^2= Ph, 2-Pyr	toluene (dry), N_2, reflux, 1-10 h	80-95	279
3		toluene (dry), N_2, reflux, 10 h	90	279
4	 R = $C_8H_{17}O$, $C_{12}H_{25}O$	THF, rt	79, 77	280
5	 Ar=  R= 2-ethylhexyl	dichlorobenzene, $POCl_3$, N_2, 130-170 °C, 6 h	81, 91	281
6		toluene (dry), $POCl_3$, reflux, 2 h	67	282
7	 R= 3-Me, 4-Me, 4-Br, 2-EtO R^1= 3-Me, 4-Me, 2-Cl, 4-EtO	MW, 6-16 min	74-91	283
8	 R= 4-$MeOC_6H_4$	dioxane, reflux, 3 h	48	284
9	 R= C_mH_{2m+1} m = 8,10,12,16	dioxane, reflux, 8 h	97	285
10	 R= $CH_3C(O)O(CH_2)_{n=3,6,11}O$- R^1= $PhCH(CH_3)CH_2O$-	THF, reflux, 1 h	64	286
11		toluene (dry), reflux, 45 min.	34	287

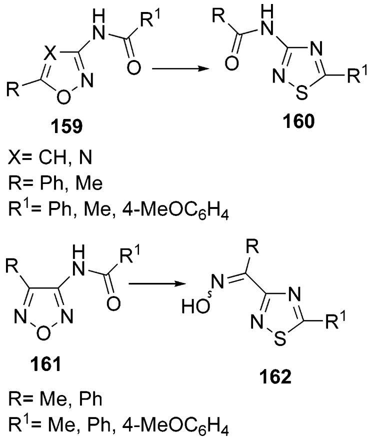
Table 8 (Continued)

Entry	Product	Reaction conditions	Yield (%)	ref
12	 R= $C_{7,9,11,15}H_{15,19,23,31}$, $C_{5,8,9}H_{11,17,19}$ -O- $C_{10}H_{21}$-, C_6H_{13}-	toluene (dry), reflux	-	288
13	 R = H, CH_3, *i*-Pr, *t*-Bu, Ph R^1= H, CH_3, *i*-Pr, *t*-Bu, Ph	xylene, reflux, 1 -3.5 h	44 - 100 R= R_1= *t*-Bu, trace	289
14	 R= Cl, Me	toluene, N_2, reflux, 4 h	51, 58	257
15		MW	81%	290
16		MW, 7 min	95%	250

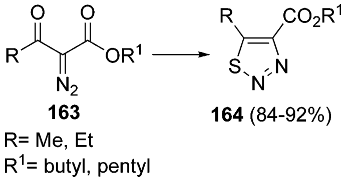
Scheme 46. General Reaction Scheme of Thiadiazoles with LR



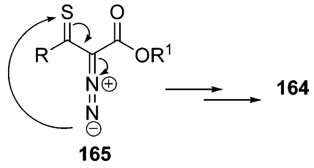
Scheme 47. Synthesis of Thiadiazoles from Acyl/Aroylaminooxazoles



Scheme 48. Reaction of α-Diazo-*β*-ketoesters with LR



Scheme 49. Possible Reaction Mechanism of 164



intramoleculer reaction of which with azide resulted in the production of **164** (Scheme 49).

Reactions of dialkylhydrazones **166** with LR in refluxing benzene were reported to produce 1,3,4-thiadiazines **167** (Scheme 50).[293,294]

Its proposed mechanism included initial production of thione from the oxo groups, and then the rearrangement gave **167** (Scheme 51).

2.9. Aldehydes

Contrary to ketones, esters, and amides, there are few examples of conversion of oxo groups of aldehydes to thione using LR. An example appeared that refluxing the aldehyde **168** with LR in dry benzene under argon in dark for 45 min yielded the thioaldehyde **169** in 75% (Scheme 52).[173]

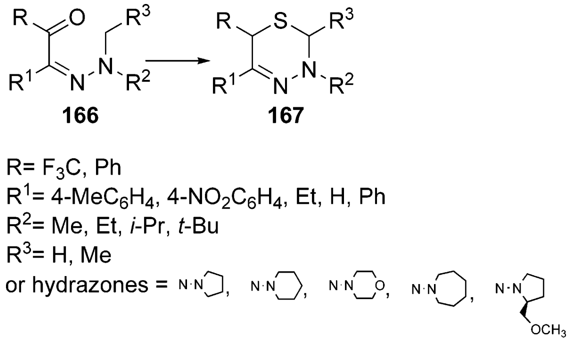
Similarly, refluxing the aldehyde **170** with LR in dry benzene under argon gave the thioformyl pyrole **171** in 53%, together with thioformyl pyrole **172** in 24% (Scheme 53).

The aldehyde moiety of the porphyrin **173** was reported to be converted to the thioaldehyde **174** in 78% (Scheme 54).[33] The reaction was performed in refluxing degassed benzene under argon for 10 min.

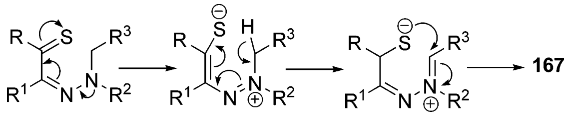
Pentafluorobenzaldehyde **175** was observed to react with anthracene in refluxing benzene in the presence of LR to give **176** in 59% along with **177** in 3.5% (Scheme 55).[295]

It was claimed that when benzaldehyde **178** was allowed to react with LR in refluxing toluene, formation of a polymeric material was observed.[296] On the other hand, when the reaction was repeated in the presence of trimethyl or triethyl phosphite and ethyl acrylate **179**, **180** and **181**, respectively, were isolated (Scheme 56).

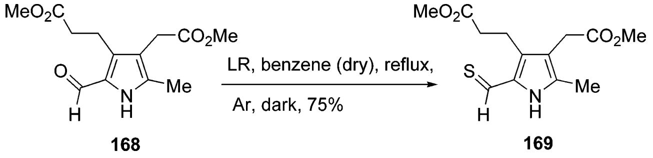
Scheme 50. Reaction of LR with Dialkylhydrazones 166



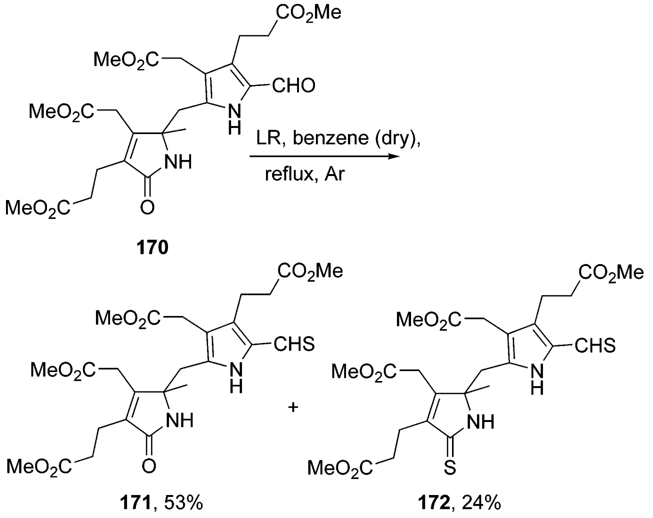
Scheme 51. Possible Reaction Mechanism of 167



Scheme 52. Conversion of the Aldehyde 168 to the Thioaldehyde 169



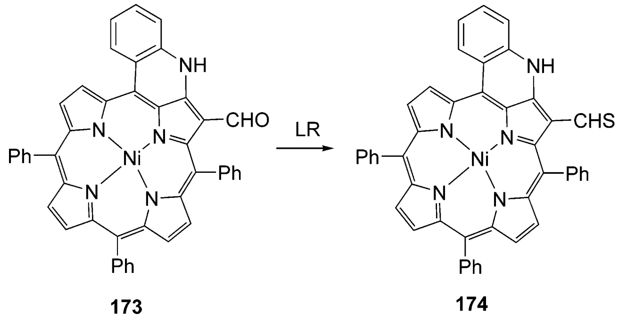
Scheme 53. Conversion of the Aldehyde 170 to Thioformyl Pyrole 171 and Thioformyl Thiopyrole 172



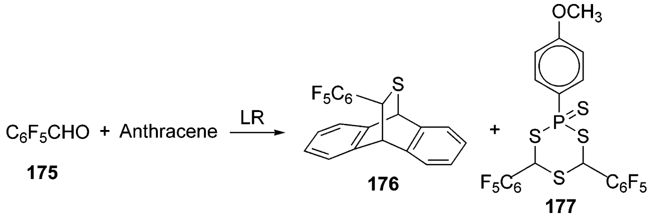
Self-coupling of the aldehydes **182**, **184**, and **185** was achieved by treatment with LR in refluxing toluene, which yielded highly conjugated systems **183** (11%), **186** (16%), and **187** (17%), respectively (Scheme 57).[297]

Unexpected products were obtained in an attempt to synthesize ethenethiols from ketones **44** and **45** (see section 2.1., Ketones, Scheme 15), and the aldehyde **188**, which resulted in the production of divinyl sulfide **189** and a ring formation product **190** of two molecules of the thioaldehyde and 4-MeOC$_6$H$_4$PS$_2$ (Scheme 58).[61]

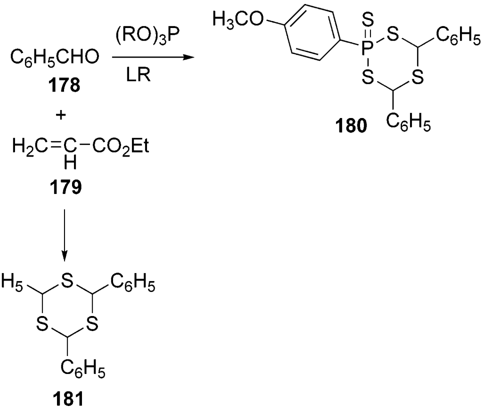
Scheme 54. Conversion of the Aldehyde Moiety of the Porphyrin 173 to Thioaldehyde 174



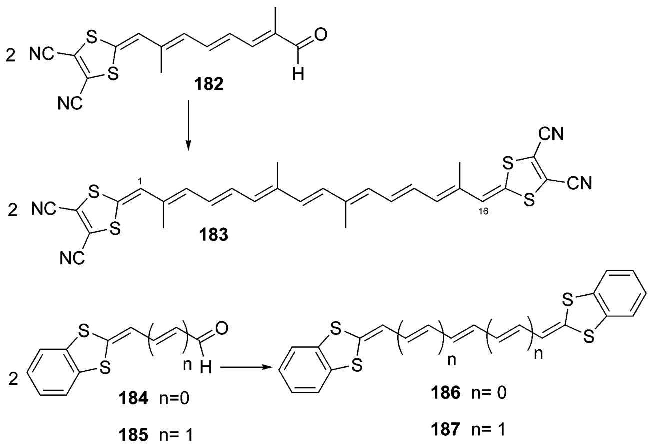
Scheme 55. Reaction of 175 with Anthracene in the Presence of LR



Scheme 56. Reaction of Benzaldehyde with LR in the Presence of Alkyl Phosphite and Ethyl Acrylate



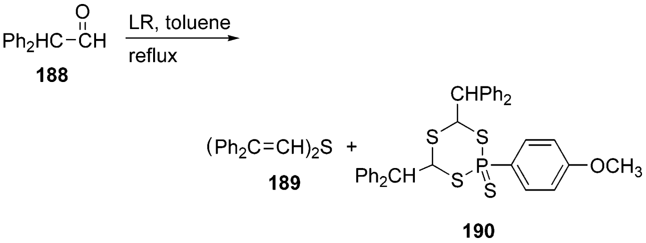
Scheme 57. Self-Coupling Reactions of the Aldehydes



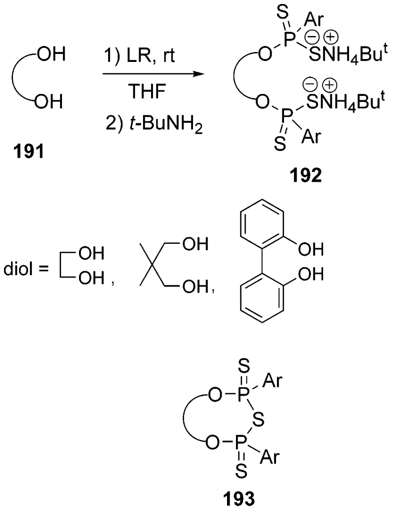
2.10. Alcohols

Some examples in the literature indicate that the conversion of the hydroxyl groups to thiol, even in the presence of ketone, amide, and ester moieties, is possible (Table 9). On the other hand, there are many examples showing that hydroxyl groups react with LR to give 5−8-membered heterocycles incorporating part of the LR if they have nucleophilic or electrophilic centers in proper proximity to the hydroxyl group (see section 2.11. Heterocyclic Rings Incorporating Part of LR, Table 11).

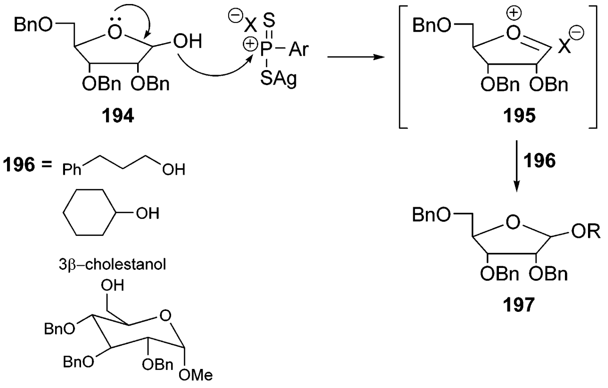
Scheme 58. Reaction of the Aldehyde 188 with LR



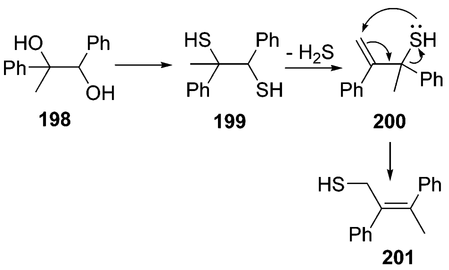
Scheme 59. Formation of Bis-anisyldithiophosphonic Acids



Scheme 60. Reaction of Ribofuranose 194 with Alcohols in the Presence of LR

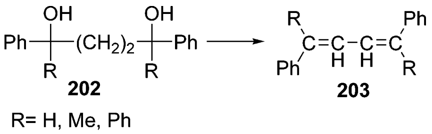


Scheme 61. Reaction of 1,2-Diol 198 with LR

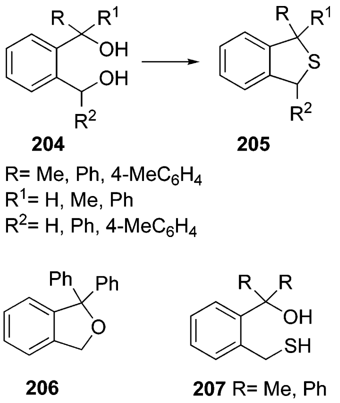


It was reported that when the diols **191** were reacted with LR at room temperature, rather than the heterocyclic products **193**, as suggested earlier,[345,346] corresponding bis-anisyldithiophosphonic acids were formed, which were isolated as their *tert*-butylammonium salts **192** (Scheme 59).[301]

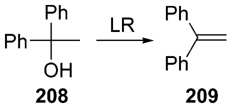
Scheme 62. Reaction of 1,4-Diols with LR



Scheme 63. Reaction of 1,2-Dihydroxymethylbenzene with LR



Scheme 64. Reaction of a Tertiary Alcohol with LR



Ribofuranoside **197** was reported to be synthesized by treatment of 2,3,5-tri-*O*-benzyl-D-ribofuranose **194** with various alcohols **196** in the presence of LR and $AgClO_4$ combination in 79−97% yields (Scheme 60).[303] Its mechanism was claimed to involve the intermediate **195** which underwent a nucleophilic attack by alcohol to yield **197**.

Treatment of 1,2- **198** and 1,4- **202**, diols with LR gave an unexpected product **201** and the expected product **203**, respectively (Schemes 61 and 62).[299] An explanation for the possible mechanism of the former was that hydroxyl groups were initially converted to thiols **199**. Then, elimination of H_2S yielded **200**, rearrangement of which resulted in the formation of **201** (Scheme 61).

Formation of rings **205** were observed when *o*-bis(hyroxymethyl)benzene derivatives **204**, two hydroxyl groups of which were located on the same side as 1,4- to each other, were treated with LR (Scheme 63).[299] In the case when R and R_1 are Ph and R_2 is H, **206** was obtained. Finally the reaction of **207** with LR yielded the corresponding compounds **205**.

Treatment of tertiary alcohol **208**, having two phenyl groups, with LR resulted in the elimination reaction to give the olefin **209** (Scheme 64).[46]

2.11. Heterocyclic Rings Incorporating Part of LR

Reaction of LR with the compounds having nucleophilic centers such as hydroxyl, amine, and thiol may lead to heterocyclic rings having "S" and "P" atoms introduced by LR itself. The size of the rings varies from 4 to 8, although the sizes concentrate at 5- and 6-membered rings (Tables 10 and 11). It appears that the mechanisms of the formation of such rings mainly follow two paths. One of them involves two nucleophilic centers **210** which sequentially attack phosphorus to yield a heterocycle **211** consisting of phosphorus of LR in the ring (Scheme 65).

In the second mechanism, the compound **212**, which reacts with LR, involves a nucleophilic center and an electrophilic center/a leaving group. An initial attack to the phosphorus

Table 9. Conversion of the Corresponding Hydroxyl Groups to Thiols

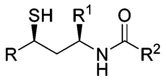
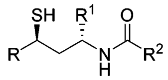
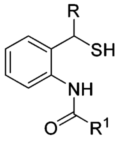
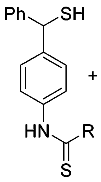
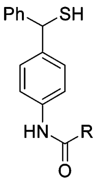
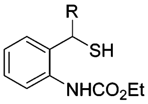
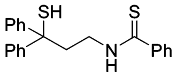
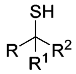
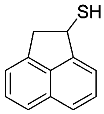
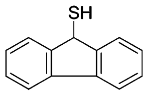
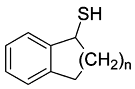
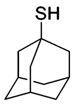
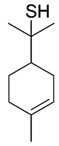
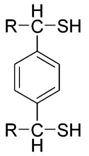
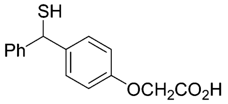
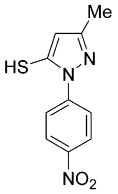
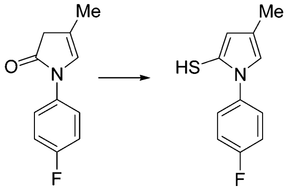
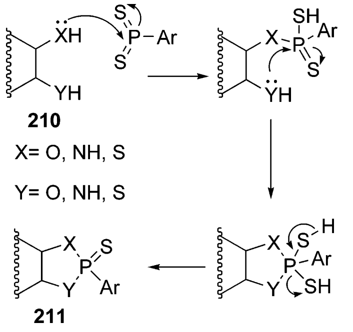
Entry	Product	Reaction conditions	Yield (%)	ref
1	 **A**  **B**	0.5 mol LR, toluene, Ar, reflux, 15 min	A 20-52 B 32-49	262
2	R= Ph, 4-MeC$_6$H$_4$ R^1 = Ph, 4-MeC$_6$H$_4$, Me R^2= 4-MeC$_6$H$_4$, *p*-ClC$_6$H$_4$			
3	 R= Ph, Me R^1= *t*-Bu, 4-MeC$_6$H$_4$, α-napthyl	0.5 mol LR, toluene, Ar, reflux 15–30 min	59-87	264
4	 +  **A** **B**	toluene, Ar, reflux, 15–30 min	A + B Eq LR 76 trace 0.5 LR 10 54	264
5	 R = Ph, Me	toluene, Ar, reflux, 15–30 min	R= Ph= 94 R= M = 64	264
6		toluene, Ar, reflux, 30 min	26	264
7	 R= Ph, PhCH$_2$, PhCH=CH R^1= H, Ph, Me, Et R^2= H, Ph, Me	DME, rt or toluene, reflux, Ar, 0.2-48 h	9-100	298
8		toluene, reflux, Ar, 0.5 h	-	298
9		toluene, Ar, reflux, 0.5 h	18	298
10		toluene, Ar, reflux, 3 h	n= 1 67 n= 2 65	298
11		toluene, Ar, reflux, 3 h	23	298

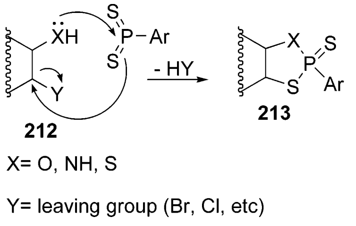
Table 9 (Continued)

Entry	Product	Reaction conditions	Yield (%)	ref
12		toluene, Ar, reflux, 0.5 h	20	299
13	 R= Me, Ph	toluene, Ar, reflux, 0.5 h	R= Me, 17 R$_1$= Ph, 52	299
14		THF or DME, Ar, rt, 24 h	quant.	300
15		toluene (dry), 3.5 h	58	302
16		toluene (dry), 3-5 h	62	302

Scheme 65. Possible Reaction Mechanism of the Phosphorus Heterocycle 211

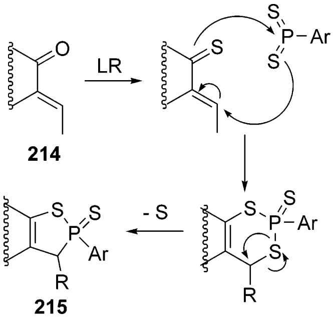


Scheme 66. Possible Reaction Mechanism of the Phosphorus Heterocycle 213



of LR is followed by a nucleophilic attack from sulfur of LR to the electrophilic center to yield the heterocycle **213**, having phosphorus and sulfur atoms of LR (Scheme 66).

