A Berzelius Reagent, Phosphorus Decasulfide (P_4S_{10}), in Organic Syntheses

Turan Ozturk,*,† Erdal Ertas,‡ and Olcay Mert§

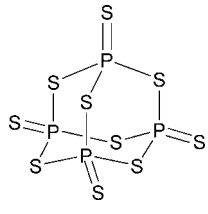
Istanbul Technical University, Science Faculty, Chemistry Department, Organic Chemistry, 34469 Maslak, Istanbul, Turkey, Tubitak Marmara Research Centre, Fl, 41470 Gebze-Kocaeli, Turkey, Middle East Technical University, Department of Chemistry, Organic Chemistry, Ankara, Turkey, and TUBITAK UME, Chemistry Group Laboratories, PBox 54, 41470, Gebze-Kocaeli, Turkey

Received July 6, 2009

Contents

1. Introduction

Syntheses of organic compounds having a sulfur heteroatom have been in the interest of many groups. This has been performed mainly through the reactions of thionating agents, among the oldest and the most important ones of which is phosphorus decasulfide (P_4S_{10}), **1** (also called phosphorus pentasulfide, P_2S_5).



1

Although it was claimed[1] that the reaction between phosphorus and sulfur was first indicated nearly three hundred years ago,[2] possibly such a reaction had been known even earlier but had not been noted. On the other hand, the first reports on the synthesis of P_4S_{10} appeared in 1843 and were authored by J. Berzelius.[3,4] The discoverer of P_4S_{10} is understood to be the famous Swedish chemist Jóns Jacob Berzelius (1779−1848), who is considered among the fathers of modern chemistry. His works include the discovery of chemical elements such as silicon, selenium, thorium, and cerium. Moreover, he is the first person to make a distinction between organic compounds, containing carbon, and inorganic compounds. He also worked on chemical formula notation, such as isomers.

Berzelius synthesized P_4S_{10} by a violent reaction of white phosphorus and sulfur. A more controlled reaction was later obtained using red phosphorus. P_4S_{10} can also be formed by reaction of elemental sulfur or pyrite (FeS_2) with ferrophosphorus (Fe_2P), which is a byproduct of P_4 production from phosphate rock.

Since then, P_4S_{10} has been used widely in organic syntheses for a wide range of purposes, primarily as a thionating agent of organic (also inorganic) compounds and

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 Lawesseon's reagent and P_4S_{10}. He took up a position at TUBITAK MRC, Turkey, and 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 the development of new organic reactions, particularly the new reactions of Lawesson's reagent and P4S10.

* To whom correspondence should be addressed. Telephone: +90 212 285 69 94. E-mail: ozturktur@itu.edu.tr.
† Istanbul Technical University.
‡ Tubitak Marmara Research Centre.
§ Middle East Technical University.
|| TUBITAK UME.

10.1021/cr900243d
Published on Web 04/29/2010

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 at 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 for 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 formulations.

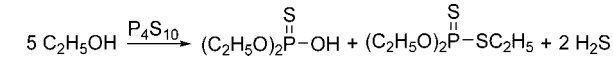
Olcay Mert was born in Saray, Tekirdag, Turkey. He graduated from the Chemistry Department of Kocaeli University, Turkey, in 2002 with the first rank in his class. He is currently a Ph.D. student in the Polymer Science and Technology Program at Middle East Technical University, Ankara, Turkey. His research area includes injectable biodegrable polymers for the delivery of camptothecin family anticancer drugs and syntheses of pyrrole and thiophene based monomers and their electrochemical polymerizations. He was a visiting scientist at the Chemical & Biomolecular Engineering Department of Johns Hopkins University, USA, between February of 2008 and February of 2009.

for the syntheses of various heterocycles, including thiophenes, thiazines, thiazoles, thiazolines, imidazolines, pyrimidines, imides, dithiazoles, thiadiazoles, and dithiins. Additionally, it has widespreadly been applied in thionations of peptides, nucleosides, purines, and pyrimidines, and in reductions of sulfoxides to sulfides.