Scheme 67. Possible Reaction Mechanism of the α,β-Unsaturated Compounds 214 with LR Leading to the Heterocycle 215



α,β-Unsaturated compounds **214** could have a mechanism similar to the one which has nucleophilic and an electrophilic centers, although its initial step is replacement of the oxo group by thione which act as a nucleophile while sulfur of LR attacks the α,β-unsaturated bond (Michael addition). Elimination of elemental sulfur could result in the formation of five-membered ring **215**, incorporating sulfur and phosphorus atoms of LR (Scheme 67).

The smallest rings possessing part of LR were obtained as 4-membered heterocycles **218** upon the reaction of α,β-unsaturated nitriles **216** with LR as minor products (Scheme 68).[338] Thioamide **217** was the major product.

Table 10. Formation of Phosphorus Heterocycles (Ar = 4-MeOPh)

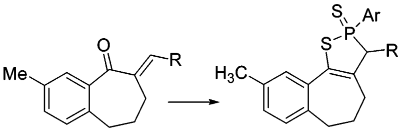
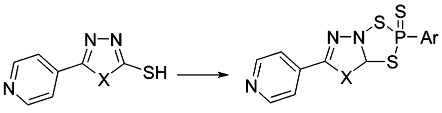
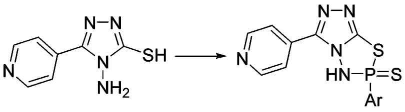
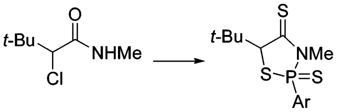
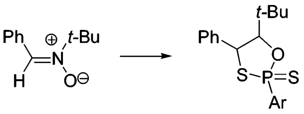
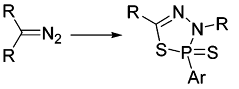
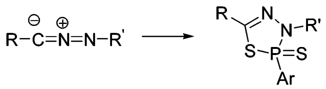
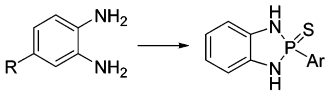
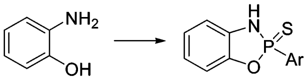
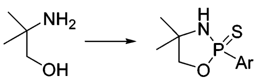
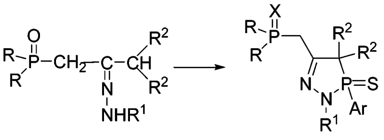
Entry	Reaction	Reference
1	 R= Aryl	304
2	 X= O, S	305
3		305
4		306
5		307
6	 R= Me_3Sn, $(i\text{-}Pr_2N)_2P$	307
7	 R= $(i\text{-}Pr_2N)_2P{=}S$, $(i\text{-}Pr_2N)_2B$ R'= $(i\text{-}Pr_2N)_2P$, $Me(i\text{-}Pr_2N)_2P^{\oplus}$	307
8	 R= H, CH_3, Cl	308
9		308
10		308
11	 R= Aryl, R^1= H, Alkyl, Aryl R^2= H, Alkyl, Aryl X= O, S	309, 310

Table 10 (Continued)

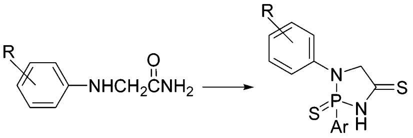
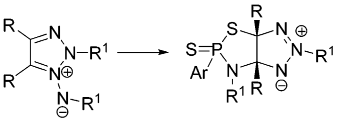
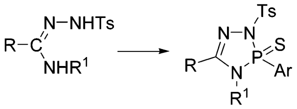
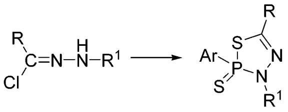
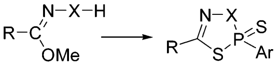
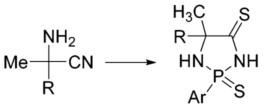
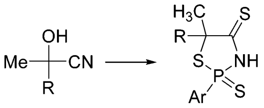
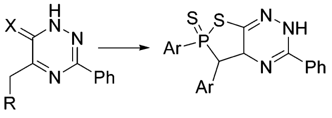
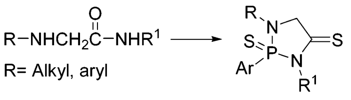
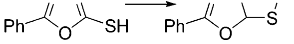
Entry	Reaction	Reference
12	 R= H, 2-Me, 3-Me, 4-Me, 2-Cl, 2,4-Cl, 2-Br, 4-Br 2-NO_2, 3-NO_2, 4-NO_2, 2,4-NO_2	311
13	 R= Ph, R,R= $(CH_2)_4$ R^1= Ph, 4-MeC_6H_4, 4-BrC_6H_4, 4-$NO_2C_6H_4$	312
14	 R= Me, CH_2CH_3 R^1= Aryl, alkyl	313
15	 R= CO_2Me, CO_2Et R^1= Aryl	314
16	 X= N-Ph, O R= H, Alkyl	315
17	 R= Alkyl	316
18	 R= Alkyl	316
19	 X= O, S R= Aryl	317
20	 R= Alkyl, aryl R^1= Alkyl, aryl	318-320
21		321

Table 10 (Continued)

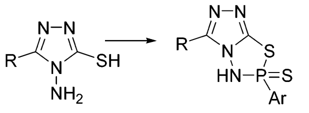
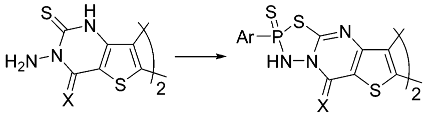
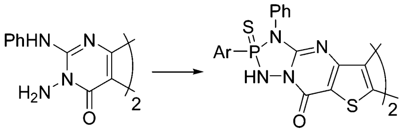
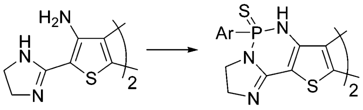
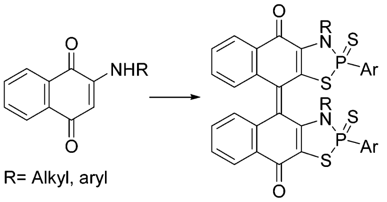
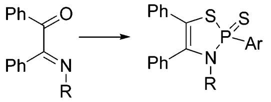
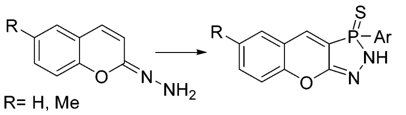
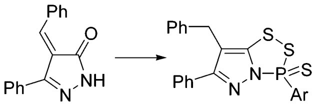
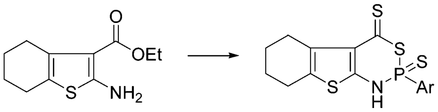
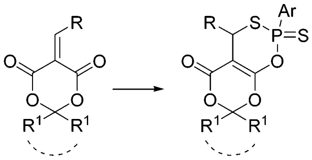
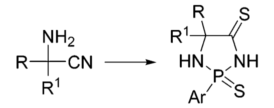
Entry	Reaction	Reference
22	 R= Me, Et, Ph	321
23	 X= O, S	322
24		322
25		323
26	 R= Alkyl, aryl	324
27	 R= Alkyl	325
28	 R= H, Me	326
29		56
30		56
31	 R= Aryl R^1= Me, Cyclopentyl	56
32	 R= H, Me R^1= Alkyl	327

Table 10 (Continued)

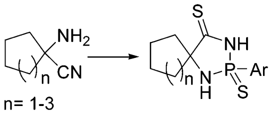
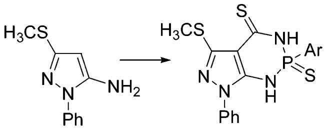
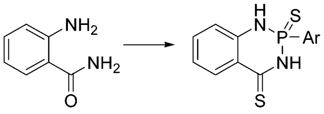
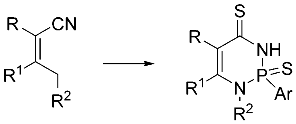
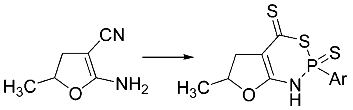
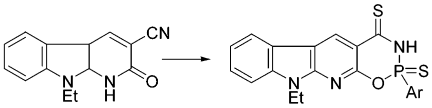
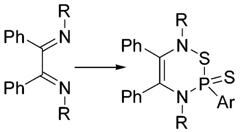
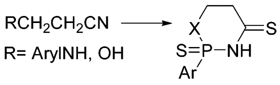
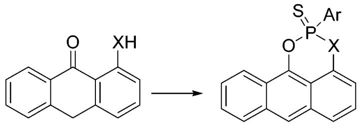
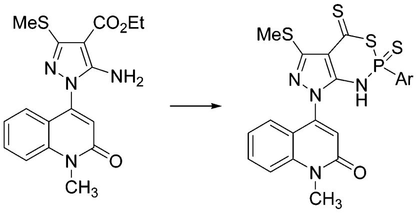
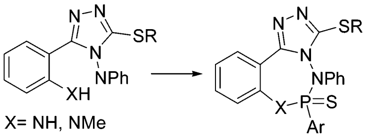
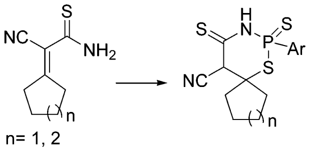
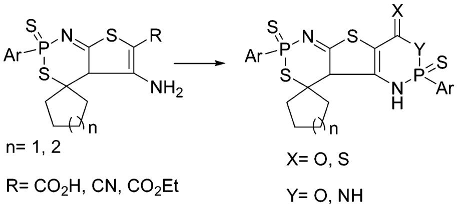
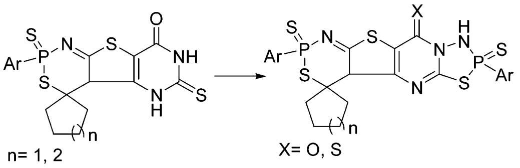
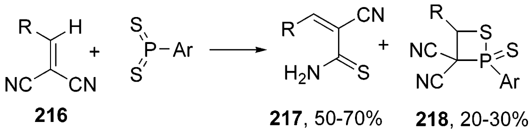
Entry	Reaction	Reference
33	 n= 1-3	327
34		327
35		328
36		329
37		329
38		330
39	 R= Aryl	331
40	 RCH_2CH_2CN R= ArylNH, OH X= ArylN, O	332
41	 X= NH, NMe, NPh, NCOMe	333
42		334
43	 X= NH, NMe R= H, Me	335, 336

Table 10 (Continued)

Entry	Reaction	Reference
44		337
45		337
46		337

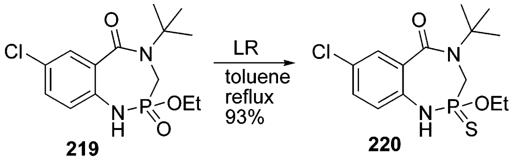
Scheme 68. Formation of the Smallest Ring 218



216 **217**, 50-70% **218**, 20-30%

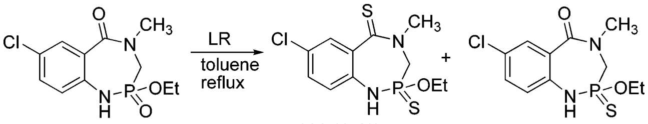
R= 2-HOPh, 4-MeOPh, 4-NO$_2$Ph, thienyl

Scheme 69. Conversion of P═O to P═S



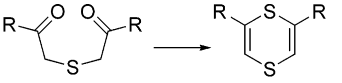
219 **220**

Scheme 70. Reaction of 221 with LR

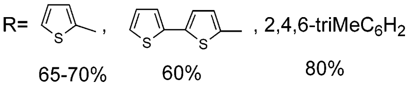


221 **222** (45%) **223** (16%)

Scheme 71. Treatment of 1,5-Diketone with LR



224 **225**

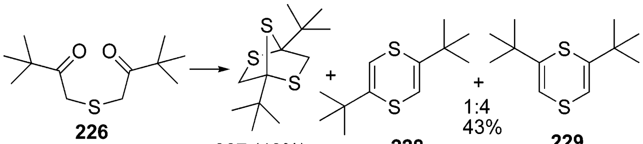


The biggest ring, which is an 8-membered ring, was obtained with 1,6- and 1,3-dinucleophilic systems. While the first one possessed half of LR, the latter had the whole LR in the ring (Table 11, entries 24 and 25, respectively).

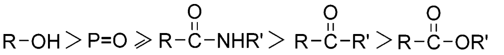
2.12. P═O to P═S

Use of LR for the replacement of the oxo group of phosphorus (P═O) with the thio (P═S) is commonly applied (Table 12). It appears that such a conversion can be accomplished without affecting the other functional groups such as imide, amide, lactam, and ester so that the Nishio's[23] relative reactivity order toward LR can be reorganized as follows.

Scheme 72. Reaction of 226 with LR



226 **227** (42%) **228** **229**



$$\text{R-OH} > \text{P=O} \gg \text{R-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-NHR'} > \text{R-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-R'} > \text{R-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-OR'}$$

The reaction is carried out in general fashion, i.e., refluxing toluene, xylene, benzene, or acetonitrile. In some cases, in CH_2Cl_2 at room temperature and a prolonged reaction time (~12 h) gave the result.[363]

Thionation of **219** using LR in refluxing toluene smoothly produced **220** in high yield (Scheme 69).[366] On the other hand, when the *t*-Bu group was replaced with a small group, methyl, **221**, two products **222** and **223** in 45 and 16% yields, respectively, were obtained (Scheme 70).

2.13. Dithiins

Similar to the synthesis of thiophenes from 1,4-diketones, treatment of the 1,5-diketones **224**, with LR in refluxing benzene, toluene, or chlorobenzene smoothly produced the 1,4-dithiins **225** as the sole products (Scheme 71).[367,368]

However, replacement of aromatic groups of **224** with *t*-Bu (**226**) and refluxing in toluene was reported to result in a mixture of products **227**, **228**, and **229** (Scheme 72).[368]

An interesting reaction, which led to the production of 1,4-dithiins as major and thiophenes as minor products, appeared as a result of the reaction of 1,8-diketones **230** with either LR or P_4S_{10} in refluxing toluene (Scheme 73).[369−375]

Table 11. Formation of Phosphorus Heterocycles (Ar= 4-MeOPh)

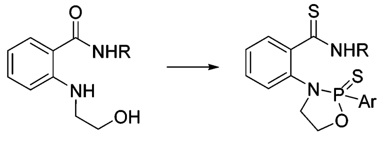
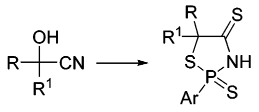
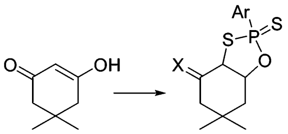
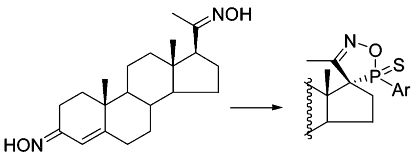
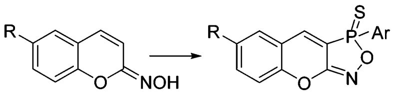
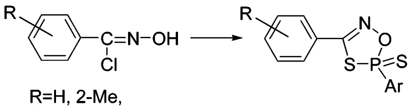
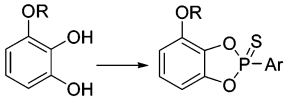
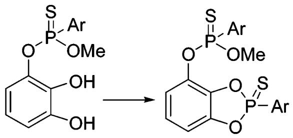
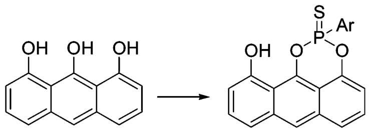
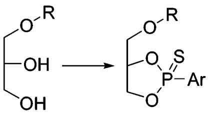
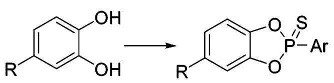
Entry	Reaction	Reference
1		339, 340
2	 R= Alkyl, H R^1= Alkyl	341, 342
3	 X= O, S	57
4		343
5	 R=H, Me	336
6	 R=H, 2-Me, 3-Me, 4-Me	54
7	 R= H, Me	53
8		53
9		53
10	 R= Alkyl	344
11	 R= alkyl, aryl	345

Table 11 (Continued)

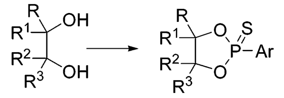
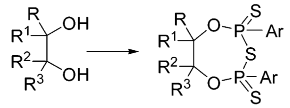
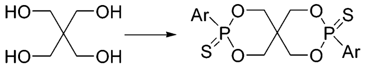
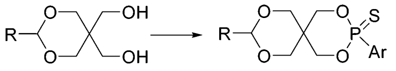
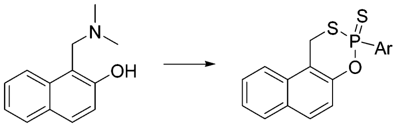
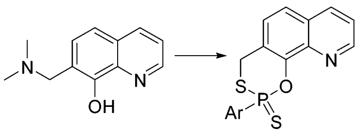
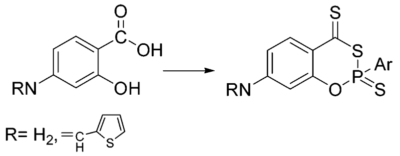
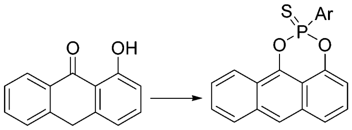
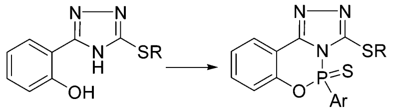
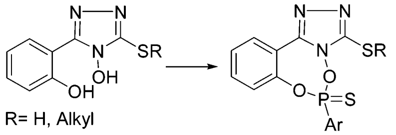
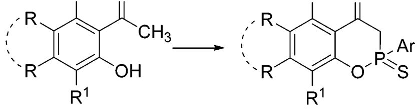
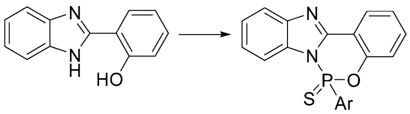
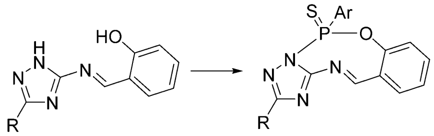
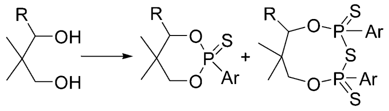
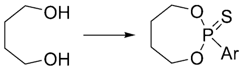
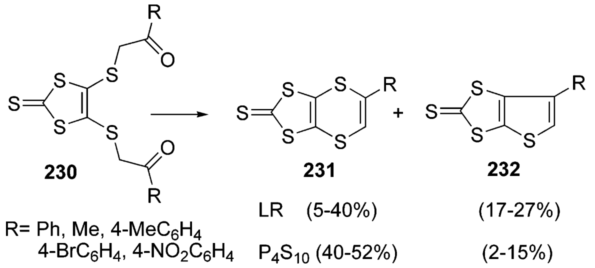
Entry	Reaction	Reference
12	 R, R^1, R^2, R^3= H, alkyl	346
13	 R, R^1, R^2, R^3= H, alkyl	346
14		347
15	 R=Ph, 4-MeC$_6$H$_4$	347
16		348
17		348
18		349
19		333
20	 R= H, Alkyl	335, 336
21	 R= H, Alkyl	335, 336
22	 R= H, Furyl R^1= H, OMe	350

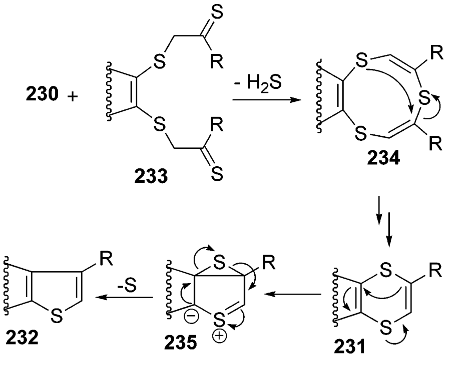
Table 11 (Continued)

Entry	Reaction	Reference
23		351
24	 R= H, CO$_2$Me	351
25	 R= Ph, Furyl, 4-ClC$_6$H$_4$, 2-ClC$_6$H$_4$, 3-NO$_2$C$_6$H$_4$ 4-MeC$_6$H$_4$, 4-FC$_6$H$_4$	352
26		346

Scheme 73. Reaction of 1,8-Diketone with LR and P_4S_{10}



Scheme 74. Possible Reaction Mechanism of Formation of Dithiins 231 and Thiophenes 232

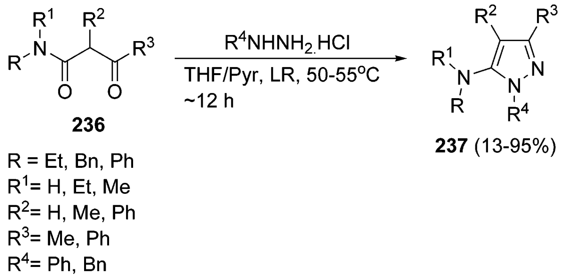


Its possible reaction mechanism was suggested to involve a nine-membered ring **234** formed after initial thionation of carbonyl groups **233** and elimination of H_2S (Scheme 74). The formed dithiin ring **231** then rearranges through **235**, and after elimination of elemental sulfur forms the thiophene heterocycle **232**.

2.14. Pyrazoles

Synthesis of 5-aminopyrazoles **237** having various alkyl and aryl groups was achieved by reacting *β*-ketoamide **236** with an alkyl or aryl hydrazine and LR combination in dry THF/pyridine (95/5) mixture at 55−60 °C (Scheme 75).[376]

Scheme 75. Formation of 5-Aminopyrazole 237



The success of this synthesis was based on the use of the advantages of the faster reaction of ketones with hydrazines compared with that of amides, and faster oxygen exchange with sulfur of amides compared to that with ketones.

The same group applied a similar reaction to the solid-phase synthesis of 5-*N*-arylamino pyrazoles **240** (Scheme 76).[377] Treatment of resin-immobilized *β*-ketoamide **238** with the same reagent mixture (arylhydrazine/LR/THF/Pyr) at 50−55 °C for 40 h gave resin-bound intermediate **239**, hydrolysis of which with trifluoroacetic acid yielded **240**.

2.15. Reduction

There are a few examples available in the literature indicating that treatment of sulfoxides with LR in solvents such as CH_2Cl_2 or THF at room temperature or in some cases even in lower temperatures in a shorter reaction time (15−30 min) produces sulfides (Table 13). Such a conversion was achieved in the presence of functional groups such as esters, hydroxides, tosyl, nitro, and halogens, which were not affected.

In a few special cases reductions of lactam carbonyl and benzoyl carbonyl to alkyl groups were reported. Treatment of the tetrahydroindol-2-one **241** with LR in refluxing benzene−DME mixture for 15 min gave the tetrahydroindol **242** (Scheme 77).[383]

Table 12. Conversion of P=O Group of the Corresponding Compound to P=S

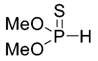
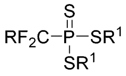
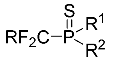
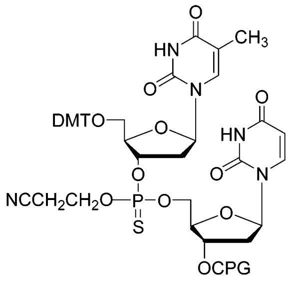
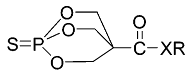
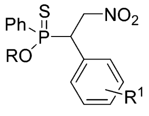
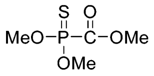
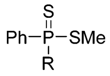
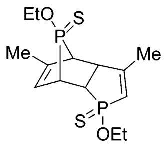
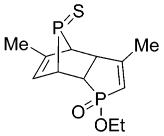
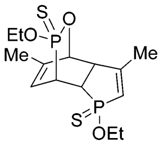
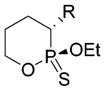
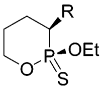
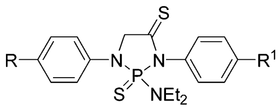
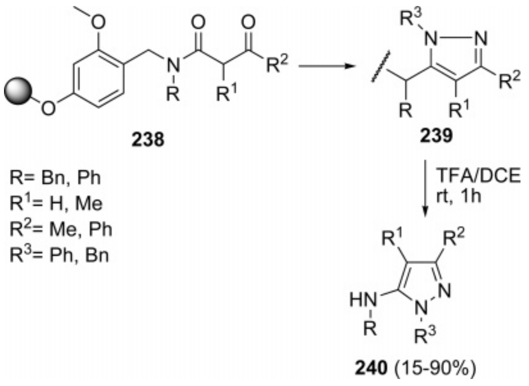
Entry	Product	Reaction conditions	Yield (%)	ref
1	 $\mathrm{\overset{MeO}{MeO}{>}\overset{S}{\overset{\|}{P}}{-}H}$	benzene, heat, 85-90 °C, 45 min	46	353
2	 $\mathrm{RF_2C{-}\underset{SR^1}{\overset{S}{\overset{\|}{P}}}{-}SR^1}$ R= H, Br, $C_{12}H_{25}$, c.C_6H_{11} $C_9H_{19}(CH_3)CH$, $PPhCH_2OC_6H_4CO$ R^1= CH_3CH_2, $PhCH_2$, $(CH_3)_3C$, Ph, Me	toluene (dry), Ar, reflux, 2 h	68-93	354,355, 356
3	 $\mathrm{RF_2C{-}\overset{S}{\overset{\|}{P}}{<}^{R^1}_{R^2}}$ R= *c*.C_6H_{11}, $C_9H_{19}CHCH_3$ R^1= Me, C_6H_5 R^2= OC_2H_5, C_6H_5	toluene, 100 °C, 120 min	91-96	356
4	 DMT = 4,4'-dimethoxytrityl CPG = Solid-phase controlled pore glass	CH_3CN, rt, 5 min	-	357
5	 X= O, S, NH, NBu^n, NMe, , NPr^i R= Me, *t*-Bu, *i*-Pr, Ph, Et, *i*-Bu, Bn, *n*-Pr, $CH_3(CH_2)_4$, $CH_3(CH_2)_7$	xylene (dry), 135 °C, 15 h	X= O, S 75-90 X= N, no rxn	358
6	 R= *n*-Bu, *n*-Pr,*i*-Pr, Et R^1= H, 4-MeO, 4-Me_2N, 3-PhO	toluene (dry), 95 °C, 15 h	76-88	359
7	 $\mathrm{MeO{-}\underset{OMe}{\overset{S}{\overset{\|}{P}}}{-}\overset{O}{\overset{\|}{C}}{-}OMe}$	acetonitrile, Ar, reflux, 6 h	good yield	360, 361
8	 $\mathrm{Ph{-}\underset{R}{\overset{S}{\overset{\|}{P}}}{-}SMe}$ R = *t*-Bu, 1-naphthyl	toluene, reflux	90, 76	362
9		benzene (dry), rt, 2 days	63	363

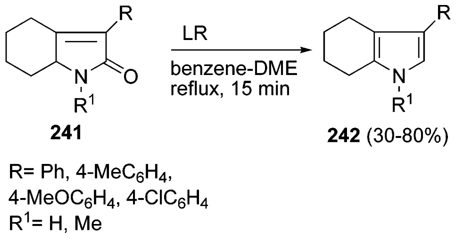
Table 12 (Continued)

Entry	Product	Reaction conditions	Yield (%)	ref
10		¼ LR, benzene (dry), rt, 7 h	76	363
11		CH_2Cl_2, rt, 12 h	-	363
12	 R= Me, Ph, $PhCH_2$	toluene, reflux, 3 h	20-68	364
13	 R= Me, Ph, $PhCH_2$	toluene, reflux, 3 h	17-68	364
14	 R= H, Me, Cl, Br R^1= H, Me, Cl, Br	toluene (dry), N_2, reflux	60	365

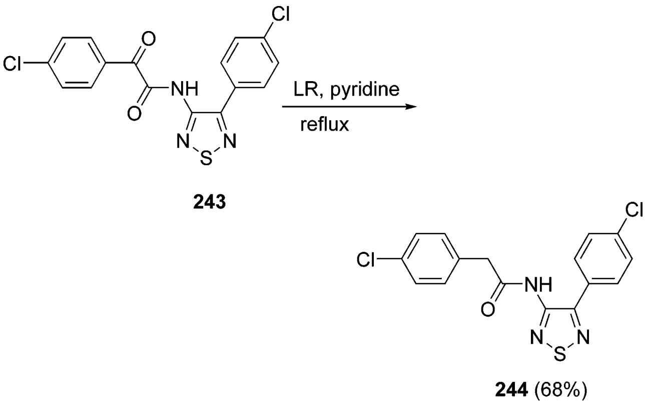
Scheme 76. Solid-State Synthesis of 5-Amino Pyrazoles



Scheme 77. Reaction of Indolone to Indol



Scheme 78. Reduction of 243



Reduction of the benzoyl carbonyl functional group to alkyl was achieved upon reacting **243** with LR in refluxing pyridine for 3.5 h to yield **244** in 68% (Scheme 78).[384]

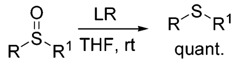
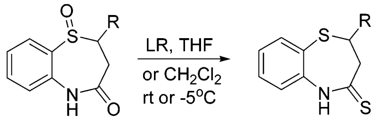
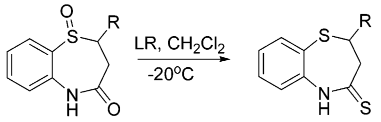
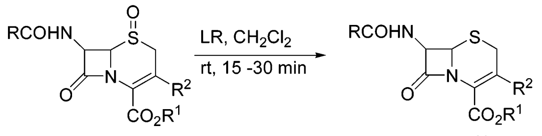
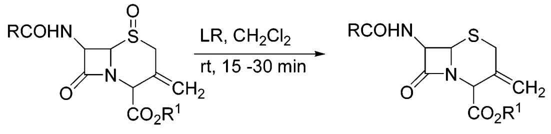
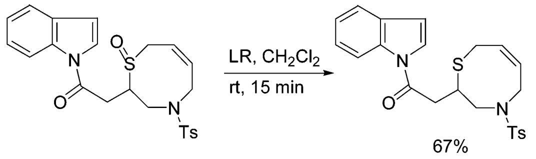
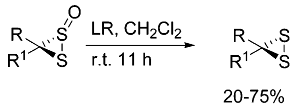
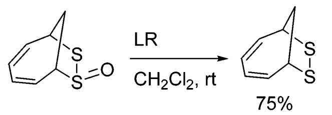
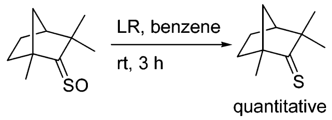
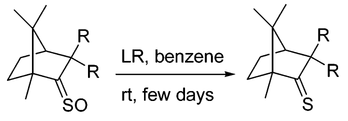
An example of the removal of disulfide with the action of LR or P_4S_{10} was reported.[385] The reaction of **245** with LR or P_4S_{10} in toluene at room temperature gave **246** in 44% yield (Scheme 79). Interestingly, the product **246** indicated that, rather than breaking the S−S bond, C−S bond breaking takes place. Moreover, the disulfide in the ring was not affected.

While the reduction of dithiirane 1-oxide with LR was successfully achieved (Table 13, entry 7),[381] an attempt to reduce **247** and **248** yielded the α-dithiones **249** and **250**, respectively (Scheme 80).[386]

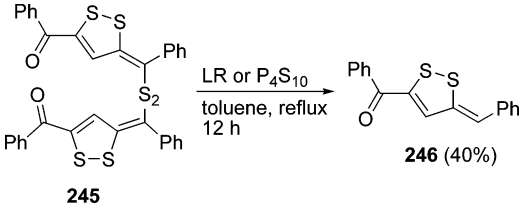
2.16. Peptides

LR was widely employed particularly for the selective transformation of amide groups of aminoacids and peptides to thioamides using the advantage of easier transformation of amides compared with other functional groups such as

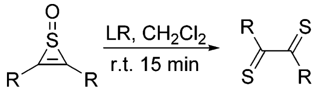
Table 13. Reduction of Sulfoxides to Sulfides with LR

Entry	Reaction	reference
1	 R= Ph, Bz CH_3SCH_2, R^1= Ph, Bz, Me CH_2CH, CH_2CO_2Me	378
2	 R= H, Ph	378
3	 R= H, Ph	378
4	 R= Bz, $PhOCH_2$ R^1= 4-$NO_2C_6H_4CO$, Bz R^2= Cl, Me, OH	379
5	 R= Bz, $PhOCH_2$ R^1= 4-$NO_2C_6H_4CO$,	379
6		380
7	 R = 1-Adamantyl, *t*-Bu, Ph R^1= *t*-Bu, 1- Adamantyl	381
8		382
9		39
10	 R-R= -$(CH_2)_4$- R-R= -$CH_2(2\text{-}C_6H_4)CH_2$-	39

Scheme 79. Reaction of Disulfide 245 with LR



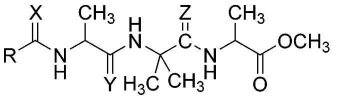
Scheme 80. Synthesis of α-Dithiones 249 and 250



247 R= 1-adamantyl **249** R= 1-adamantyl

248 R= *t*-Bu **250** R= *t*-Bu

ketones and esters, as Nishio et al. reported.[23] Due to the presence of various functional groups, peptide chains require adequate protection before the transformation is initiated. In most cases the thionation with LR was conducted in the presence of urethane, ketone, ester, and hydroxyl groups. Such a selective study was reported on protected, short, model peptide chains Boc-S-Ala-Aib-S-Ala-OMe **251** and Ac-S-Ala-Aib-S-Ala-OMe **252**.[387] Reaction of **251** with LR in toluene at 100 °C for 45 min gave a mixture of **253** (27%) and **254** (14%). On the other hand replacing the *tert*-butoxy group with methyl **252** and then subjecting it to the thionation reaction with LR in THF at room temperature for overnight yielded the thionation of peripheral amide group **255**. In all cases ester and urethane groups remained untouched. Similar reactions of LR with peptides having different chain lengths were reported.[388−396]

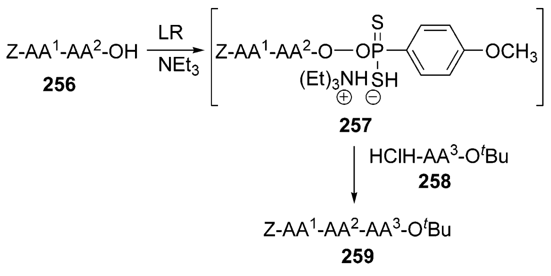


251 R= $(CH_3)_3C$-O, X= Y= Z= O
252 R= CH_3, X= Y= Z= O
253 R= $(CH_3)_3C$-O, X= Z= O, Y= S
254 R= $(CH_3)_3C$-O, X= O, Y= Z= S
255 R= CH_3, X= S, Y= Z= O

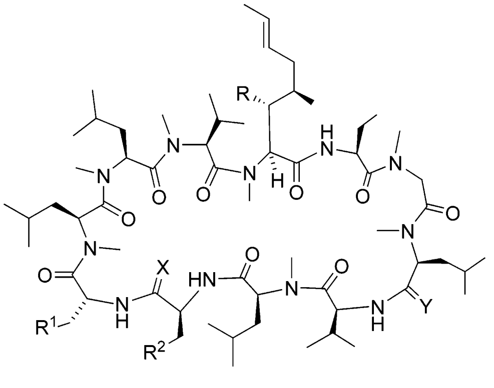
In the synthesis for elongation of peptides, LR was used as a coupling reagent.[397] It was reported that at −15 °C LR was added to *N*-protected amino acid or peptide **256** dissolved in a triethylamine/CH_2Cl_2 mixture (Scheme 81). It was then reacted with amino acid ester hydrochloride **258** to yield the peptide **259** through the intermediate **257**.

Thionation of peptides is not limited only to the short-chain peptides. There are examples indicating that macrocyclic peptides could be thionated as well. Indepth studies on the thionation of cyclosporine A **260** were reported wherein selective thionation of lactam amides was achieved either by refluxing in xylene for 30 min (**261**−**263**)[398,399] or in DMPU (3,4,5,6-tetrahydro-1,3-dimethylpyrimidin-2-(1*H*)-one) for 2−4 days which yielded various thionated products including the hydroxyl group.[400]

Scheme 81. Use of LR as a Coupling Reagent in Peptide Synthesis



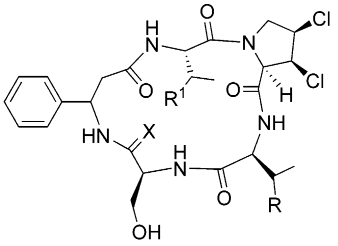
AA^1-AA^2-AA^3 = Pro-Val-Pro, Leu-Phe-Val



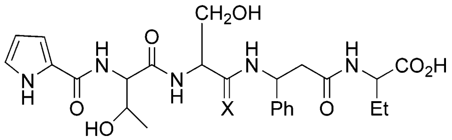
260 R= OH, R^1= R^2= H, X= Y= O
261 R= OAc, R^1= R^2=H, X= Y= S
262 R= OAc, R^1= R^2= H, X= S, Y= O
263 R= OAc, R^1= R^2= H, X= O, Y= S
264 R= SH, R^1= R^2= H, X= Y= O

Selective conversion of the hydroxyl group of cyclosporin A to thiol **264** was achieved by refluxing in toluene with LR for 30 min.[401]

Thionation of cyclic peptides astins A **265**, B **266**, C **267**, and a cyclic astin B **271** was performed in dioxane at 50 °C for 12 h which resulted in the formation of thionated analogues **268**, **269**, **270**, and **272**, respectively.[402,403]



265 R= H, R^1= OH, X= O
266 R= OH, R^1= H, X= O
267 R= R^1= H, X= O
268 R= H, R^1= OH, X= S
269 R= OH, R^1= H, X= S
270 R= R^1= H, X= S

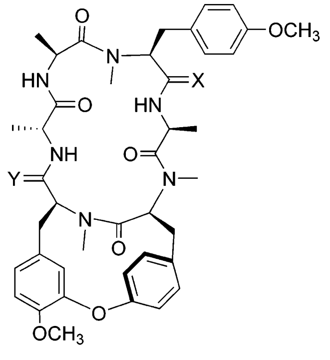


271 X= O
272 X= S

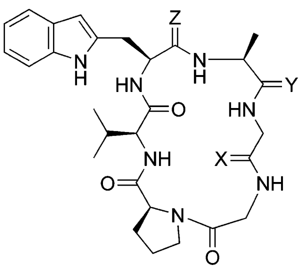
In a similar fashion, the same group reacted the cyclic peptides RA-VII **273**[404,405] and Segatalins A **274** and B **275**[406] with LR in dioxane at 50 °C for 72 h and 30 min, respectively, to produce their thionated analogues **276**−**281**.