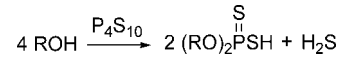
In 1854, Kekule employed P_4S_{10} for thionation of some compounds, including diethyl ether, anhydrides, and ethanol.[5] In 1859, Carius re-examined the reactions and reported that, contrary to Kekule's findings, rather than obtaining ethylmercaptan from ethyl alcohol, the reaction in Scheme 1 took place.[6] Moreover, a general scheme obtained through the further investigations is depicted in Scheme 2.[7]

In 1878, Hofmann applied P_4S_{10} to convert amides to thioamides, the products of which included $HCSNH_2$ (30−50%), CH_3CSNH_2 (35−40%), $(CH_3)_2CHCSNH_2$ (30−50%), 3,4-$(CH_3O)_2C_6H_3NHCSCH_3$ (%55), nonylthiolactam (50−90%), 4-$ClC_6H_4NHCSCH_3$ (54%), 4-$NO_2C_6H_4CSNH_2$ (70−90%), 4-$H_2NC_6H_4CSNHC_6H_5$ (5%), and thionsaccharin (90%).[8]

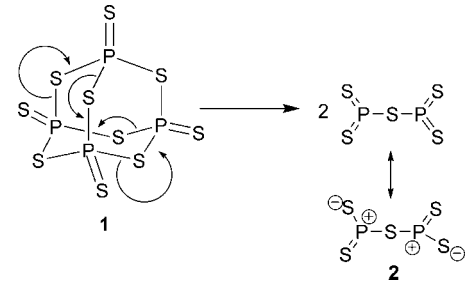
Scheme 1. Carius' Postulation of the Reaction of Ethyl Alcohol with P_4S_{10}



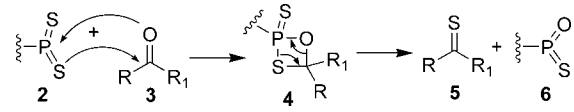
Scheme 2. General Reaction Scheme of Alcohol with P_4S_{10}



Scheme 3. Dissociation Mechanism of P_4S_{10}



Scheme 4. Thionation Mechanism of P_4S_{10}



P_4S_{10} is now a commercially available compound, and not only is it used for thionation reactions and constructing heterocycles, it is also used for industrial applications such as production of additives for lubricants, oil, flotation agents, and insecticides, etc.[9]

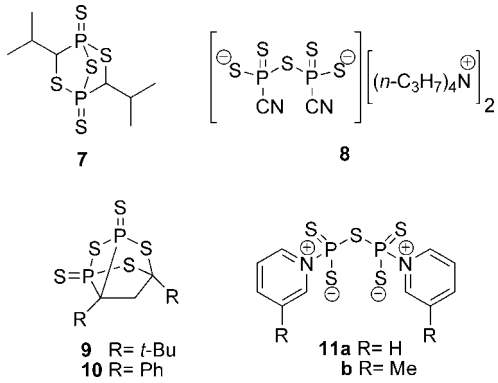
The usual method of thionation using P_4S_{10} is conducted in refluxing solvents such as benzene, toluene, dioxane, xylene, THF, pyridine, acetonitrile, and CS_2. On the other hand, there are examples where the reactions were carried out at 0 °C to room temperature even in low boiling solvents such as dichloromethane and diethyl ether. Moreover, addition of some bases, such as $NaHCO_3$, Na_2CO_3, Na_2SO_3, pyridine, and Et_3N, is widely applied as well as addition of Al_2O_3. More importantly, incorporation of hexamethyldisiloxane (HMDO) into the reaction mixture resulted in the improvement of the yield (see P_4S_{10} vs Lawesson's reagent, LR, part).

Although there is not a clear-cut report for the thionation mechanism of P_4S_{10}, it is generally accepted that, particularly in the reactions conducted under refluxing solvents, P_4S_{10} dissociates into P_2S_5, **2** (Scheme 3).[10−12]

The decomposition product **2** can then react with functional groups such as carbonyl **3** to form four-membered ring **4**, which decomposes to the corresponding thioketone **5** and to the thermodynamically more stable product **6**, having a P═O bond (Scheme 4).