2.17. Nucleosides, Purines, and Pyrimidines

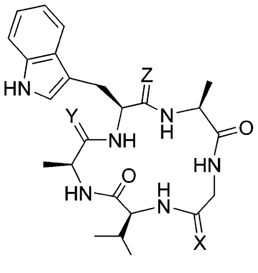
Thionation of nucleosides, purines, and pyrimidines with LR is widely applied to obtain their sulfur analogues, mainly



273 X= Y= O
276 X= S, Y= O (80%)
277 X= Y= S (3%)



274 X= Y= Z= O
278 X= Z= S, Y= O
279 X= Y= S, Z= O

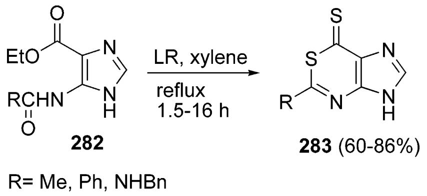


275 X= Y= Z= O
280 X= Y= S, Z= O
281 X= Z= S, Y= O

for biological purposes (Table 14). To avoid the side reactions, the hydroxyl groups are properly protected as ethers or esters. It appears that when two oxo groups are present in pyrimidine at the 2- and 4-positions, the use of LR as a thionating agent for the oxo group at the 4-position is quite convenient. An excess of LR helps for thionation of both oxo groups (Table 14, entry 9). It is also applicable to purines that, in the presence of two oxo groups, thionation of one of them is widespread.

Treatment of the imidazole **282**, having ester and amide groups, with LR yielded the purine analogue **283** with a dithiolactone ring (Scheme 82).[421]

Scheme 82. Reaction of the Imidazole 282 with LR

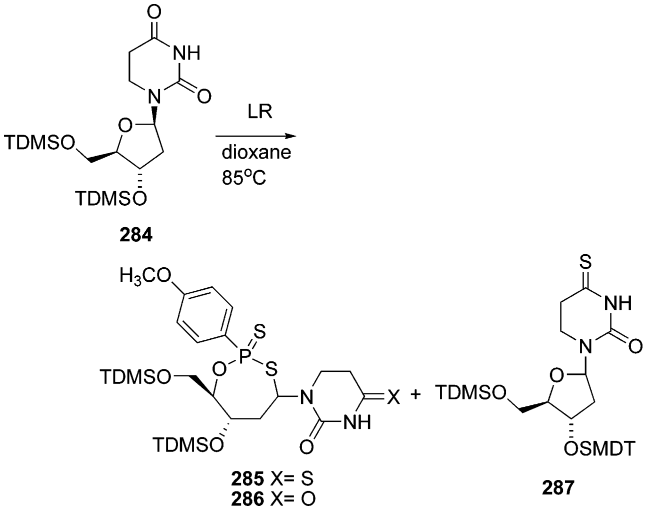


The reaction of the nucleoside **284** with LR resulted in some interesting products (Scheme 83).[421] The reaction was performed in dioxane at 85 °C which yielded a mixture of products **285**−**287** in 30 min. On the other hand extension of the reaction time resulted in the complete conversion to **287**. A possible mechanism for **285** and **286** was suggested as the following. An initial attack from oxygen to the LR formed the **288**, which caused ring-opening product **289**. Then, the nucleophilic attack of the sulfur ion to the imine yielded the products **285** and **286** (Scheme 84).

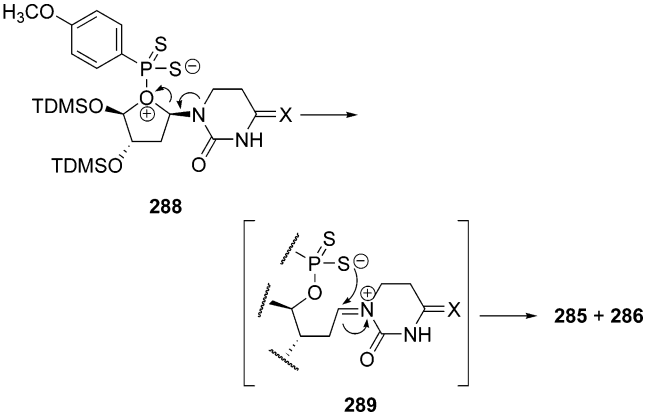
2.18. Miscellaneous

Phenanthrene rings were introduced into polymer **293** chains through cyclization of 2,2′-dibenzoylbiphenyl **290** units using LR (Scheme 85).[423−427] The reactions were either performed in refluxing toluene or 1,1,2,2-tetrachloroethane under N_2 atmosphere. The possible reaction mechanism was suggested to involve an initial conversion of oxo groups to thiones **291**, which was followed by intramolecular cyclization to give **292** and then elimination of sulfur to produce the phenanthrene ring in the polymer chain.

Scheme 83. Reaction of 284 with LR



Scheme 84. Possible Reaction Mechanism of 284



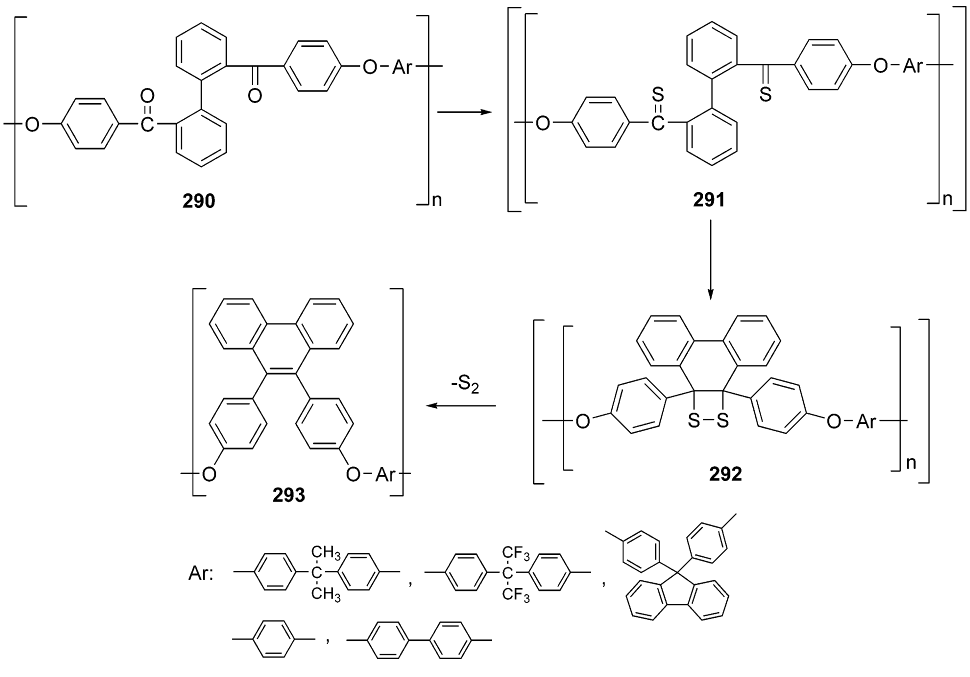
Thionation of polyamides was carried out to obtain poly(*N*,*N*′-didecyldodecanedithioamide) (PTA-12.10), poly(*N*,*N*’-didecyl-4,9-dioxadodecanedithioamide) (PTA-dioxa12.10), and poly(*N*,*N*′-didecyl-4,7,10-trioxatridecanedithioamide (PTA-trioxa13.10).[428] It was reported that complete thionation was achieved in toluene at 100 °C when the polymer samples were finely divided. Ether−amide block copolymer, poly(ether-*block*-amide), PEBA, could be used as pellets for partial modification.

During the synthesis of a potent α-adrenergic agent, LR was used to construct its imidazole ring.[429] Treatment of the aminolactam **294** with LR in the presence of d-10 camphorsulfonic acid in refluxing xylene for 72 h under nitrogen atmosphere afforded the imidazole ring **295** in 38% (Scheme 86).

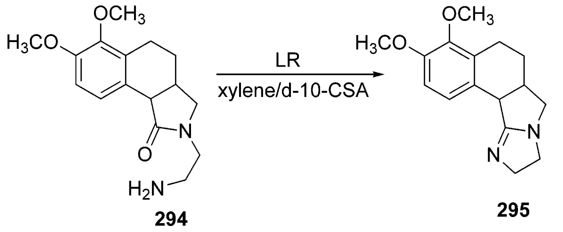
Conversion of oxathiazine-*S*-oxides into dithiazoles upon reaction with LR was reported.[430] Reaction of *S*-oxides **296** with LR in refluxing toluene for 1 h produced the dithiazoles **297**, the possible reaction mechanism of which is depicted in Scheme 87.

An interesting reaction of LR together with elemental sulfur was reported in which the unsaturated carbonyl compounds **298** or **299** produce trithiapentalene **300** (Scheme

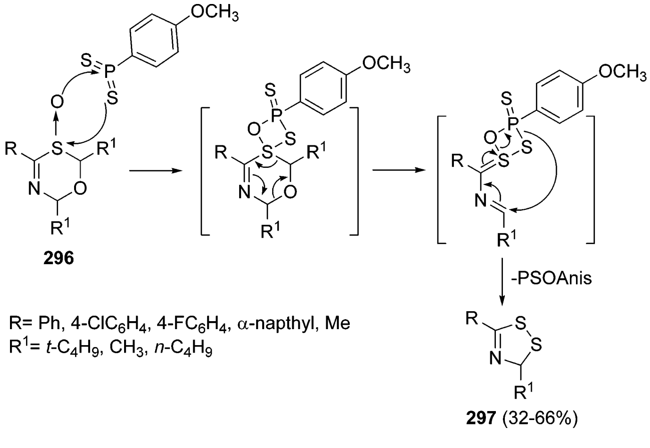
Scheme 85. Suggested Reaction Mechanism for 293



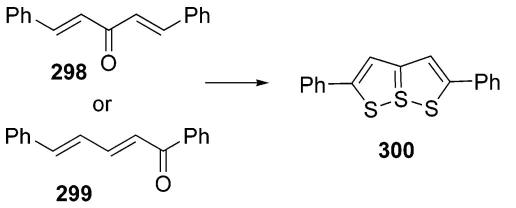
Scheme 86. Construction of Imidazole Ring Using LR



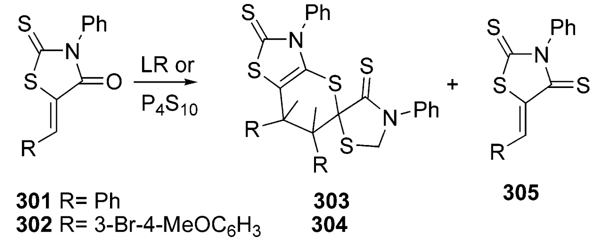
Scheme 87. Conversion of Oxathiazine-*S*-oxides into Dithiazoles



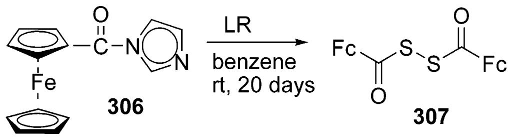
Scheme 88. Formation of Trithiapentalene 300



Scheme 89. Thionation of 301 and 302



Scheme 90. Synthesis of Diferrocenyl Disulfide 307



88).[431] The carbonyl compounds were initially allowed to react with LR in acetonitrile at room temperature for 30 min, and then addition of sulfur and TEA led to the formation of **300**.

Thionation reaction of **301** and **302** with either P_4S_{10} or LR in refluxing xylene for 2 h yielded unexpected spiro-type products **303** and **304**, respectively, along with **305** (Scheme 89).[432]

Treatment of ferrocenoyl imidazole **306** with LR in benzene at room temperature for 20 days resulted in the production of the dimer diferrocenoyl disulfide **307** in 52% (Scheme 90).[433]

Synthesis of poly(ferrocenylanthracene), having disulfide units, was reported.[434] Reaction of 2-ferrocenylanthraquinone **308** and 2,6-diferrocenylanthraquinone **309** with LR in refluxing chlorobenzene for 1−5 h yielded the polymers **310** and **311** in 45 and 81% yields, respectively.

Dimerization of furan-2,3-diones **312** and pyrrole-2,3-diones **313** was observed when they were reacted with LR in xylene at 60−70 °C for 2 h in between 40−50 and 30−45% yields, respectively (Scheme 91).[435]

Thioanalogues of squarylium dyes (SQ) were obtained upon treatment of SQs **314** with LR (or P_4S_{10}) in the presence

Table 14. Thionation Products of the Corresponding Nucleosides, Purines, and Pyrimidines

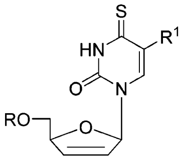
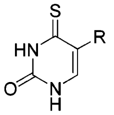
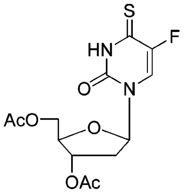
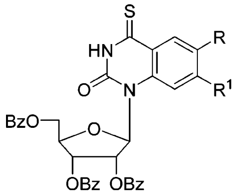
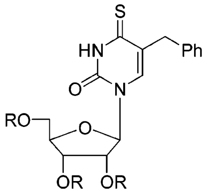
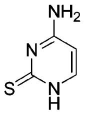
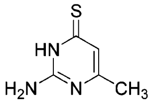
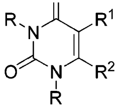
Entry	Product	Reaction conditions	Yield (%)	ref
1	 R= Bz, H R^1= Me, H	toluene, 80 °C, N_2, 12 h	75-94	407
2	 R= H, F, Me	i- HMPA (dry), Ar, 100-120 °C, 1-4 h ii- pyridine, Ar, 140 °C, 2-8 h	i- 64-78 ii- 69-78	408
3		dioxane (dry), reflux,1 h	94	409
4	 R= H, Me, OMe, Cl, Br R^1= H, Me, OMe	toluene, reflux, 20 h	57-99	410
5	 R= Bz, Tol	1,2-dichloroethane, reflux, Ar, 5-8 h	65-81	411
6		dioxane, 100 °C, 16 h	80	412
7		dioxane, 100 °C, 0.5 h	74	412
8	 R= H, Me R^1= H, F, Me, Cl R^2= H, Me, Et, Pr, *i*-Pr, CF_3, CH_2Cl, CH_2F	2 eq LR, dioxane, 100 °C, 0.5-3 h	80-90	412

Table 14 (Continued)

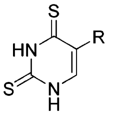
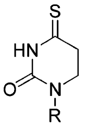
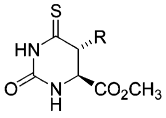
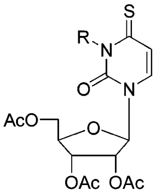
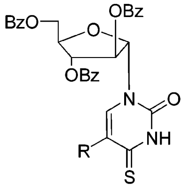
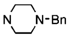
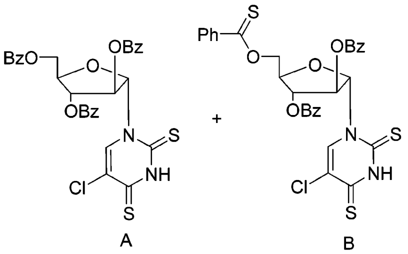
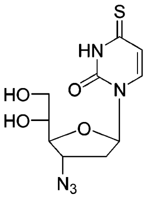
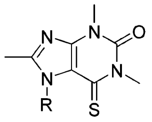
Entry	Product	Reaction conditions	Yield (%)	ref
9	 R= Me, F	2 eq (or excess) LR, dioxane, 100 °C, 16 h	90	412
10	 R= H, Me	THF, rt, 16 h	83-88	412
11	 R= Me, Et, propyl	THF(dry), rt, 36 h	61-69	413
12	 R= CH_2Ph, $CH(CH_3)Ph$ $COCH_2Ph$, CH_2-3,4-diMeC_6H_3	benzene (dry), reflux, overnight	52-90	414
13	 R= Cl, Me, 	toluene, N_2, 80 °C, 4-15 h	43-84	415
14		toluene, N_2, 80 °C, 24 h	A= 29 B= 14	415
15		i- CH_3CN, Ac_2O, 4-(dimethylamino)pyridine, rt, 30 min ii-evaporate all the solvent, LR, dichloroethane, reflux, 45 min	34	416
16	 R= β-D-(2,3,4,6-tetra-O-acetyl) glucopyranosyl β-D-(2,3,4,6-tetra-O-acetyl) glacto pyranosyl	toluene, reflux	70	417, 418

Table 14 (Continued)

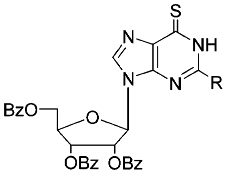
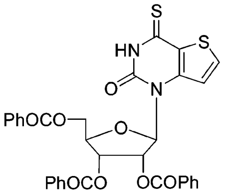
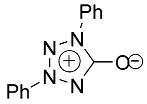
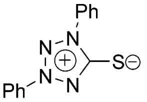
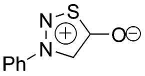
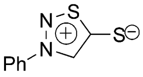
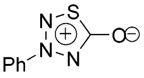
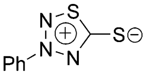
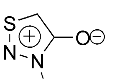
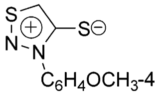
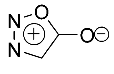
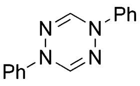
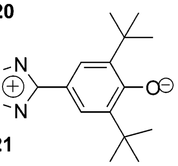
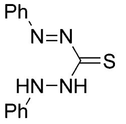
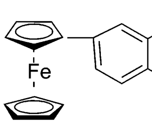
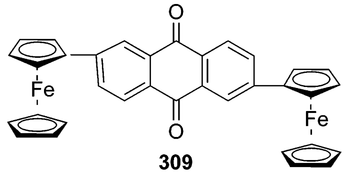
Entry	Product	Reaction conditions	Yield (%)	ref
17	 R= H, NHBz	pyridine, reflux, 6 h	90,86	419
18		toluene, reflux, 24 h	62	420

Table 15. Thionation of Mesoionic Olates with LR

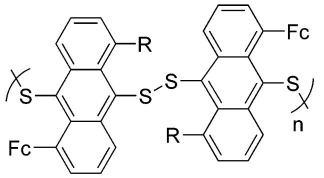
 **316**	 **322** (93%)
 **317**	 **323** (98%)
 **318**	 **324** (93%)
 **319**	 **325** (16%)
 **320**	 **326** (100%)
 **321**	 **327** (100%)



308

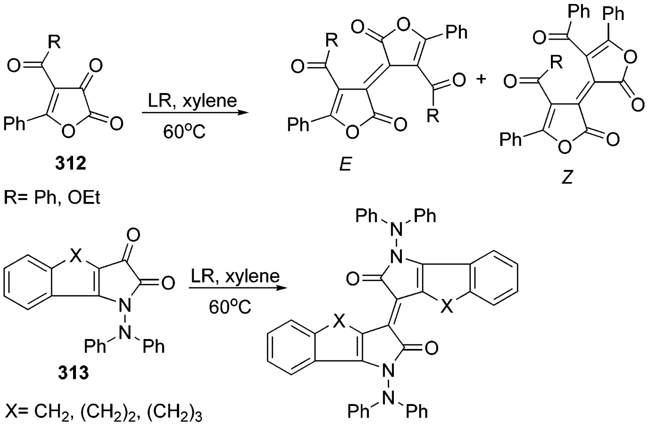


309

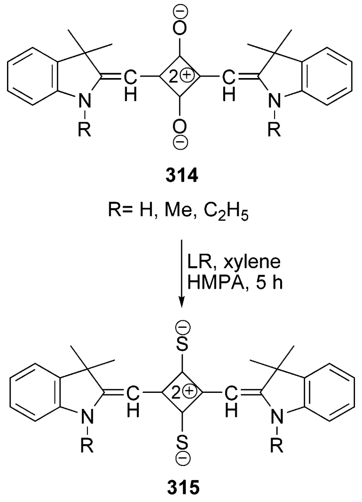


310 R= H
311 R= Ferrocenyl

Scheme 91. Dimerization Reactions of 312 and 313



Scheme 92. Thionation of SQ Dyes

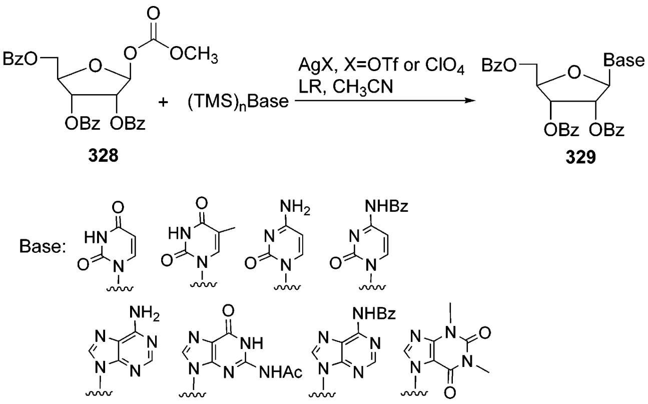


of HMPA in refluxing xylene for 5 h, which yielded the analogue **315** in 32−46% yield (Scheme 92).[436]

Reaction of mesoionic olates **316**−**319** with LR in refluxing toluene from 30 min to 18 h produced their thiolate analogues **322**−**325** (Table 15).[437] On the other hand the reactions of **320** and **321** with LR did not give the expected products. They yielded **326** and **327**, respectively.

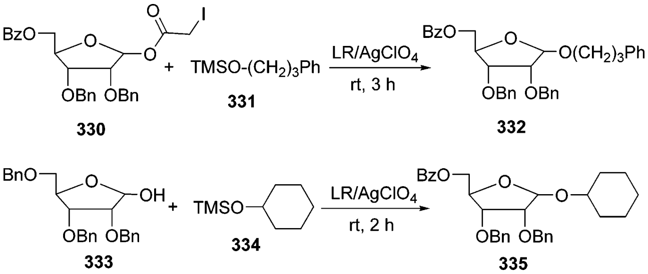
Combinations of LR and silver salts such as $AgClO_4$ and AgOTf were successfully applied for the synthesis of *β*-D-

Scheme 93. Synthesis of Ribonucleosides Using Combination of Silver Salts and LR



328
329

Scheme 94. Synthesis of Ribofuranosides Using LR/AgClO$_4$ Combination



330
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332
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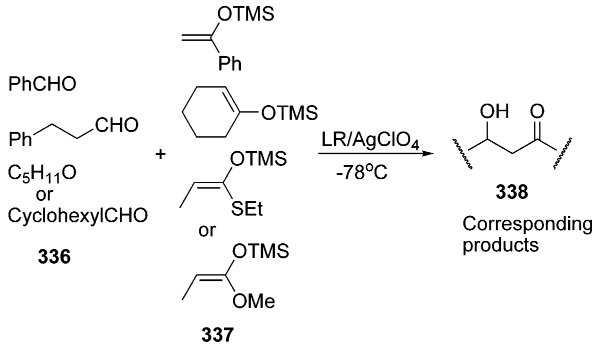
335

Scheme 95. Aldol Reactions Using LR/AgClO$_4$ Combination



336
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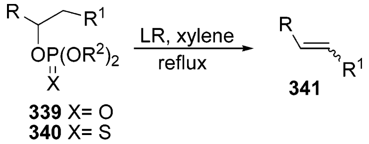
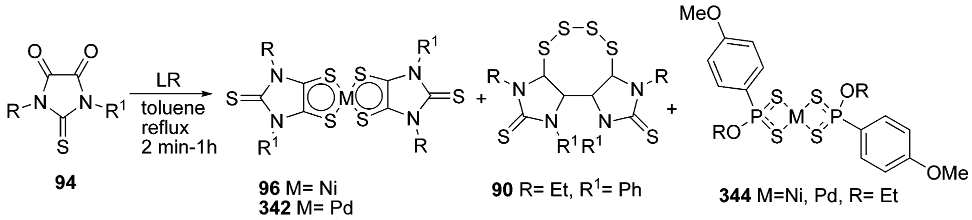
338

Scheme 96. Synthesis of Olefins from Phosphates or Thiophosphates



339 X= O
340 X= S
341

Scheme 97. Synthesis of Metal Dithiolanes



94

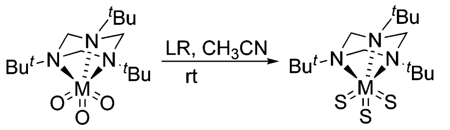
R = Me, Et
R^1= Et,*i*-Pr, *n*-pentyl,
Ph, 4-ClC$_6$H$_4$, 4-MeOC$_6$H$_4$,
n-nonyl, 4-NO$_2$C$_6$H$_4$

96 M= Ni
342 M= Pd
343 M= Pt

90 R= Et, R^1= Ph

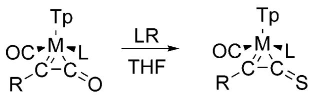
344 M=Ni, Pd, R= Et

Scheme 98. Thionation of the Complexes 345 and 346



345 M= Mo
346 M= W
347 M= Mo (52%)
348 M= W (51%)

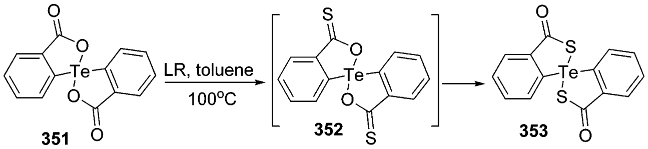
Scheme 99. Synthesis of Thioketenyl Complexes 350



349
350

L= PPh$_3$, P(OMe)$_3$, PMe$_2$Ph
R= 4-MeC$_6$H$_4$
Tp=κ^3-HB(pz)$_3$
M= W(PPh)$_3$, Mo(PPh)$_3$
W(PMe$_2$Ph), Mo{P(OMe)$_3$}

Scheme 100. Synthesis of Spirotellurane Having Sulfur Atoms



351
352
353

ribonucleosides,[438,439] and in aldol[440] and Diels–Alder[441] reactions. Reaction of ribofuranosyl carbonate **328** with various trimethylsilylated bases such as uracil, thymine, theophylline, *N*^{4}-*N*^{4}-benzoylcytosine, *N*^{6}-benzoyladenine, and *N*^{2}-acetylguanine at 60–80 °C for 4–6.5 h yielded the ribonucleosides **329** from 81% to quantitative yields (Scheme 93).[438]

Syntheses of α-D- and *β*-D-ribofuranosides **332**, **335** were achieved from the reaction of ribofuranoses **330** and **333** with trimethylsilylated nucleophiles **331** and **334**, respectively, applying the same LR/AgClO$_4$ combination (Scheme 94).[439] The reaction was performed in various solvents such as CH$_2$Cl$_2$, 1,2-dichloroethane, benzene, toluene, (Et)$_2$O, and CH$_3$CN at room temperature, which yielded the products in between 77–93% (Scheme 94).

Aldol reactions of various aldehydes **336** with trimethylsilyl enol ethers **337**, using the LR/AgClO$_4$ combination in CH$_2$Cl$_2$, toluene, or EtCN at −78 °C gave the corresponding products **338** in 59–89% yields (Scheme 95).[440]

LR was applied for the synthesis of olefins **341** from phosphates **339** and thiophosphates **340** in refluxing xylene, toluene, or benzene in 50–79% yields (Scheme 96).[442]

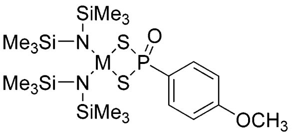
On the way to synthesize new metal dithiolenes **96**, **342**, **343** from imidazolidine-2-thione-4,5-diones **94**, treatment of **94** with LR in the presence of desired metals as powder or in chloride form in refluxing toluene between 20 min to 1 h yielded **96**, **342**, and **343** along with **90** and **344** (Scheme 97).[443]

Conversion of the oxo groups of various ligands to thio with LR was reported. Treatment of the complexes **345** and **346** with LR in acetonitrile at room temperature gave the fully thionated products **347** and **348** in 52 and 51% yields, respectively (Scheme 98).[444]

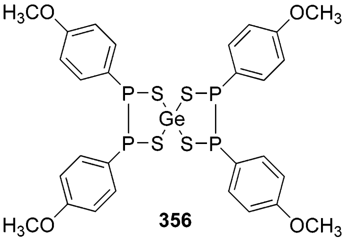
Thioketenyl complexes **350** were synthesized in high yields upon reacting **349** with LR in THF (Scheme 99).[445]

Synthesis of spirotellurene having two sulfur atoms was reported wherein the reaction of **351** with LR in toluene at 100 °C for 2 days gave the unexpected product **353** in 17% yield. It was believed that the product was obtained through the intermediate **352** (Scheme 100).[446]

Cleavage of LR was observed during the preparation of metal complexes. Treatment of LR with bis[bis(trimethylsilyl)amino]germanium(II) and bis[bis(trimethylsilyl)amino]tin(II) produced the complexes **354** and **355**.[447] On the other hand, the reaction with 1,3-di-*tert*-butyl-1,3,2-diazagermol-2-ylidene yielded a spiro product **356**.



354 M= Ge
355 M= Sn

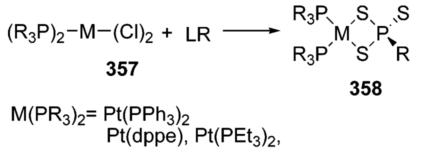


356

It was reported that the reaction of LR with bis-phosphine-dihalide complexes of Ni, Pd, and Pt **357** resulted in the cleavage of LR to produce **358** (Scheme 101).[448]

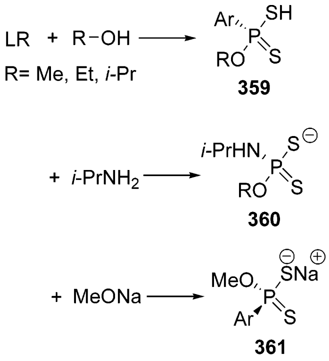
In some cases, preparation of metal complexes of LR was performed after cleavage of LR with bases and nuclephiles. Treatment of LR with alcohols,[449] amine, and base[450,451] resulted in the production of dithiophosphonic acids **359**, phosphonodithioate **360**, and amidophosphonodithioate **361** (Scheme 102). Their reactions with chelating agents yielded the metal complexes **362**, **363**, and **364** (Scheme 103).

Scheme 101. Reaction of Bis-phosphine-dihalide Complexes with LR



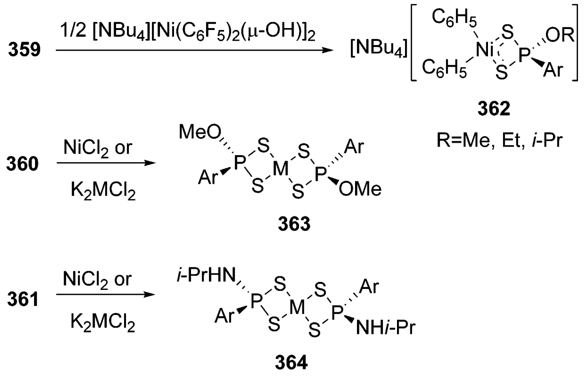
$M(PR_3)_2$= $Pt(PPh_3)_2$
$Pt(dppe)$, $Pt(PEt_3)_2$,
$Pt(PMe_2Ph)_2$, $Pd(dppe)$
$Pd(PMe_2Ph)_2$, $Ni(dppe)$

Scheme 102. Cleavage of LR with Bases and Nucleophiles

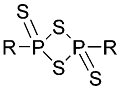


Ar= 4-MeOC_6H_4

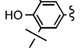
Scheme 103. Formation of Metal Complexes of 359, 360, and 361

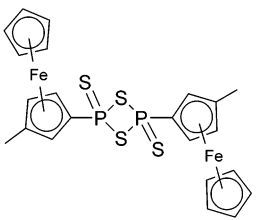


Various analogues of LR were reported to be synthesized. Modification was performed with the replacement of the anisole moiety of LR with some groups such as MeS (Davy's reagent) **365**,[452,453] PhS (Yokoyama's reagent) **366**,[305,453−455] 4-$C_6H_5OC_6H_4$ **367**,[456,457] Ph, *t*-Bu, *i*-BuS, EtS, 4-EtOC_6H_5, Et_2N, CH_3CH_2, 3,5-di-*tert*-butyl-4-hydroxyphenyl **368**,[453] ferrocenyl **369a**, **369b**,[458,459] and naphthalenyl **370**, **371a**−**371c**.[460]

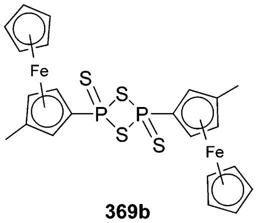


365 R= MeS (Davy's reagent)
366 R= PhS (Yokoyama's reagent)
367 R= 4-$C_6H_5OC_6H_4$
368 R= Ferrocenyl, Ph, *t*-Bu, *i*-BuS,
4-EtOC_6H_4, Et_2N, EtS, CH_3CH_2,

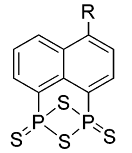




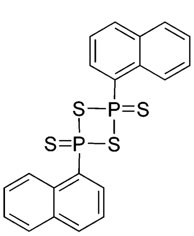
369a



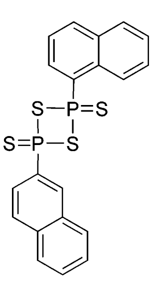
369b



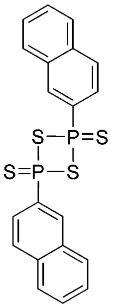
370 (R= H, MeO)



371a



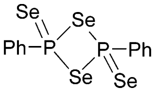
371b



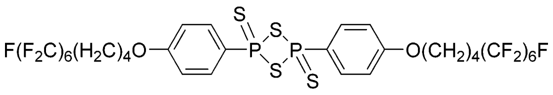
371c

A selenium analogue of LR, which is called Woollins reagent **372**, was reported to be synthesized by the reaction of $(PhP)_5$ with selenium in refluxing toluene.[461,47] It was successfully applied for the synthesis of seleno amides[462,463] and benzoselenophenes.[464]

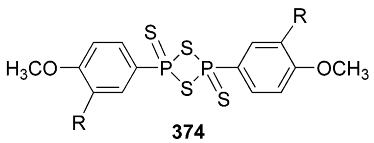
Recently, two fluorous analogues of LR **373**[465] and **374**[466] were reported. They were indicated to be successfully used for the thionation of carbonyl compounds.



372 (Woollins reagent)



373



374

R= $(CH_2)_5(CF_2)_7CF_3$

3. Conclusion

Lawesson's reagent has now been an indispensable reagent for sulfur chemistry particularly for converting almost all kinds of oxo groups to thios, which are important functional groups to perform various organic reactions or to use them as end products in material, medicinal, etc. chemistry. Lawesson's reagent fast and slow reactions toward the functional groups such as alcohols, P═Os, amides, ketones, and esters provide the synthetic chemists with a tool of designing their synthetic methodology accordingly. Moreover, LR is widely applied for the synthesis of almost all kinds of heterocyclic compounds incorporating sulfur atom(s). Its range varies form thiophene to thiazole, thiazine, thiadiazole, thiadiazine, dithiin and pyrazoles. It finds widespread application in thionation reactions of peptides, nucleosides, purines and pyrimidines. Reduction of sulfoxides to sulfides could be concluded as another useful reaction of LR.

LR is a reagent that can make surprises by giving unexpected reactions, results of which lead the chemists to new methodologies and reactions.

4. Acknowledgment

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5. References

(1) Campaigne, E. *Chem. Rev.* **1946**, *39*, 1.
(2) Cava, M. P.; Levinson, M. I. *Tetrahedron* **1985**, *41*, 5061.
(3) Cherkasov, R. A.; Kutyrev, G. A.; Pudovik A. N. *Tetrahedron* **1985**, *41*, 2567.
(4) Nagaoka, J. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 1138.
(5) Brillon, D. *Sulfur Rep.* **1992**, *12*, 297.
(6) Jesberger, M.; Davis, T. P.; Barner, L. *Synthesis* **2003**, 1929.
(7) Scheibye, S.; Pedersen, B. S.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 229.
(8) Pedersen B. S.; Scheibye, S.; Nilson, N. H.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223.
(9) Scheibye, S.; Pedersen, B.S.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 299.
(10) Pedersen B. S.; Scheibye, S.; Nilson, N. H.; Clausen, K.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 293.
(11) Henry, L. *Ann. Chem. Pharm.* **1869**, *148*, 152.
(12) Wislicenus, J. *Z. Chem.* **1869**, 324.
(13) Polshettiwar, V. *Synlett* **2004**, 2245.
(14) Lecher, H. Z.; Greenwood, R. A.; Whitehouse, K. C.; Chau, T. H. *J. Am. Chem. Soc.* **1956**, *78*, 5018.
(15) Perregaard, J.; Scheibye, S.; Meyer, H. J.; Thomsen, I.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1977**, *86*, 679.
(16) Ozturk T. Unpublished results.
(17) Oshida, H.; Ishii, A.; Nakayama, J. *Tetrahedron Lett.* **2004**, *45*, 1331.
(18) Fay, P.; Lankelma, H. P. *J. Am. Chem. Soc.* **1952**, *74*, 4933.
(19) Hoffman, H.; Schumacher, G. *Tetrahedron Lett.* **1967**, *31*, 2963.
(20) Mazitova, F. N.; Khairullin, V. K. *ZhOKn* **1981**, *51*, 958.
(21) Kempe, R.; Sieler, J.; Beckmann, H.; Ohms, G. *Z. Kristallogr.* **1992**, *202*, 159.
(22) Grossmann, G.; Ohms, G.; Krüqer, K.; Jeschke, G. *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, *107*, 57.
(23) Ori, M.; Nishio, T. *Heterocycles* **2000**, *52*, 111.
(24) Moriyama, S.; Karakasa, T.; Motoki, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2540.
(25) Karakasa, T.; Moriyama, S.; Motoki, S. *Chem. Lett.* **1988**, 1029.
(26) Markovic, R.; Rasovic, A.; Baranac, M.; Stojanovic, M.; Steel, P. J.; Jovetic, S. *J. Serb. Chem. Soc.* **2004**, *69*, 909.
(27) Mishra, M.; Chowdhury, S. K. D.; Mahalanabis, K. K. *Synth. Commun.* **2004**, *34*, 2681.
(28) Fu, T. Y.; Scheffer, J. R.; Trotter, J. *Tetrahedron Lett.* **1996**, *37*, 2125.
(29) Pandey, R. K.; Isaac, M.; MacDonald, I.; Medforth C. J.; Senge, M. O.; Dougherty, T. S.; Smith, K. M. *J. Org. Chem.* **1997**, *62*, 1463.
(30) Dannhardt, V. G.; Geyer, Y.; Obergrusberger, R.; Ziereis, K. *Chem.-Ztg.* **1987**, *111*, 237.
(31) Khan, A. Z. Z.; Isaksson, R.; Sandstrom, J. *J. Chem. Soc., Perkin Trans. 2* **1987**, 491.
(32) Doussot, J.; Guy, A.; Roncali, J. *Tetrahedron Lett.* **1999**, *40*, 1811.
(33) Richeter, S.; Jeandon, C.; Gisselbrecht, J. P.; Graff, R.; Ruppert, R.; Callot, H. J. *Inorg. Chem.* **2004**, *43*, 251.
(34) Bonini, B. F.; Comes-Franchini, M.; Fochi, M.; Mazzanti, G.; Ricci, A.; Varchi, G. *Tetrahedron Lett.* **1999**, *40*, 6473.
(35) Sato, M.; Asai, M. *J. Organomet. Chem.* **1992**, *430*, 105.
(36) Vallée, Y.; Masson, S.; Ripoll, J. L. *Tetrahedron* **1990**, *46*, 3921.
(37) Read, C. E.; Martins, F. J. C.; Viljoen, A. M. *Tetrahedron Lett.* **2004**, *45*, 7655.
(38) Martinez, A. G.; Vilar, E. T.; Jiménez, F. M.; Bilbao, C. M. *Tetrahedron* **1997**, *8*, 3031.
(39) Shimada, K.; Kodaki, K.; Aoyagi, S.; Takikawa, Y.; Kabuto, C. *Chem. Lett.* **1999**, 695.
(40) Montenegro, E.; Echarri, R.; Claver, C.; Castillon, S.; Moyano, A.; Pericas, M. A.; Riera, A. *Tetrahedron: Asymmetry* **1996**, *7*, 3553.
(41) Nawwar, G. A. M.; Haggag, B. M.; Yakout, E.-S. M. A. *Z. Naturforsch., B: Chem. Sci.* **1992**, *47*, 1639.
(42) Marchand, E.; Morel, G. *Bull. Soc. Chim. Fr.* **1996**, *133*, 903.
(43) Weiss, D.; Gaudig, U.; Beckert, R. *Synthesis* **1992**, 751.
(44) Strehlow, T.; Voss, J.; Spohnholz, R.; Adiwidjaja, G. *Chem. Ber.* **1991**, *124*, 1397.
(45) Müller, M.; Heileman, M. J.; Moore, H. W.; Schaumann, E.; Adiwidjaja, G. *Synthesis* **1996**, 50.
(46) Foreman, M. S.; Slawin, A. M. Z.; Woolins, J. D. *Heteroat. Chem.* **1999**, *10*, 651.
(47) Gray, I. P.; Bhattacharyya, P.; Slawin, A. M. Z.; Woolins, J. D. *Chem. Eur. J.* **2005**, *11*, 6221.
(48) Varma, R. S.; Kumar, D. *Org. Lett.* **1999**, *1*, 697.
(49) Curphey, T. J. *J. Org. Chem.* **2002**, 67, 6461.
(50) Lakshmikantham, M. V.; Levinson, M.; Menachery, M.; Cava, M. P. *J. Org. Chem.* **1986**, *51*, 411.
(51) Raasch, M. S. *J. Org. Chem.* **1979**, *44*, 632.
(52) Yousif, N. M.; Shabana, R.; Lawesson, S.-O. *Bull. Soc. Chim. Fr.* **1986**, 283.
(53) Shabana, R.; Boulos, L. S.; Shaker, Y. M. *Heteroat. Chem.* **1999**, *10*, 25.
(54) El-Barbary, A. A.; Shabana, R.; Lawesson, S.-O. *Phosphorus, Sulfur Silicon Relat. Elem.* **1985**, *21*, 375.
(55) Rufanov, K. A.; Stepanov, A. S.; Lemenovskii, D. A.; Churakov, A. V. *Heteroat. Chem.* **1999**, *10*, 369.
(56) Mohamed, N. R.; El-Saidi, M. M. T.; Abdallah, T. A.; Nada, A. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 2387.
(57) Mohamed, N. R. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *161*, 123.
(58) Dolling, W.; Vogt, A.; Baumeister, U.; Hartung, H. *Eur. J. Org. Chem.* **1998**, 2647.
(59) Karakasa, T.; Satsumabayashi, S.; Motoki, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 335.
(60) Markovic, R.; Baranac, M.; Jovetic, S. *Tetrahedron Lett.* **2003**, *44*, 7087.
(61) Selzer, T.; Rappoport, Z. *J. Org. Chem.* **1996**, *61*, 5462.
(62) El-Kateb, A. A.; Hennawy, I. T.; Shabana, R.; Abdel-Malek, H. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1991**, *63*, 13.