P_2S_5 produced in the reaction medium was trapped by various research groups, and the X-ray diffractions were reported, **7**−**10**.[13−15] Moreover, the reactions performed in the presence of bases such as pyridine were reported to form a pyridine−P_2S_5 complex **11**.[16−18]

X-ray diffraction,[1,19−21] mass, NMR,[1,22−24] infrared, Raman,[12,25−27] ESR,[28] and XPS[29] spectroscopic studies of P_4S_{10} were conducted. Additionally, solubility,[30] sublimation,[31] and vaporization[32] behaviors were investigated in-



depth. Phosphorus pentasulfide having the phosphorus-32 isotope was reported to be prepared.[33]

Interestingly, to our best knowledge, a comprehensive review has not appeared so far, although some organosulfur related reviews included P_4S_{10} as short sections.[34−42] In this review, considering its widespread use in organic syntheses, P_4S_{10} has been reviewed in-depth.

2. Reactions of P_4S_{10}

2.1. Ketones

Ketones **12** are converted to thioketones **13** (Scheme 5) with P_4S_{10}, even in the presence of some functional groups such as aromatic and heterocyclic rings, halogens, ethers, amines, ferrocyl, and tosyl groups (Table 1).

Various reaction conditions are applied, including pyridine, toluene, CH_2Cl_2, CH_3CN, THF, diglyme, xylene, CS_2, and dioxane as solvent, 0 °C to reflux as the reaction temperature, and in some cases in the presence of Al_2O_3 (Table 1, entries 9−12), $NaHCO_3$ (Table 1, entries 18, 19) and Et_3N (Table 1, entry 28). The reaction is not preferentially carried out under inert atmosphere. There are a number of examples where the reactions were performed open to atmosphere.

It is not unusual that the use of P_4S_{10} results in unexpected products. It could be concluded that, in general, when α,β-unsaturated ketones are treated with P_4S_{10}, various products are obtained, including dimerization (Table 2, entries 1, 2−9) and new ring formations (Table 2, entries 2, 10, 11). It looks as though dimerization and a new ring formation are likely products of the reaction of α,β-unsaturated ketones with P_4S_{10}.

Reaction of α,β-unsaturated ketone **14** with P_4S_{10} in CS_2 gave an intramolecular Diels−Alder reaction to yield the cyclo adduct **16**, possibly through the thione intermediate **15** (Scheme 6).[74]

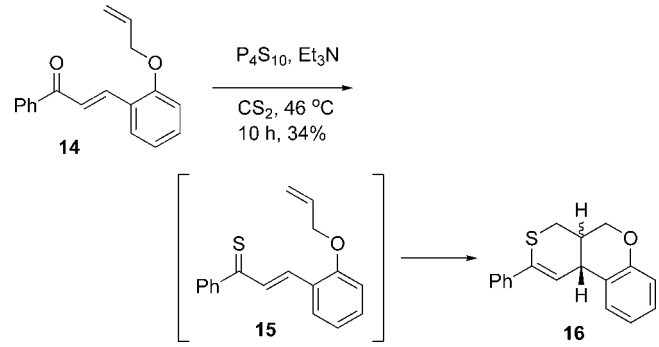
Treatment of the diketone **17**, having an α,β-unsaturated unit with P_4S_{10} in pyridine (dry), for 3−5 h at room temperature resulted in the formation of thiopyran ring **18** (Scheme 7).[75] On the other hand, it was reported that the treatment of the same ketone with P_4S_{10} in refluxing xylene yielded trithiapentalene **19**.[76]

Thiopyran **21** ring was also obtained when 1,5-diketones **20** were reacted with P_4S_{10} (Scheme 8, Table 3).

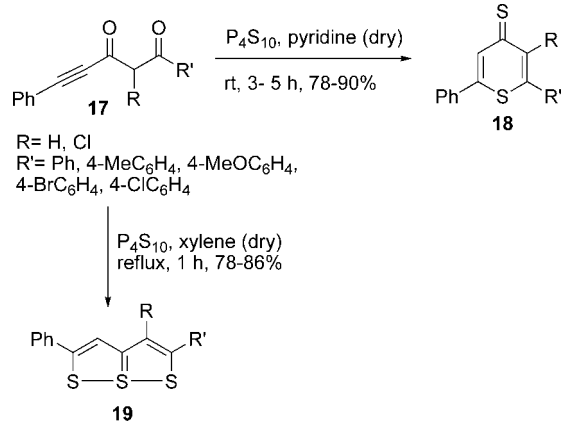
Trithiapentalenes were reported to be obtained from 1,3,5-triketones.[81,82] Treatment of the triketones **22**−**24** with P_4S_{10} in refluxing toluene yielded the trithiapentalenes **25**−**27** (Scheme 9).