(63) Eychenne, V.; Mouloungui, Z. *J. Am. Oil Chem. Soc.* **2001**, *78*, 229.
(64) Nicolaou, K. C.; Hwang, C. K.; Duggan, M. E.; Nugiel, D. A.; Abe, Y.; Reddy, K. B.; DeFrees, S. A.; Reddy, D. R.; Awartani, R. A.; Conley, S. R.; Rutjes, F. P. J. T; Theodorakis, E. F. *J. Am. Chem. Soc.* **1995**, *117*, 10227.
(65) Nicolaou, K. C.; Redy, K. R.; Skokotas, G.; Sata, F.; Xiao, X. Y.; Hwang, C. K. *J. Am. Chem. Soc.* **1993**, *115*, 3558.
(66) Bunnelle, W. H.; McKinnis, B. R.; Narayanan, B. A. *J. Org. Chem.* **1990**, *55*, 768.
(67) Barrett, A. G. M.; Bezuidenhoudt, B. C. B.; Howell, A. R.; Lee, A. C.; Russell M. A. *J. Org. Chem.* **1989**, *54*, 2275.
(68) Kanagassabapathy, S.; Sudalai, A.; Benicewicz, B. C. *Tetrahedron Lett.* **2001**, *42*, 3791.
(69) Josse, O.; Labar, D.; Brynaert, J.-M. *Synthesis* **1999**, 404.
(70) Moriyama, S.; Motoki, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2056.
(71) Steliou, K.; Salama, P.; Yu, X. P. *J. Am. Chem. Soc.* **1992**, *112*, 1456.
(72) Nicolaou, K. C.; Hwang, C. K.; Marron, B. E.; DeFrees, S. A.; Couladouros E. A.; Abe, Y.; Carroll, P. J.; Synder, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 3040.
(73) Nicolaou, K. C.; McGarry, D. G.; Somers, P. K.; Kim, B. H.; Ogilvie, W. W.; Yiannikouros, G.; Prasad, C. V. C.; Veale, C. A.; Hark, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6263.
(74) Sviripa, V. N.; Brovarets, V. S.; Drach, B. S. *Russ. J. Gen. Chem.* **2004**, *74*, 639.
(75) Brunner, A.; Kühnle, F. N. M.; Seebach, D. *Helv. Chim. Acta* **1996**, 319.
(76) Clyne, D. S.; Weiler, L. *Tetrahedron* **1999**, *55*, 13659.
(77) Böge, A.; Voss, J. *Chem. Ber.* **1990**, *123*, 1733.
(78) Hamad, A. S. S.; Hashem, A. I.; El-Kafrawy, A. F.; Saad, M. M. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000,** *159*, 157.
(79) Filippi, J. J.; Fernandez, X.; Lizzani-Cuvelier, L.; Loiseau, A. M. *Tetrahedron Lett.* **2002**, *43*, 6267.
(80) Pirkle, W. H.; Spence, P. L. *J. Chromatogr., A* **1997**, *775*, 81.
(81) Takano, S.; Tomita, S.; Takahashi, M.; Oqasawara, K. *Synthesis* **1987**, 1116.
(82) Ray, S.; Paul, S. K. *J. Indian Chem. Soc.* **2005**, *82*, 236.
(83) Hirano, K.; Oderaotoshi, Y.; Minakata, S.; Komatsu, M. *Chem. Lett.* **2001**, 1262.
(84) Iwanaga, H.; Naito, K.; Sunohara, K.; Okajima, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1719.
(85) Letcher, R. M.; Kwok, N. C.; Lo, W. H.; Ng, K. W. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1715.
(86) Bringmann, G.; Wuzik, A.; Schupp, O.; Peters, K.; Peters, E.-M. *Z. Naturforsch., B: Chem. Sci.* **1997**, *52*, 355.
(87) Peters, K.; Peters E. M.; Bringmann, G.; Schupp, O. *Z. Naturforsch., B: Chem. Sci.* **1996**, *51*, 431.
(88) Bringmann, G.; Schöner, B.; Schupp, O.; Schenk, W. A.; Reuther, I.; Peters, K.; Peters, E. M.; Von Schnering, H. G. *J. Organomet. Chem.* **1994**, *472*, 275.
(89) Kahne, D.; Yang, D.; Lim, J. J.; Miller, R.; Paguaga, E. *J. Am. Chem. Soc.* **1988**, *110*, 8716.
(90) Levai, A.; Szabo, Z. *J. Chem. Res., Synop.* **1992**, 380.
(91) Levai, A. *J. Chem. Res., Synop.* **1992**, 163.
(92) Levai, A. *Heterocycl. Commun.* **1999,** *5*, 419.
(93) Levai, A.; Szabo, Z. *Bull. Soc. Chim. Fr.* **1991**, *128*, 976.
(94) Levai, A.; Jeko, J. *J. Heterocycl. Chem.* **2005**, *42*, 739.
(95) Gadre, J. N.; Audi, A. A.; Karambelkar, N. P. *Indian J. Chem., Sect. B* **1996**, *35*, 60.
(96) Filippi, J.-J.; Fernandez, X.; Lizzani-Cuvelier, L.; Loiseau, A.-M. *Flavour Fragrance J.* **2006**, *21*, 175.
(97) Filippi, J.-J.; Fernandez, X.; Lizzani-Cuvelier, L.; Loiseau, A.-M. *Tetrahedron Lett.* **2003**, *44*, 6647.
(98) Brayton, D.; Jacobsen, F. E.; Cohen, S. M.; Farmer, P. J. *Chem. Commun.* **2006**, 206.
(99) Aqad, E.; Lakshmikantham, M. V.; Cava, M. P. *Org. Lett.* **2004**, *6*, 3039.
(100) Okuma, K.; Shigetomi, T.; Nibu, Y.; Shioji, K.; Yoshida, M.; Yokomori, Y. *J. Am. Chem. Soc.* **2004**, *126*, 9508.
(101) Adam, W.; Hasemann, L. *Chem. Ber.* **1990**, *123*, 1449.
(102) Adam, W.; Albert, R.; Hasemann, Ş.; Salgado, V. O. N.; Nestler, B.; Peters, E.-M.; Peters, K.; Prechtl, F.; von Schnering, H. G. *J. Org. Chem.* **1991**, *56*, 5782.
(103) Aimar, M. L.; Kreiker, J.; de Rossi, R. H. *Tetrahedron Lett.* **2002**, *43*, 1947.
(104) Closs, F.; Srdanov, G.; Wudl, F. *J. Chem. Soc., Chem. Commun.* **1989**, 1716.
(105) Khan, A. Z.; Sandstrom, J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2085.
(106) Nair, S. K.; Jose, A. M.; Asokan, C. V. *Synthesis* **2005**, 1261.
(107) Gompper, R.; Knieler, R.; Polborn, K. *Z. Naturforsch., B: Chem. Sci.* **1993**, *48*, 1621.
(108) Robert, J. M. H.; Robert-Piessard, S.; Courant, J.; LeBaut, G.; Robert, B.; Lang, F.; Petit, J. Y.; Grimaud, N.; Welin, L. *Eur. J. Med. Chem.* **1995**, *30*, 915.
(109) Drew, M. G. B.; Beer, P. O.; Ogden, M. I. *Acta Crystallogr.* **1997**, *C53*, 472.
(110) Katritzky, A. R.; Chen, J.; Yang, Z. J. *J. Org. Chem.* **1995**, *60*, 5638.
(111) Sifferlen, T.; Rueping, M.; Gademann, K.; Juan, B.; Seebach, D. *Helv. Chim. Acta* **1999**, *82*, 2067.
(112) Zacharie, B.; Lagraoui, M.; Dimarco, M., Penney, C. L.; Gagnon, L. *J. Med. Chem.* **1999**, *42*, 2046.
(113) Fruit, C.; Turck, A.; Plé, N.; Quéguiner, G. *Heterocycles* **1999**, *51*, 2349.
(114) Okumura, K; Suziki, T.; Shin, C. *Heterocycles* **2000**, *53*, 765.
(115) Nonoyama, M.; Nakajima, K.; Mizuno, H.; Hayashi, S. *Inorg. Chim. Acta* **1994**, *215*, 91.
(116) Vicentini, C. B.; Veronese, A. C.; Guarneri, M.; Manfrini, M.; Giori, P.; Guccione, S. *J. Heterocycl. Chem.* **1994**, *31*, 1477.
(117) Johnson, J. E.; Canseco, D. C.; Rowe, J. E. *Aust. J. Chem.* **2004**, *57*, 549.
(118) Davies, D. J.; Faust, R.; Garratt, P. S.; Marivingt-Mounir, C.; Davidson, K.; Teh, M. T.; Sugden; D. *Bioorg. Chem.* **2004**, *32*, 1.
(119) Hilty, F. M.; Brun, K. A.; Heimgartner, H. *Helv. Chim. Acta* **2004**, *87*, 2539.
(120) Ach, D.; Reboul, V.; Metzner, P. *Eur. J. Org. Chem.* **2003**, 3398.
(121) Aguirre, G.; Cerecetto, H.; Maio, R. D.; Gonzalez, M.; Porcal, W.; Seoane, G.; Ortega, M. A.; Aldana, I.; Monge, A.; Denicola, A. *Archiv Der Pharmazie* **2002**, *335*, 15.
(122) Blass, B. E.; Coburn, K. R.; Faulkner, A. L.; Liu, S.; Ogden, A.; Portlock, D. E.; Srivastava, A. *Tetrahedron Lett.* **2002**, *43*, 8165.
(123) Boeglin, D.; Cantel, S.; Martinez, J.; Fehrentz, J.-A. *Tetrahedron Lett.* **2003,** *44*, 459.
(124) Krinkova, J.; Dolezal, M.; Hartl, J.; Buchta, V.; Pour, M. *Farmoco* **2002**, *57*, 71.
(125) Tiecco, M.; Bagnoli, L.; Santi, C.; Tomassin, C.; Marini, F.; Bagnoli, L.; Temperini, A. *Tetrahedron: Asymmetry* **2002**, *13*, 429.
(126) No, K.; Lee, J. H.; Yang, S. H.; Yu, S. H.; Cho, M. H.; Kim, M. J.; Kim, J. S. *J. Org. Chem.* **2002**, *67*, 3165.
(127) Arena, G.; Contino, A.; Longo, E.; Sciotto, D.; Spoto, G. *J. Chem. Soc., Perkin Trans. 2* **2001**, 2287.
(128) Fruit, C; Turck, A.; Plé, N.; Mojovic, L.; Quéguiner, G. *Tetrahedron* **2002**, *58*, 2743.
(129) Breitenmoser, R. A.; Heimgartner, H. *Helv. Chim. Acta* **2002**, *85*, 885.
(130) Breitenmoser, R. A.; Hirt, T. R.; Luykx, R. T. N.; Heimgartner, H. *Helv. Chim. Acta* **2001**, *84*, 972.
(131) Schwarzer, K.; Wojczewski, C.; Engels, J. W. *Nucleosides & Nucleotides* **2001**, *20*, 879.
(132) Wojczewski, C.; Schwarzer, K.; Engels, J. W. *Helv. Chim. Acta* **2000**, *83*, 1268.
(133) Bobsikova, M.; Clegg, W.; Coles, S. J.; Dandarova, M.; Hursthouse, M.B.; Kiss, T.; Krutosikova, A.; Liptaj, T.; Pronayova, N.; Ramsden, C. A. *J. Chem. Soc., Perkin Trans. 1* **2001**, 680.
(134) Arevalo, M. J.; Avalos, M.; Babiano, R.; Cabanillas, A.; Cintas, P.; Jimenez, J. L.; Palacios, J. C. *Tetrahedron*: *Asymmetry* **1995**, *11*, 1985.
(135) Nishio, T. *Helv. Chim. Acta* **1998**, *81*, 1207.
(136) Arnaud-Neu, F.; Barret, G.; Corry, D.; Cremin, S.; Ferguson, G.; Gallagher, J. F.; Harris, S. J.; McKervey, M. A.; Schwing-Weill, M.-J. *J. Chem. Soc., Perkin Trans. 2* **1997**, 575.
(137) Cobben, P. L. H. M.; Egberink, R. J. M.; Bomer, J. G.; Bergveld, P.; Verboom, W.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1997**, *36*, 10573.
(138) van Wageningen, A. M. A.; Timmermnan, P.; van Duynhoven, J. P. M.; Verboom, W.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Chem. Eur. J.* **1997**, *13*, 639.
(139) Beer, P. D.; Graydon, A. R.; Johnson, A. O. M.; Smith, D. K. *Inorg. Chem.* **1997**, *36*, 2112.
(140) Jang, Y. C.; Bartsch, R. A. *J. Heterocycl. Chem.* **1995**, *32*, 1441.
(141) Blagbrough, I. S.; Moya, E. *Tetrahedron Lett.* **1994,** *35*, 2057.
(142) Hartl, J.; Dolezal, M.; Krinkova, J.; Lycka, A.; Odlerova, Z. *Collect. Czech. Chem. Commun.* **1996**, *61*, 1109.
(143) Van Hemel, J. V.; Esmans, E. L.; De Groot, A.; Dommisse, R. A.; Balzarini, I. M.; De Clercq, E. D. *Nucleosides Nucleotides* **1996**, *15*, 1203.
(144) Van Hemel, J.; Esmans, E. L.; Alderweireldt, F. C.; Dommisse, R. A.; De Groot, A.; Balzarini, J.; De Clercq, E. *Nucleosides Nucleotides* **1994**, *13*, 2345.
(145) Olsson, R.; Hansen, H. C.; Andersson, C.-M. *Tetrahedron Lett.* **2000**, *41*, 7947.
(146) Pons, J.-F.; Mishir, Q.; Nouvet, A.; Brookfield, F. *Tetrahedron Lett.* **2000**, *41*, 4965.
(147) Thompson, M. J.; Heal, W.; Chen, B. *Tetrahedron Lett.* **2006**, *47*, 2361.