Scheme 5. General Reaction of P_4S_{10} with Ketones

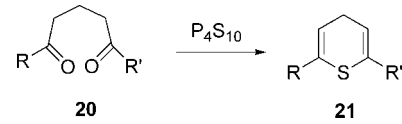
Scheme 6. Reaction of α,β-Unsaturated Ketone 14 with P_4S_{10}



Scheme 7. Reaction of α,β-Unsaturated Diketone 17 with P_4S_{10}



Scheme 8. General Reaction of 1,5-Diketones with P_4S_{10}



The reaction of keto dienamine with P_4S_{10} led to the formation of bridged trithiapentalene. Treatment of the dienamine **28**, prepared from the reaction of 4-phenylcyclohexanone and dimethylamino-*tert*-butoxymethane (Bredereck's Reagent), with P_4S_{10} (or Lawesson's reagent, LR **566**) in refluxing benzene or toluene yielded the trithiapentalene **29** in 41% (Scheme 10).[83] It was reported that this methodology was extended to the synthesis of various bridged trithiapentalenes **30**.

Another unexpected product of P_4S_{10} is the production of 1,2,4-trithiolane from the reaction of some ketones with P_4S_{10}. In an attempt to convert the oxo group of the ketone **31** to thio, two trithiolanes, *cis*-**32** and *trans*-**33**, were isolated (Scheme 11) along with the desired thioketone **34** (Table 1, entry 27).[64]

A similar result was obtained on treatment of the ketones **35** and **36** with P_4S_{10}. 1,2,4-Trithiolanes **37** and **38** were isolated after performing the reaction in pyridine at 40 °C in 79 and 41% yields, respectively (Scheme 12).[84] On the other hand, the reaction of the ketone **39** with P_4S_{10} under the same conditions gave the dimer **40** in 78% yield.

Thionation of 1,1′-dibenzoferrocene **41** with P_4S_{10} in a refluxing mixture of CH_2Cl_2/Et_2O (1:1) for 1 h gave 1,2,4-trithiolane **42** in a yield of less than 1%, along with 1,1′-bis(thiobenzoyl)ferrocene **43** in 40% yield (Table 1, entry 20) (Scheme 13).[57] Its mechanism suggested that the initial step

Table 1. Products of the Corresponding Ketones with P_4S_{10}

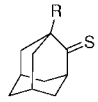
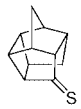
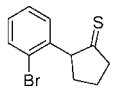
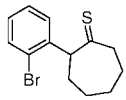
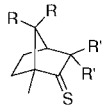
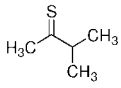
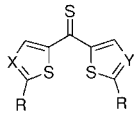
Entry	Product	Conditions	Yield (%)	Ref.
1	 R= H, Me, Et	pyridine, 90 °C, 5 h	85	43, 44
2		pyridine, 60- 80 °C, 5 h	73	44
3	 R= 2-BrPhenyl, 2-ClC_6H_4 2,4-Br,FC_6H_4	toluene (dry), N_2, 90 °C, 18 h	40-71	45
4		toluene (dry), N_2, 90 °C, 18 h	38	45
5		toluene (dry), N_2, 90 °C, 18 h	40	45
6	 R= H, Me, Ph, NH_2, NHMe OH, OMe, SMe	Et_3N, CCl_4, CH_2Cl_2, CH_3CN, 0-20 °C, 30 min-3 h	62-98	46, 47
7	 R= Ph, 4-MeC_6H_4 4-$(CH_3)_2NC_6H_4$, *t*-C_4H_9 R^1= Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$	CH_3CN, diglyme, 30 °C, reflux, 3-24 h	18-45	48
8		diglyme, 120 °C, 5 h	70	48
9	 R= Ph, 4-MeC_6H_4 4-ClC_6H_4, $Me_2NC_6H_4$ R^1= Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4 $Me_2NC_6H_4$, 3-NH_2-5-ClC_6H_3	Al_2O_3, CH_3CN, reflux, 0.5- 2 h	82-95	49
10	 A: R=R=H R'=R'= Me B: R=R= Me R'=R'= H	Al_2O_3, CH_3CN, reflux, 2 h	A= 88 B= 68	49
11		Al_2O_3, CH_3CN, reflux, 2 h	73	49
12		Al_2O_3, CH_3CN, reflux, 2 h	65	49
13	 X=Y= CH X= CH, Y= N X=Y= N R= Morpholino, $(C_6H_5)_2N$, $(CH_3)_2N$, N-methylanilino	pyridine, reflux, 1 h	48-96	50

Table 1. Continued

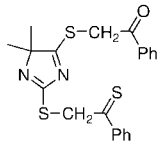
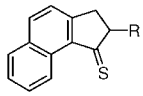
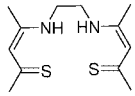
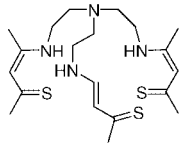
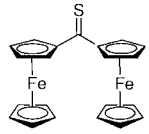
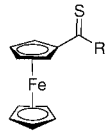
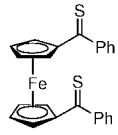
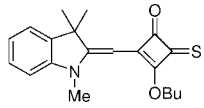
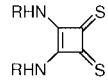
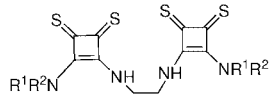
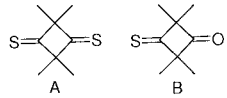
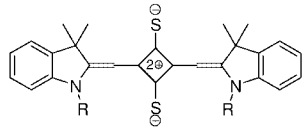
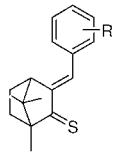
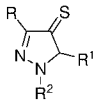
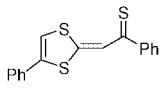
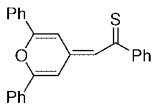
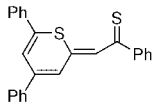
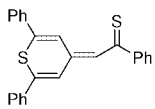
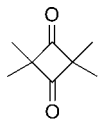
Entry	Product	Conditions	Yield (%)	Ref.
14		dioxane, reflux, 1 h	36	51
15	 R= ^{i}Pr, ^{t}Bu, Me	toluene, 111 °C	67-78	52
16		pyridine (dry), N_2, rt, 5 h	34	53, 54
17		pyridine (dry),N_2, rt, 5 h	21	54
18		CH_3CN, $NaHCO_3$, Ar, ultrasonic bath, 3 h	98	55
19	 R= Me, propionyl, 2-methylpropionyl 2,2-dimethylpropionyl, Ph	CH_2Cl_2/$(C_2H_5)_2O$ (1:1), $NaHCO_3$, Ar, reflux, 3h	79, R= Ph	56
20		CH_2Cl_2/$(C_2H_5)_2O$ (1:1), reflux,1 h	40	57
21		pyridine, rt, 6.5 h	42	58
22	 R= cyclohexyl, cyclopentyl, *n*-butyl	CH_2Cl_2, rt, 4 min-16 h	41-55	59
23	 A: R^1= R^2= ethyl B: R^1= R^2= n-butyl C: R^1= n-butyl, R^2= H	A=B= CH_2Cl_2 (dry), N_2, rt, 23 h, 16 h, respectively C= pyridine (dry), N_2, reflux, 45 min	A= 32 B= 34 C= 56	60
24		A: pyridine, reflux, 1.5 h, 1eq. P_4S_{10} B: pyridine, reflux, 45 min, 0.45 eq. P_4S_{10}	A= 50 B= 40	61
25	 R= H, CH_3	pyridine, reflux, 5 h	R= H, 93 R= CH_3, 53	62