(148) Bochu, C.; Couture, A.; Grandclaudon, P. *J. Org. Chem.* **1988**, *53*, 4852.
(149) Petrie, C. R.; Revankar, G. R.; Dalley, N. K.; George, R. D.; McKernan, P. A.; Hamill, R. L.; Robins, R. K. *J. Med. Chem.* **1986**, *29*, 268.
(150) Nishio, T.; Sekiguchi, H. *Heterocycles* **2002**, *58*, 203.
(151) Nishio, T.; Ori, M. *Helv. Chim. Acta* **2001**, *84*, 2347.
(152) Jenny, C.; Heimgartner, H. *Helv. Chim. Acta* **1986**, *69*, 374.
(153) Nishio, T. *Tetrahedron Lett.* **1995**, *36*, 6113.
(154) Nishio, T.; Sekiguchi, H. *Tetrahedron* **1999**, *55*, 5017.
(155) Delcros, J.-G.; Tomasi, S.; Duhieu, S.; Foucault, M.; Martin, B.; Le Roch, M.; Eifler-Lima, V.; Renault, J.; Uriac, P. *J. Med. Chem.* **2006**, *49*, 232.
(156) Elwahy, A. H. M.; Masaret, G. S. *J. Heterocycl. Chem.* **2004**, *41*, 711.
(157) Unterhalt, B.; Moghaddam, S. *Pharmazie* **1994**, *49*, 115.
(158) Jarecka, D.; Besch, A.; Otto, H.-H. *Monatsh. Chem.* **2003,** *134*, 901.
(159) Nieschalk, J.; Schaumann, E. *Liebigs Ann.* **1996**, 141.
(160) Mendez, L.; Delpiccolo, C. M. L.; Mata, E. G. *Synlett* **2005**, 1563.
(161) Sakamota, M.; Tanaka, M.; Fukuda, A.; Aoyama, H.; Omote, Y. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1353.
(162) Verkoyen, C.; Rademacher, P. *Chem. Ber.* **1985**, *118*, 653.
(163) Huszthy, P.; Oue, M.; Bradshaw, J. S.; Zhu, C. Y.; Wang, T.; Dalley, N. K.; Curtis, J. C.; Izatt, R. M. *J. Org. Chem.* **1992**, *57*, 5383.
(164) Elwahy, A. H. M.; Abbas, A. A. *Tetrahedron* **2000**, *56*, 885.
(165) Huszthy, P.; Köntös, Z.; Vermes, B.; Pinter, A. *Tetrahedron* **2001**, *57*, 4967.
(166) Tubery, F.; Grierson, D. S.; Husson, H.-P. *Tetrahedron Lett.* **1987**, *28*, 6461.
(167) Niedzinski, E. J.; Lashley, M. R.; Nantz, M. H. *Heterocycles* **2001**, *55*, 623.
(168) Lee, H. B.; Han, F. *Tetrahedron Lett.* **1994**, *35*, 1135.
(169) Valaityte, E.; Martynaitis, V.; Sackus, A. *Chem. Heterocycl. Compd.* **2004**, *40*, 1465.
(170) Chowdhury, S. K. D.; Sarkar, M.; Chatterjee, A.; Mahalanabis, K. K. *Indian J. Chem., Sect. B* **2003**, *42*, 2563.
(171) Roa, L.-F.; Gnecco, D.; Galindo, A.; Juarez, J.; Teran, J.-L.; Bernes, S. *Acta Crystallogr.* **2003**, *E59*, O519.
(172) Chen, X.; Du, D.-M.; Hua, W.-T. *Tetrahedron: Asymmetry* **2002**, *13*, 43.
(173) Seki, M.; Shimizu, T. *Biosci. Biotechnol. Biochem.* **2001**, *65*, 973.
(174) Hawker, C. J.; Stark, W. M.; Spivey, A. C.; Raithby, P. R.; Leeper, F. J.; Rattersby, A. R. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1493.
(175) Grisenti, P.; Magni, A.; Manzocchi, A.; Ferraboschi, P. *Steroids* **1997**, *62*, 504.
(176) Sosnicki, J.; Jagodzinski, T. S.; Liebscher, J. *J. Heterocycl. Chem.* **1997**, *34*, 643.
(177) Mamouni, A.; Netchitailo, P.; Daich, A.; Decroix, B. *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *119*, 169.
(178) Fisera, L.; Jaroskova, L.; Matejkova, I.; Heimgartner, H. *Heterocycles* **1995**, *40*, 271.
(179) Grossi, G. C.; Di Braccio, M.; Roma, G.; Ghia, M.; Brambilla, G. *Eur. J. Med. Chem.* **1993**, *28*, 577.
(180) Roma, G.; Grossi, G. C.; Di Braccio, M.; Ghia, M.; Mattioli, F. *Eur. J. Med. Chem.* **1991**, *26*, 489.
(181) Levai, A.; Balint, Z. *Arch. Pharm. (Weinheim)*, **1993**, *326*, 73.
(182) Levai, A.; Timar, T.; Frank, L.; Hosztafi, S. *Heterocycles* **1992**, *34*, 1523.
(183) Levai, A. *Arch. Pharm. (Weinheim)* **1992**, *325*, 721.
(184) Xie, M.; Lightner, D. A. *J. Heterocycl. Chem.* **1991**, *28*, 1753.
(185) Andersen, T. P.; Rasmussen, P. B.; Thomsen, I.; Lawesson, S.-O.; Jorgensen, P.; Lindhardt, P. *Liebigs Ann. Chem.* **1986**, 269.
(186) Malik, F.; Hasan, M.; Khan, K. M.; Perveen, S.; Snatzke, G.; Duddeck, H.; Voelter, W. *Liebigs Ann. Chem.* **1996**, 127.
(187) Katoh, A.; Yoshida, T.; Ohkanda, J.; Nishio, T. *Heterocycles* **1997**, *44*, 357.
(188) Soukara, S.; Wünsch, B. *Tetrahedron* **2001**, *57*, 4359.
(189) Nada, A. A.; El-Din, K.; Gab-Allah, S. T.; Zayed, M. F. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *156*, 213.
(190) Zolotoy, A. B.; Botoshansky, M.; Kaftory, M.; Scheffer, J. R.; Yang, J. *Acta Crystallogr.* **2002**, *C58*, O220.
(191) Dorn, H.; Kreher, T. *Heterocycles* **1994**, *38*, 2171.
(192) Tong, M. K.; Papandreou, G.; Ganem, B. *J. Am. Chem. Soc.* **1990**, *112*, 6137.
(193) Hoos, R.; Naughton, A. B.; Thiel, W.; Vasella, A.; Weber, W.; Rupitz, K.; Withers, S. G. *Helv. Chim. Acta* **1993**, *76*, 2666.
(194) Karp, G. M. *J. Org. Chem.* **1999**, *64*, 8156.
(195) Kukla, M. J.; Breslin, H. J.; Diamond, C. J.; Grous, P. P.; Ho, C. Y.; Miranda, M.; Rodgers, J. D.; Sherrill, R. G.; Clercq, E. D.; Pauwels, R.; Andries, K.; Moens, L. J.; Janssen, M. A. C.; Janssen, P. A. J. *J. Med. Chem.* **1991**, *34*, 3187.
(196) Chowdhury, S. K. D.; Sarkar, M.; Chatterjee, A.; Mahalanabis, K. K. *Indian J. Chem., Sect. B* **2003**, *42*, 2563.
(197) Larsen, C.; Kragh, H.; Rasmussen, P. B.; Andersen, T. P.; Senning, A. *Liebigs Ann. Chem.* **1989**, 819.
(198) Sarac-Arneri, R.; Mintas, M.; Pustet, N.; Manschreck, A. *Monatsh. Chem.* **1994**, *125*, 457.
(199) Nishio, T.; Okuda, N.; Mori, Y. I.; Kashima, C. *Synthesis* **1989**, 396.
(200) Atzrodt, J.; Beckert, R.; Günther, W.; Görls, H. *Eur. J. Org. Chem.* **2000**, 1661.
(201) Bigoli, F.; Deplano, P.; Devillanova, F. A.; Lippolis, V.; Lukes, P. J.; Mercuri, M. L.; Pellinghelli, M. A.; Trogu, E. F. *J. Chem. Soc., Chem. Commun.* **1995**, 371.
(202) Sharp, M. J.; Heathcock, C. H. *Tetrahedron Lett.* **1994**, *35*, 3651.
(203) Speelman, J. C.; Talma, A. G.; Kellogg, R. M. *J. Org. Chem.* **1989**, *54*, 1055.
(204) Cow, N. C.; Harrison, P. H. *J. Org. Chem.* **1997**, *62*, 8834.
(205) Hamad, A.-S. S.; Derbala, H. A. Y. *J. Heterocycl. Chem.* **2001**, *38*, 939.
(206) Costi, R.; Santo, R. D.; Artico, M.; Massa, S. *J. Heterocycl. Chem.* **2002**, *39*, 81.
(207) Marinov, M.; Minchev, S.; Stoyanov, N.; Ivanova, G.; Spassova, M.; Enchev, V. *Croat. Chem. Acta* **2005**, *78*, 9.
(208) Milewska, M. J.; Giöaniec, M.; Maluszynska, H.; Polonski, T. *Tetrahedron: Asymmetry* **1998**, *9*, 3011.
(209) Orzeszko, A.; Maurin, J. K.; Melon-Ksyta, D. *Z. Naturforsch., B: Chem. Sci.* **2001**, *56*, 1035.
(210) Milewska, M. J.; Bytner, T.; Polonski, T. *Synthesis* **1996**, 1485.
(211) Tominaga, Y.; Komiya, K.; Itonaga, S.; Yoshioka, N.; Kataoka, S.; Sasaki, K.; Hirota, T. *Heterocycles* **1997**, *46*, 41.
(212) Ostrowska, K.; Zankowska-Jasinska, W.; Ciechanowicz-Rutkowska, M.; Pilati, T. *J. Chem. Res. Synop.* **1996**, 236.
(213) Bialecka-Floryańczyk, E.; Orzeszko, A. *J. Mater. Chem.* **2000**, *10*, 1527.
(214) Melon-Ksyta, D.; Orzeszko, A.; Borys, W.; Czuprynski, K. *J. Mater. Chem.* **2002**, *12*, 1311.
(215) Rico-Gomez, R.; Najera, F.; Lopez-Romero, J. M.; Canada-Rudner, P. *Heterocycles* **2000**, *53*, 2275.
(216) Abdel-Ghany, H.; Khodairy, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *166*, 45.
(217) Bigoli, F.; Pellinghelli, M. A.; Atzei, D.; Deplano, P.; Trogu, E. F. *Phosphorus Sulfur* **1988**, *37*, 189.
(218) Arca, M.; Cornia, A.; Devillanova, F. A.; Fabretti, A. C.; Isaia, F.; Lippolis, V.; Verani, G. *Inorg. Chim. Acta* **1997**, *262*, 81.
(219) Arca, M.; Demartin, F.; Devillanova, F. A.; Garau, A.; Isaia, F.; Lelj, F.; Lippolis, V.; Pedraglio, S.; Verani, G. *J. Chem. Soc., Dalton Trans.* **1998**, 3731.
(220) Noe, C. R.; Knollmüller, M.; Wagner, E. *Monatsh. Chem.* **1986**, *117*, 621.
(221) Pouwer, K. L.; Vries, T. R.; Havinga, E. E.; Meijer, E. W.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1988**, 1432.
(222) Baierweck, P.; Simmross, U.; Müllen, K. *Chem. Ber.* **1988**, *121*, 2195.
(223) Merrill, B. A.; LeGoff, E. *J. Org. Chem.* **1990**, *55*, 2904.
(224) Tenhoeve, W.; Wynberg, H.; Havinga, E. E.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 5887.
(225) Merz, A.; Ellinger, F. *Synthesis* **1991**, 462.
(226) Ishii, A.; Nakayama, J.; Kazami, J.-I.; Ida, Y.; Nakamura, T.; Hoshino, M. *J. Org. Chem.* **1991**, *56*, 78.
(227) Brettle, R.; Dunmur, D. A.; Marson, C. M.; Pinol, M.; Toriyoma, K. *Chem. Lett.* **1992**, 613.
(228) Johnson, M. R.; Miller, D. C.; Bush, K.; Becker, J. J.; Ibers, J. A. *J. Org. Chem.* **1992**, *57*, 4414.
(229) Joshi, M. V.; Hemler, C.; Cava, M. P.; Cain, J. L.; Bakker, M. G.; McKinley, A. J.; Metzger, R. M. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1081.
(230) Jiang, Z.; Sanganeria, S.; Sen, A. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 841.
(231) Kuroda, M.; Nakayama, J.; Hoshino, M.; Furusho, N.; Ohba, S. *Tetrahedron Lett.* **1994**, *35*, 3957.
(232) Hörndler, C.; Hansen, H.-J. *Helv. Chim. Acta* **1997**, *80*, 2520.
(233) Ueda, M.; Hayakawa, T.; Haba, O.; Kawaguchi, H.; Inoue, J. *Macromolecules* **1997**, *30*, 7069.
(234) Ong, C. W.; Chen, C. M.; Wang, L. F. *Tetrahedron Lett.* **1998**, *39*, 9191.
(235) Lin, S.-C.; Yang, F.-D.; Shiue, J.-S.; Yang, S.-M.; Fang, J.-M. *J. Org. Chem.* **1998**, *63*, 2909.
(236) Hempenius, M. A.; Langeveld-Voss, B. M. W.; van Haare, A. E. H.; Janssen, R. A. J.; Sheiko, S. S.; Spatz, J. P.; Möller, M.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 2798.
(237) Prokop, P.; Richter, R.; Beyer, L. *Z. Naturforsch., B: Chem. Sci.* **1999**, *54*, 849.
(238) Schweiger, L. F.; Ryder, K. S.; Morris, D. G.; Glidle, A.; Cooper, J. M. *J. Mater. Chem.* **2000**, *10*, 107.
(239) Lichtenthaler, F. W.; Brust, A.; Cunny, E. *Green Chem.* **2001**, *3*, 201.

(240) Sonpatki, V. M.; Herbert, M. R.; Sandvoss, L. M.; Seed, A. J. *J. Org. Chem.* **2001**, *66*, 7283.
(241) Kim, E. K.; Lee, K. U.; Cho, B. Y.; Kim, Y. B.; Kang, K.-T. *Liq. Cryst.* **2001**, *28*, 339.
(242) Kang, K.-T.; U, Jong. S. *Synth. Commun.* **1995**, *25*, 2647.
(243) Ertas, E.; Ozturk, T. *Tetrahedron Lett.* **2004**, *45*, 3405.
(244) Synder, C. A.; Slegue, J. P.; Tice, N. C.; Wallace, C. E.; Blankenbuehler, M. T.; Parkin, S.; Allen, K. D. E.; Beck, R. T. *J. Am. Chem. Soc.* **2005**, *127*, 15010.
(245) Raposo, M. M. M.; Sampaio, A. M. B. A.; Kirsch, G. *Synthesis* **2005**, 199.
(246) Yadav, I. S.; Reddy, B. V. S.; Eeshwaraiah, B.; Gupta, M. K. *Tetrahedron Lett.* **2004**, *45*, 5873.
(247) Read, C. E.; Martins, F. J. C.; Viljoen, A. M. *Tetrahedron Lett.* **2004**, *45*, 5953.
(248) Mehta, G.; Gagliardini, V.; Schaefer, C.; Gleiter, R. *Org. Lett.* **2004**, *6*, 1617.
(249) Wu, C.-Y.; Lin, H.-C.; Wang, Z.; Wu, H.-J. *J. Org. Chem.* **2001**, *66*, 4610.
(250) Kiryanov, A. A.; Sampson, P.; Seed, A. J. *J. Org. Chem.* **2001**, *66*, 7925.
(251) Omar, M. T.; El-Aasar, N. K.; Saied, K. F. *Synthesis* **2001**, 413.
(252) Ishii, A.; Nakaniwa, T.; Umezawa, K.; Nakayama, I. *Tetrahedron* **1999**, *55*, 10341.
(253) Ishii, A.; Nakayama, J.; Ding, M.-X.; Kotaka, N.; Hoshino, M. *J. Org. Chem.* **1990**, *55*, 2421.
(254) Ishii, A.; Umezawa, K.; Nakayama, J. *Tetrahedron Lett*. **1997**, *38*, 1431.
(255) Ishii, A.; Akazawa, T.; Ding, M.-X.; Honjo, T.; Maruta, T.; Nakamura, S.-Y.; Nagaya, H.; Ogura, M.; Teramoto, K.; Shiro, M.; Hoshino, M.; Nakayama, J. *Bull. Chem. Soc. Jpn*. **1997**, *70*, 509.
(256) Gordon, T. D.; Singh, J.; Hansen, P. E.; Morgan, B. A. *Tetrahedron Lett.* **1993**, *34*, 1901.
(257) Kotian, P.; Mascarella, S. W.; Abraham, P.; Lewin, A. H.; Boja, J. W.; Kuhar, M. J.; Carroll, F. I. *J. Med. Chem.* **1996**, *39*, 2753.
(258) Uchikawa, O.; Fukatsu, K.; Aono, T. *J. Heterocycl. Chem.* **1994**, *31*, 877.
(259) Uchikawa, O.; Fukatsu, K.; Suno, M.; Aono, T.; Doi, T. *Chem. Pharm. Bull.* **1996**, *44*, 2070.
(260) Davies, J. R.; Kane, P. D.; Moody, C. J. *Tetrahedron* **2004**, *60*, 3967.
(261) Nishio, T.; Ori, M. *Helv. Chim. Acta* **2001**, *84*, 2347.
(262) Nishio, T.; Konno, Y.; Ori, M.; Sakamoto, M. *Eur. J. Org. Chem.* **2001**, 3553.
(263) Nishio, T., Sekiguchi, H. *Heterocycles* **2002**, *58*, 203.
(264) Nishio, T. *J. Org. Chem.* **1997**, *62*, 1106.
(265) Thompson, D. K.; Suzuki, N.; Hegedus, L. S.; Satoh, Y. *J. Org. Chem.* **1992**, *57*, 1461.
(266) Tarraga, A.; Molina, P.; Curiel, D.; Bautista, D. *Tetrahedron*: *Asymmetr*y **2002**, *13*, 1621.
(267) Molina, T.; Tarraga, A.; Curiel, D. *Synlett* **2002**, 435.
(268) Nishio, T.; Kodama, Y.; Tsurumi, Y. *Phosphorus, Sulfur Silicon Relat. Elem.* **2005**, *180*, 1449.
(269) Golankiewicz, B.; Januszczyk, P. *Tetrahedron* **1985**, *41*, 5989.
(270) Golankiewicz, B.; Januszczyk, P. *Nucleosides Nucleotides* **1995**, *14*, 313.
(271) Savarino, P.; Viscardi, G.; Carpignano, R.; Borda, A.; Barni, E. *J. Heterocycl. Chem*. **1989**, *26*, 289.
(272) Jenny, C.; Heimgartner, H. *Helv. Chim. Acta*. **1986**, *69*, 374.
(273) Jenny, C.; Heimgartner, H. *Helv. Chim. Acta*. **1987**, *70*, 1001.
(274) Jenny, C.; Heimgartner, H. *Helv. Chim. Acta* **1989**, *72*, 1639.
(275) Ori, M.; Nishio, T. *Heterocycles* **2001**, *54*, 201.
(276) Mitra, R. B.; Muljiani, Z.; Deshpande, R. *Heterocycles* **1988**, *27*, 2297.
(277) Bochu, C.; Couture, A.; Grandclaudon, P. *J. Org. Chem*. **1988**, *53*, 4852.
(278) Okada, E.; Masuda, R.; Hojo, M. *Heterocycles* **1994**, *37*, 157.
(279) Gierczyk, B.; Zalas, M. *Org. Prep. Proced. Int.* **2005**, 37, 213.
(280) Bradly, P.; Sampson, P.; Seed, A. J. *Liq. Cryst. Today* **2005**, *14*, 15.
(281) Janietz, S.; Barche, J.; Wedel, A.; Sainova, D. *Macromol.Chem. Phys.* **2004**, *205*, 187.
(282) Barche, J.; Janietz, S.; Ahles, M.; Schmechel, R.; Von Seggern, H. *Chem. Mater.* **2004**, *16*, 4286.
(283) Huang, H.-M.; Yu, H.-T.; Chen, P.-L.; Han, J.; Meng, J.-B. *Chin. J. Org. Chem.* **2004**, *24*, 502.
(284) Sato, M.; Notsu, M.; Nakashima, S.; Uemota, Y. *Makromol. Chem., Rapid Commun.* **2001**, *22*, 681.
(285) Sato, M.; Yamauchi, K.; Handa, M.; Kasuqa, K. *Makromol. Chem., Rapid Commun.* **2000**, *21*, 1234.
(286) Lee, J.; Hong, S. I. *Macromol. Chem. Phys.* **1997**, *198*, 391.
(287) Tully, W. R.; Gardner, C. R.; Gillespie, R. J.; Westwod, R. *J. Med. Chem.* **1991**, *34*, 2060.
(288) Tschierske, C.; Girdziunaite, D. *J. Prakt. Chem.* **1991**, *333*, 135.
(289) Rasmussen, P. B.; Pedersen, U.; Thomsen, I.; Yde B, Lawesson S.-O. *Bull. Soc. Chim. Fr.* **1985**, 62.
(290) Huang, H.-M.; Yu, H.-T.; Chen, P.-L, Meng, J.-B. *Acta Crystallogr.* **2004**, *E60*, 0881.
(291) Buscemi, S.; Vivona, N. *Heterocycles* **1994**, *38*, 2423.
(292) Caron, M. *J. Org. Chem*. **1986**, *51*, 4075.
(293) Kamitori, Y.; Hojo, M.; Masuda, R.; Kawamura, Y.; Numai, T. *Synthesis* **1990**, 491.
(294) Charrier, J.-D.; Reliquet, A.; Meslin, C. *Tetrahedron: Asymmetry* **1998**, *9*, 1531.
(295) Hasserodt, J.; Pritzkow, H.; Sundermeyer, W. *Chem. Ber*. **1993**, *126*, 1701.
(296) El-Kateb, A. A.; El-Rahman, N. M. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2006**, *181*, 249.
(297) Markl, G.; Aschenbrenner, N.; Baur, A.; Rastorfer, C.; Kreitmeier, P. *Helv. Chim. Acta* **2003**, *86*, 2589.
(298) Nishio, T. *J. Chem. Soc., Chem. Commun*. **1989**, 205.
(299) Nishio, T. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1113.
(300) Rajagopalan, S.; Radke, G.; Tomich, J. *Synth. Commun*. **1997**, *27*, 187.
(301) Przychodzen, W. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 1621.
(302) Tagawa, Y.; Minami, S.; Yoshida, T.; Tanaka, K.; Sato, S.; Goto, Y.; Yamagata, K. *Arch. Pharm. Med. Chem.* **2002**, *335*, 99.
(303) Shimomura, N.; Mukaiyama, T. *Chem. Lett*. **1993**, 1941.
(304) Venkateswarlu, P.; Venkata, S. C. *Tetrahedron Lett*. **2004**, *45*, 3207.
(305) Fahmy, A. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *68*, 139.
(306) Quast, H.; Aldenkortt, S.; Heller, E.; Schafer, P.; Schmitt, E. *Chem. Ber*. **1994**, *127*, 1699.
(307) Dubau-Assibat, N.; Baceiredo, A.; Bertrand, G. *J. Org. Chem*. **1995**, *60*, 3904.
(308) Shabana, R.; Atrees, S. S. *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, *105*, 57.
(309) Boukraa, M.; Ayed, N.; Akacha, A. B.; Zantour, H.; Baccar, B. *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, *105*, 57.
(310) Touil, S.; Dhia, M. T. B.; Zantour, H.; Baccar, B. *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *119*, 295.
(311) He, L. N.; Chen, R.-Y. *Phosphorus, Sulfur Silicon Relat. Elem.* **1997**, *129*, 111.
(312) Butler, R. N.; McKenna, E. C.; Grogan, D. C. *Chem. Commun*. **1997**, 2149.
(313) Mosbah, M. B.; Chouaib, H.; Kossentini, M.; Salem, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **2003**, *178*, 1433.
(314) Mohamed, N. R.; El-Saidi, M. M. T.; Hasaneen, H. M.; Erian, A. W. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 521.
(315) Boukraa, M.; El-Efrit, L.; Zantour, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *157*, 145.
(316) Deng, S. L.; Liu, D. Z.; Chen, R. Y. *Chin. Chem. Lett.* **2001**, *12*, 1065.
(317) Ibrahim, Y. A.; Kadry, A. M.; Ibrahim, M. R.; Lisgarten, J. N.; Potter, B. S.; Palmer, R. A. *Tetrahedron* **1999**, *55*, 13457.
(318) He, L.-N.; Zhuo, R.-X.; Chen, R.-Y.; Li, K.; Zhang, Y.-J. *Heteroat. Chem*. **1999**, *10*, 105.
(319) He, L.-N.; Li, K.; Liu, X.-P.; Luo, Y.-P.; Lu, A.-H.; Ding, M.-W. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *158*, 117.
(320) He, L.-N.; Zhuo, R.-X.; Liu, X.-P.; Cai, F. *Phosphorus, Sulfur Silicon Relat. Elem.* **1999**, *144*, 453.
(321) He, L.-N.; Chen, R.-Y. *Heterocycl. Commun*. **1997**, *3*, 461.
(322) Khodairy, A.; Abdel-Ghany, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *162*, 259.
(323) Abd-Allah, O. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2003**, *178*, 1115.
(324) Boulos, L.; Abd-El-Malek, H. A. *Heteroat. Chem*. **1999**, *10*, 488.
(325) Shabana, R.; Mahran, M. R.; Hafez, T. S. *Phosphorus, Sulfur Silicon Relat. Elem.* **1987**, *31*, 1.
(326) Ghattas, A.-B. A. G.; Abd-Allah, O. A.; Moustafa, H. M. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *157*, 1.
(327) Deng, S. L.; Liu, D. Z. *Synthesis*, **2001**, 2445.
(328) Bryce, M. R.; Matthews, R. S. *J. Organomet. Chem*. **1987**, *325*, 153.
(329) Testa, M. G.; Perrini, G.; Chiacchio, U.; Corsaro, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *86*, 75.
(330) Golovko, T.V.; Soloveva, N. P.; Granik, V. G. *Mendeleev Commun*. **1995**, 191.
(331) Shabana, R.; Atrees, S. S. *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, *102*, 9.
(332) Deng, S.-L.; Chen, R.-Y. *Monatsh. Chem*. **2004**, *135*, 1113.
(333) Loskutov, V. A.; Mamatyuk, V. I. *Russ. Chem. Bull*. **1995**, *44*, 137.
(334) Abass, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **2003**, *178*, 1413.
(335) Moustafa, H. M. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *164*, 11.
(336) Moustafa, H. M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1999**, *148*, 131.