Table 1. Continued

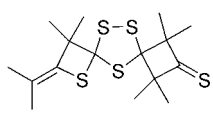
Entry	Product	Conditions	Yield (%)	Ref.
26	 R= H, 4-Br, 4-MeO, 4-Me 2-F, 2-MeO, 2-Me	benzene, reflux, 1 h	-	63
27		pyridine, reflux, 48 h	23	64
28	 A: R= R'= Ph B: R= Me, R'= Ph	Et_3N, CS_2, 1 h A: reflux B: 10-15 °C	A: 76 B: 27	65
29	 R= Ph, 4-$(Me)_2$NPh, *t*-Bu	With or without HMDO, xylene, or toluene, 110 °C reflux, 0.25-12 h	50-97	66
30	 R= Ph, 4-ClC_6H_4, 4-$NO_2C_6H_4$ 4-$CH_3C_6H_4$ R^1= Ph, 4-BrC_6H_4, 4-ClC_6H_4, 4-MeC_6H_4 R^2= Ph, 2,4-$NO_2C_6H_4$	AcCN, P_4S_{10}, $(Et)_3N$, rt, 24 h	17-85	93
31		CS_2, reflux, 1-15 h	57	97
32		pyridine, reflux, 20 min	29	97
33		benzene, reflux, 1-15 h	29	97
34		CS_2, reflux, 1-15 h	12	97

involved the exchange of carbonyl oxygenes with sulfur to give **44** and then addition of H_2S to the two thioketones formed the dithiol **45**, oxidation of which resulted in the 1,2,4-trithiolane **42**.

On the way to converting the oxo groups of **46** (Table 1, entry 24) to thiones, a dimerized product **47** in 2.8% yield, consisting of a 1,2,4-trithiolane unit, was isolated along with the products containing thione groups (figures in entry 24).[61]



46



47

On the other hand, treatment of **46** with P_4S_{10} in refluxing pyridine for 12 h, rather than 1.5 h done previously,[61] resulted in the formation of **48** in quantitative yield, and heating **46** with P_4S_{10} up to 200 °C under reduced pressure yielded **49** in 72% yield (Scheme 14).[85]

Reductive coupling, resulting in the formation of the peropyrene **51**, took place upon treatment of the ketone, phenalenone **50**, with P_4S_{10} (or LR) in refluxing benzene (Scheme 15).[86] It was suggested that its mechanism involves the conversion of the oxo group to the thione **52**, which was followed by the formation of a carbene intermediate **53**. Its coupling gives the final product **51**.

A series of coupling products were obtained when the dione **54** was reacted with P_4S_{10} in refluxing toluene (Scheme 16).[87] The mechanism was proposed to involve the replacement of the oxygens with sulfurs to give **55**, which was then decomposed to **56** and **57**, from which the coupling products **58**, **59**, and **60** were formed, respectively.

Table 2. Reaction of α,β-Unsaturated Ketones with P_4S_{10}

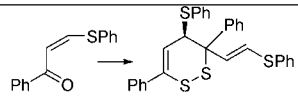
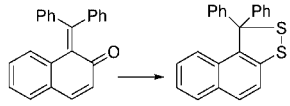
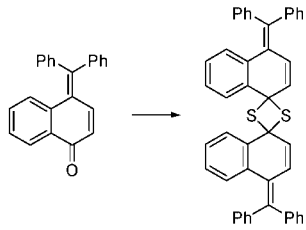
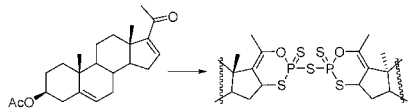
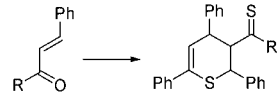
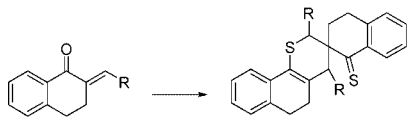
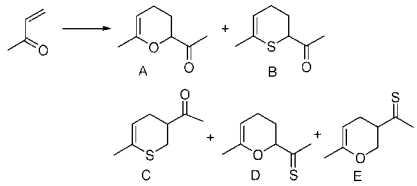
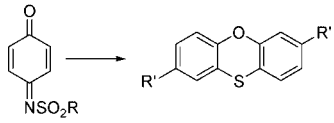
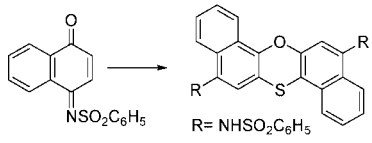
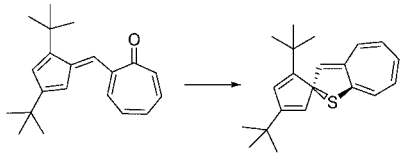
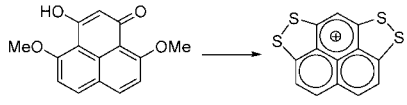
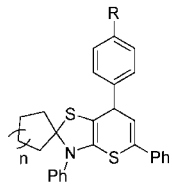
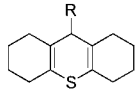
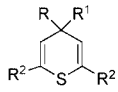
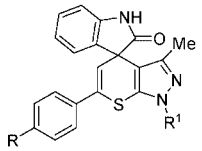
Entry	Product	Conditions	Yield (%)	ref
1		Et_3N, CS_2, rt, 6 d.	3.9	67
2		toluene, reflux	60	68
3		toluene, reflux, 12 h	50	68
4		benzene, reflux, 4 h	78	69
5	 R= Ph, 4-CH_3OPh	Et_3N, CS_2, 20-25 °C, 1 d.	Ph= 38 4-CH_3OPh= 50	65
6	 R= Ph, 4-CH_3OPh, 4-ClPh	Et_3N, CS_2, 20-25 °C, 1 week	45-62	65
7		pyridine, reflux, 20 h	A= 15, B= 30, C= 41, D= 13, E= 7	70
8	 R= Me, Ph R'= $NHSO_2CH_3$, $NHSO_2C_6H_5$	toluene (dry), reflux, 10 h	80, 85	71
9	 R= $NHSO_2C_6H_5$	toluene (dry), reflux, 10 h	80	71
10		Et_3N, 0 °C, 30 min	49	72
11		i) toluene (dry), N_2, reflux, 12 h ii) HCl, reflux, N_2, 1 h	63	73

Table 3. Synthesis of Thiopyrans from 1,5-Diketones

Entry	Product	Conditions	Yield (%)	ref
1	 n= 1,2 R= H, Cl, MeO, NO_2	pyridine, reflux, 0.5 h	62-73	77
2	 R= H, CH_3, C_2H_5	pyridine, N_2, 100 °C, 2 h	45-65	78
3	 R= R^1= CO_2Me R= CN, R^1=CO_2Et R^2= Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4	xylene, reflux, 3-10 h	35-62	79
4	 R= H, Me, MeO R^1= H, Ph	pyridine, reflux	55-60	80

Treatment of the α-hydroxyketones **61** and **62** with P_4S_{10} in refluxing dioxane and then addition of alkylating agent such as MeI, BzBr gives the dithiolene thiophosphoryl thiolates **63**, **64**, and **65**, respectively (Scheme 17).[88]

In a similar manner, the benzoins **66** (Scheme 18)[89] and **68** (Scheme 19)[90] were treated with P_4S_{10} in refluxing dioxane followed by trapping, using metal ions to form the complexes in place of alkylating agents to yield **67** and **69**.

In the case of having reactive functional units close enough to give reaction with carbonyl groups, unexpected products including addition of the part of P_4S_{10} or dimerization were obtained. Treatment of the tetrabutyl ammonium salt of camphor **70** with P_4S_{10} in refluxing toluene gave an addition product **71** (Scheme 20).[91] The reaction of 1,3-diketone **72** with P_4S_{10} in *o*-dichlorobenzene at 100 °C in the presence of Li_2CO_3 yielded the addition product **73** (Scheme 20).[15]

Treatment of β-oxo sulfenyl chlorides **74a**,**b** with P_4S_{10} in refluxing toluene for 10 h produced the dimers **75a**,**b** and 1,2,3,4-tetrathiins **76a**,**b** (Scheme 20).[92]