(337) Moustafa, H. M. *Phosphorus, Sulfur Silicon Relat. Elem.* **2003**, *178*, 1397.
(338) Khidre, M. D.; Yakout, E. M. A.; Rafet, M.; Mahran, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **1998**, *133*, 119.
(339) Deng, S.-L.; Liu, D.-Z.; Li, W. *Acta Crystallogr.* **2002**, *E58*, o1430.
(340) Deng, S.-L.; Chen, R.-Y. *Phosphorus, Sulfur Silicon Relat. Elem.* **2003**, *178*, 211.
(341) Deng, S.-L.; Chen, R.-Y. *Synthesis* **2002**, 2527.
(342) Deng, S.-L.; Liu D.-Z.; Huang, J.-M.; Chen, R.-Y.; Weng, L.-H.; Leng, X.-B. *Chin. J. Struct. Chem.* **2002**, *21*, 46.
(343) Mohamed, N. R.; Elmegeed, G. A.; Abd-El-Malek, H. A.; Younis, M. *Steroids* **2005**, *70*, 131.
(344) He, L.-N.; Zhuo, R.-X. *Synth. Commun.* **1997**, *27*, 2853.
(345) Shabana, R.; Osman, F. H.; Atrees, S. S. *Tetrahedron* **1994**, *50*, 6975.
(346) Shabana, R.; Osman, F. H.; Atrees, S. S. *Tetrahedron* **1993**, *49*, 1271.
(347) He, L.; Luo, Y.; Li, K.; Ding, M.; Lu, A.; Liu, X.; Wu, T.; Cai, F. *Synth. Commun.* **2002**, *32*, 1415.
(348) El-Kateb, A. A.; El-Rahman, N. M. A. *Phosphorus, Sulfur Silicon Relat. Elem.*, **2006**, *181*, 249.
(349) Fahmy, A. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1991**, *63*, 81.
(350) Shabana, R.; Yakout, E. M.; Atrees, S. S. *Heteroat. Chem.* **1993**, *4*, 491.
(351) He, L.; Luo, Y.; Li, K.; Yang, G.; Ding, M.; Liu, X.; Wu, T.-J. *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, *177*, 2675.
(352) He, L.-N.; Li, K.; Luo, Y.-P.; Liu, X.-P.; Ding, M.-W.; Zhou, Q.-C: Wu, T.-J.; Cai, F. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *156*, 173.
(353) Tongcharoensirikul, P.; Suarez, A. I.; Voelker, T.; Thompson, C. M. *J. Org. Chem.* **2004**, *69*, 2322.
(354) Lopin, C.; Gouhier, G.; Piettre, S. R. *Tetrahedron Lett.*, **2003**, *44*, 8837.
(355) Piettre, S. R.; Raboisson, P. *Tetrahedron Lett.* **1996**, *37*, 2229.
(356) Piettre, S. R. *Tetrahedron Lett.* **1996**, *37*, 4707.
(357) Ju, J. Y; McKenna, C. E. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 1643.
(358) Zhou, H.-J.; Han, J.-X.; Li, Y.-G.; Ye, T.-G.; Wang, J.-L.; Miao, F.-L. *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *112*, 281.
(359) Zhou, H.-J.; Zhang,Y.-Q.; Li, Y.-G.; Wang, J.-L.; Liu, X.-L.; Miao, F.-M.; Yang, S.-C.; Jiang, X.-C.; Feng, R.; Yan, Z.-X. *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, *102*, 185.
(360) McKenna, C. E.; Ye, T.-G.; Levy, J. N.; Pham, P.; Wen, T.; Bongartz, J.-P.; Starnes, M. C.; Cheng, Y.-C. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *49*, 183.
(361) Wen, T.; Bau, R.; MecKenna, C. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1223.
(362) Kawashima, T.; Kojima, S.; Inamoto, N. *Chem. Lett.* **1989**, 849.
(363) Quin, L. D.; Osman, F. H.; Day, R. O.; Hughes, A. N.; Wu, X.-P.; Wang, L.-O. *New J. Chem.* **1989**, *13*, 375.
(364) Polozov, A. M.; Cremer, S. E.; Fanwick, P. E. *Can. J. Chem.* **1999**, *77*, 1274.
(365) He, L.; Luo, Y.; Ding, M.; Lu, A.; Liu, X.; Wu, T.; Cai, F. *Heteroat. Chem.* **2001**, *12*, 497.
(366) Karp, G. M. *J. Org. Chem.* **1999**, *64*, 8156.
(367) Nakayama, J.; Nakamura, Y.; Murabayashi, S.; Hoshino, M. *Heterocycles* **1987**, *26*, 939.
(368) Nakayama, J.; Choi, K. S.; Yamaoka, S.; Hoshino, M. *Heterocycles* **1989**, *29*, 391.
(369) Ozturk, T. *Tetrahedron Lett.* **1996**, *37*, 2821.
(370) Turksoy, F.; Wallis, J. D.; Tunca, U.; Ozturk, T. *Tetrahedron* **2003**, *59*, 8107.
(371) Ertas, E.; Ozturk, T. *Chem. Commun.* **2000**, 2039.
(372) Ozturk, T.; Turksoy, F.; Ertas, E. *Phosphorus, Sulfur Silicon Relat. Elem.* **1999**, *153*−*154*, 417.
(373) Kaynak, F. B.; Ozbey, S.; Ozturk, T.; Ertas, E. *Acta Crystallogr.* **2001**, *C57*, 926.
(374) Kaynak, F. B.; Ozbey, S.; Ozturk, T.; Ertas, E. *Acta Crystallogr.* **2001**, *C57*, 319.
(375) Kaynak, F. B.; Ozbey, S.; Ozturk, T.; Ertas, E. *Acta Crystallogr.* **2001**, *C57*, 1125.
(376) Dodd, D. S.; Martinez, R. L. *Tetrahedron Lett.* **2004**, *45*, 4265.
(377) Dodd, D. S.; Martinez, R. L.; Kamau, M.; Ruan, Z.; Kirk, K. V.; Cooper, C. B.; Hermsmeier, M. A.; Traeger, S. C.; Poss, M. A. *J. Comb. Chem.* **2005**, *7*, 584.
(378) Bartsch; H.; Erker, T. *Tetrahedron Lett.* **1992**, *33*, 199.
(379) Tewari, N.; Kumar, Y.; Thaper, R. K.; Khanna, J. M. *Synth. Commun.* **1996**, *26*, 1169.
(380) Bates, D. K.; Li, X.; Jog, P. V. *J. Org. Chem.* **2004**, *69*, 2750.
(381) Ishii, A.; Yamashita, R.; Saito, M.; Nakayama, J. *J. Org. Chem.* **2003**, *68*, 1555.
(382) Ishii, A.; Kashiura, S.; Oshida, H.; Nakayama, J. *Org. Lett.* **2004**, *6*, 2623.
(383) Nishio, T.; Okuda, N.; Kashima, C. *J. Chem. Soc., Perkin. Trans. 1* **1992**, 899.
(384) Kong, Y. C.; Kim, K. *J. Heterocycl. Chem.* **1999**, *36*, 515.
(385) Chiacchio, U.; Corsaro, A.; Pistara, V.; Purrello, G.; Rescifina, A. *Heterocycles* **1998**, *48*, 41.
(386) Ono, Y.; Sugihara, Y.; Ishii, A.; Nakayama, J. *J. Am. Chem. Soc.* **2003**, *125*, 12114.
(387) Jensen, O. E.; Senning, A. *Tetrahedron* **1986**, *42*, 6555.
(388) Wang, L.; Phanstiel, O. *J. Org. Chem.* **2000**, *65*, 1442.
(389) Sherman, D. B.; Spatola, A. F. *J. Am. Chem. Soc.* **1990**, *112*, 433.
(390) Guziec, F. S.; Wasmund, L. M. *J. Chem. Res. Synop.* **1989**, 155.
(391) Hollosi, M.; Majer, Z.; Zewdu, M.; Ruff, F.; Kajtar, M.; Kover, K. E. *Tetrahedron* **1988**, *44*, 195.
(392) Majer, Z.; Zewdu, M.; Hollosi, M.; Seprodi, J.; Vadasz, Z.; Teplan, I. *Biochem. Biophys. Res. Commun.* **1988**, *150*, 1017.
(393) Brown, D. W.; Campbell, M. M.; Chambers, M. S.; Walker, C. V. *Tetrahedron* **1987**, *28*, 2171.
(394) Kajtar, M.; Hollosi, M.; Kajtar, J.; Majer, Z. S.; Kover, K. E. *Tetrahedron* **1986**, *42*, 3931.
(395) Jensen, O. E.; Lawesson, S.-O. *Tetrahedron* **1985**, *41*, 5595.
(396) Cho, K. *Anal. Biochem.* **1987**, *164*, 284.
(397) Thorsen, M.; Andersen, T. P.; Pedersen, U.; Yde, B.; Lawesson, S.-O.; Hansen, H. F. *Tetrahedron* **1985**, *41*, 5633.
(398) Eberle, M. K.; Jutzi-Eme, A.-M.; Nuninger, F. *J. Org. Chem.* **1994**, *59*, 7249.
(399) Eberle, M. K.; Nuninger, F. *J. Org. Chem.* **1993**, *58*, 673.
(400) Seebach, D.; Ko, S. Y.; Kessler, H.; Kock, M.; Reggelin, M.; Walkinshaw, M. D.; Bolsterli, J. J.; Bevec, D. *Helv. Chim. Acta* **1991**, *74*, 1953.
(401) Eberle, M. K.; Nuninger, F.; Weber, H.-P. *J. Org. Chem.* **1995**, *60*, 2610.
(402) Morita, H.; Nagashima, S.; Takeya, K.; Itokawa, H. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2327.
(403) Morita, H.; Nagashima, S.; Takeya, K.; Itokawa, H. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 677.
(404) Hitotsuyanagi, Y.; Suzuki, J.; Matsumoto, Y.; Takeya, K.; Itokawa, H. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1887.
(405) Morita, H.; Yun, Y. S.; Takeya, K.; Itokawa, H.; Shirota, O. *Bioorg. Med. Chem.* **1997**, *5*, 631.
(406) Hitotsuyanagi, Y.; Matsumoto, Y.; Sasaki, S.-I.; Yamaguchi, K.; Itokawa, H.; Takeya, K. *Tetrahedron Lett.* **2001**, *42*, 1535.
(407) Palomino, E.; Meltsner, B. R.; Kessel, D.; Horwitz, J. P. *J. Med. Chem.* **1990**, *33*, 258.
(408) Kaneko, K.; Katayama, H.; Wakabayashi, T.; Kumonaka, T. *Synthesis* **1988**, 152.
(409) Dzik, J. M.; Kulikowski, T.; Zielinski, Z.; Ciesla, J.; Rode, W.; Shugar, D. *Biochem. Biophys. Res. Commun.* **1987**, *149*, 1201.
(410) Dunkel, M.; Pfleiderer, W. *Nucleosides Nucleotides* **1991**, *10*, 799.
(411) Krecmerova, M.; Hrebabecky, H.; Holy, A. *Collect. Czech. Chem. Commun.* **1996**, *61*, 627.
(412) Felczak, K.; Bretner, M.; Kulikowski, T.; Shugar, D. *Nucleosides Nucleotides* **1993**, *12*, 245.
(413) Batty, C. A.; Manthey, M. K.; Kirk, J.; Mantey, M.; Christopherson, R. I. *J. Heterocycl. Chem.* **1997**, *34*, 1355.
(414) Kozai, S.; Maruyama, T.; Kimura, T.; Yamamoto, I. *Chem. Pharm. Bull.* **2001**, *49*, 1185.
(415) Jorgensen, P. T.; Pedersen, E. B.; Nielsen, C. *Synthesis* **1992**, 1299.
(416) Hrebabecky, H.; Holy, A. *Collect. Czech. Chem. Commun.* **1994**, *59*, 412.
(417) Rico-Gomez, R.; Ruiz-Mora, M. L.; Villatoro, E. P.; Rios-Ruiz, J. *Heterocycles* **1988**, *27*, 12.
(418) Rico-Gomez, R.; Lopez-Romero, J. M. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3001.
(419) Wörner, K.; Strube, T.; Engels, J. W. *Helv. Chim. Acta* **1999**, *82*, 2094.
(420) Fossey, C.; Landelle, H.; Laduree, D.; Robba, M. *Nucleosides Nucleotides* **1993**, *12*, 973.
(421) Kaneko, C.; Hara, S.; Matsumoto, H.; Takeuchi, T.; Mori, T.; Ikeda, K.; Mizuno, Y. *Chem. Pharm. Bull.* **1991**, *39*, 871.
(422) Peyrane, F.; Fourrey, J.-L.; Clivio, P. *Chem. Commun.* **2003**, 736.
(423) Wang, Z. Y.; Zhang, C. *Macromolecules* **1992**, *25*, 5851.
(424) Zhang, C.; Wang, Z. Y. *Macromolecules* **1993**, *26*, 3330.
(425) Moulinie, P.; Paroli, R. M.; Wang, Z. Y.; Delgado, A. H.; Guen, A. L.; Qi, Y.; Gao, J.-P. *Polym. Test.* **1996**, *15*, 75.
(426) Wang, Z. Y.; Zhang, C.; Arnoux, F. *Macromolecules* **1994**, *27*, 4415.
(427) Wang, Z. Y.; Franklin, J.; Venkatesan, D. *Macromolecules* **1999**, *32*, 1691.
(428) Deletre, M.; Levesque, G. *Macromolecules* **1990**, *23*, 4876.
(429) Basha, F. Z.; DeBernardis, J. F. *J. Heterocycl. Chem.* **1987**, *24*, 789.
(430) Rafiqul, I. M.; Shimada, K.; Aoyagi, S.; Fujisawa, Y.; Takikawa, Y. *Heteroat. Chem.* **2004**, *15*, 208.
(431) Chiacchio, U.; Corsaro, A.; Rescifina, A.; Testa, M. G.; Purello, G. *Heterocycles* **1993**, *36*, 223.
(432) Omar, M. T.; El-Khamry, A.; Youssef, A. M.; Ramadan, S. *Phosphorus, Sulfur Silicon Relat. Elem.* **2003**, *178*, 721.

(433) Imrie, C.; Cook, L.; Levendis, D. C. *J. Organomet. Chem*. **2001**, *637−639*, 266.
(434) Butler, I. R.; Caballero, A. G.; Kelly, G. A. *Inorg. Chem. Commun.* **2003**, *6*, 639.
(435) Kollenz, G.; Penn, G.; Theuer, R.; Fabian, W. M. F.; El-Nabi, H. A. A.; Zhang, X.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Tetrahedron* **1996**, *52*, 5427.
(436) Kim, S. H.; Han, S. K.; Kim, J. J.; Hwang, S. H; Yoon, C. M.; Keum, S. R. *Dyes Pigm*. **1998**, *39*, 77.
(437) Araki, S.; Goto, T.; Butsugan, Y. *Bull. Chem. Soc. Jpn*. **1988**, *61*, 2977.
(438) Shimomura, N.; Matsutani, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn*. **1994**, *67*, 3100.
(439) Shimomura, N.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2532.
(440) Mukaiyama, T.; Saito, K.; Kitagawa, H.; Shimomura, N. *Chem. Lett*. **1994**, 789.
(441) Mukaiyama, T.; Watanabe, K.; Shiina, I. *Chem. Lett*. **1995**, 1.
(442) Shimagaki, M.; Fujieda, Y.; Kimura, T.; Nakata, T. *Tetrahedron Lett*. **1995**, *36*, 719.
(443) Aragoni, M. C.; Arca, M.; Demantin, F.; Devillanova, F. A.; Garau, A.; Isaia, F.; Lelj, F.; Lippolis, V.; Verani, G. *J. Am. Chem. Soc*. **1999**, *121*, 7098.
(444) Partyka, D. V.; Staples, R. J.; Holm, R. H. *Inorg. Chem*. **2003**, *42*, 7877.
(445) Hill, A. F.; Malget, J. M. *Chem. Commun*. **1996**, 1177.
(446) Takaguchi, Y.; Furukawa, N. *Chem. Lett*. **1996**, 859.
(447) Carmalt, C. J.; Clyburne, J. A. C.; Cowley, A. H.; Lomeli, V.; McBurnett, R. G. *Chem. Commun*. **1998**, 243.
(448) Wood, P. T.; Woolins, J. D. *Transition Met. Chem*. **1987**, *12*, 403.
(449) Sanchez, G.; Garcia, J.; Meseguer, D. J.; Serrano, J. L.; Perez, J.; Molins, E.; Lopez, G. *Inorg. Chim. Acta* **2004**, *357*, 677.
(450) Aragoni, M. C.; Arca, M.; Demartin, F.; Devillanova, F. A.; Graiff, C.; Isaia, F.; Lippolis, V.; Tiripicchio, A.; Verani, G. *Eur. J. Inorg. Chem*. **2000**, 2239.
(451) Gray, I. P.; Slawin, M. Z.; Woolins, J. D. *Dalton Trans*. **2004**, 2477.
(452) Pashkevich, K. I.; Saloutin, V. I.; Bobrov, M. B. *J. Fluorine Chem*. **1988**, *41*, 421.
(453) Nizamov, I. S.; Sergeenko, G. G.; Popovich, A. E.; Nizamov, I. D.; Batyeva, E. S.; Al'fonsov, V. A. *Russ. J. Gen. Chem. (Engl. Transl.*) **2002**, *72*, 1356.
(454) Kessler, H.; Geyer, A.; Matter, H.; Köck, M. *Int. J. Pept. Protein Res.* **1992**, *40*, 25.
(455) Hafez, T. S. *Phosphorus, Sulfur Silicon Relat. Elem.*, **1991**, *63*, 249.
(456) Lajoie, G.; Lepine, F.; Maziak, L.; Belleau, B. *Tetrahedron Lett.* **1983**, *24*, 3815.
(457) Barrett, A. G. M.; Lee, A. C. *J. Org. Chem.* **1992**, *57*, 2818.
(458) Foreman, M. R. S. J.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1996**, 3653.
(459) Foreman, M. R. S. J.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1999**, 1175.
(460) Foreman, M. R. S. J.; Novosad, J.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1997**, 1347.
(461) Wood, P. T.; Woollins, J. D. *J. Chem. Soc., Chem. Commun.* **1988**, 1190.
(462) Bhattacharyya, P.; Woollins, J. D. *Tetrahedron Lett.* **2001**, *42*, 5949.
(463) Bethke, K.; Karaghiosoff, K.; Wessjohann, L. A. *Tetrahedron Lett.* **2003**, *44*, 6911.
(464) Mohanakrishnan, A. K.; Amaladass, P. *Tetrahedron Lett.* **2005**, *46*, 7201.
(465) Kaleta, Z.; Makowski, B. T.; Soos, T.; Dembinski, R. *Org. Lett*. **2006**, *8*, 1625.
(466) Kaleta, Z.; Tarkanyi. G.; Gömöry, A.; Kalman, F.; Nagy, T.; Soos, T. *Org. Lett*. **2006**, *8*, 1093.

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