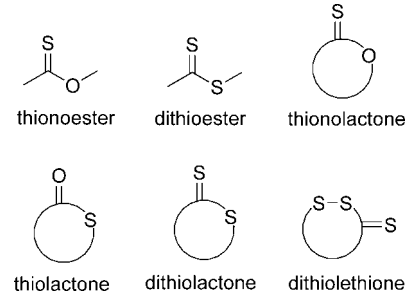
Reaction of 2,3-diphenylcyclopropenone **77** with P_4S_{10} in benzene (dry) at 50−60 °C was reported to produce the corresponding thione derivative 2,3-diphenylcyclopropenethione **78** in 68% yield (Scheme 21).[94] On the other hand, contrary to these results, depending on personal communications, a different result indicated that the reaction of **77** with P_4S_{10} gave dithiolethione **79** rather than **78**.[95] Then, a rather extensive study demonstrated that the reaction of **77** with the P_4S_{10} in benzene at 45 °C yielded both **78** and **79** in equal ratios.[96] Moreover, while the mixture was refluxed for 30 min, **79** was obtained as a sole product in 10% yield. The same reaction at room temperature for 3 h resulted in the formation of the thione **78** in 15% and **79** in trace.

Treatment of thiobenzophenone **81**, obtained by the reaction of benzophenone **80** with P_4S_{10} in $CH_3CN/NaHCO_3$ at 30 °C, with P_4S_{10} in refluxing xylene for 20 h yielded tetraphenyl ethylene **82** (Scheme 22).[98] High temperature could be the reason that tetraphenyl ethylene was obtained from thiobenzophenone, not from benzophenone.

An attempt to thionate the ketone **83**, having an epoxide moiety, surprisingly yielded the dithiole **86**, the mechanism of which was suggested to involve the intermediates **84** and **85** (Scheme 23).[99] A similar result was obtained on treatment of epoxyketone **87** with P_4S_{10}, which gave the dithiole **88** in 50% yield.[100]

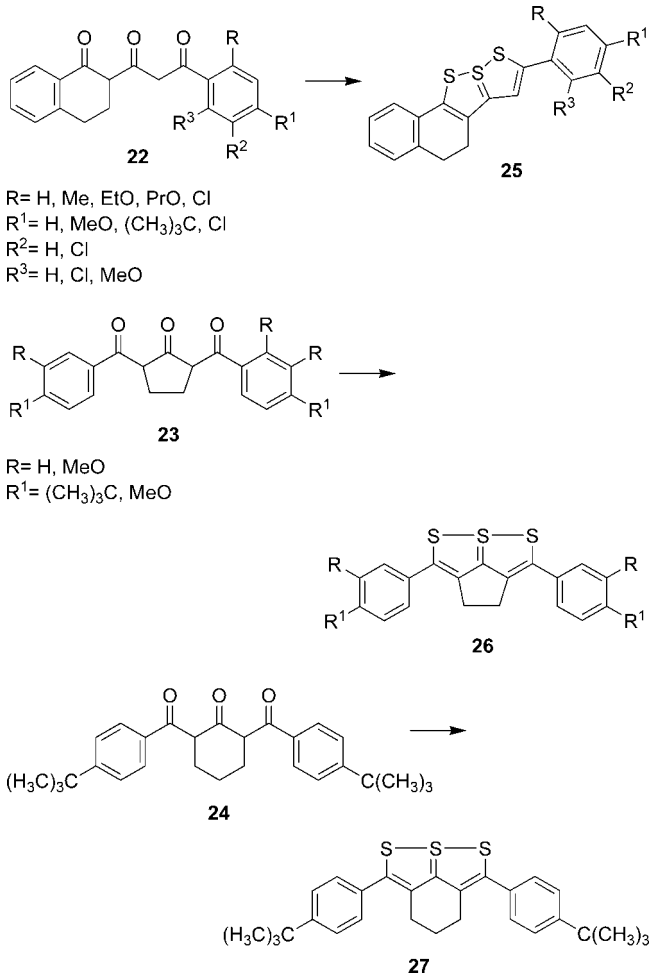
Addition of part of P_4S_{10} was observed when indigo **89** was reacted with P_4S_{10} in hot pyridine, which gave a hardly soluble dark blue solid **90** (Scheme 24).[101]

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

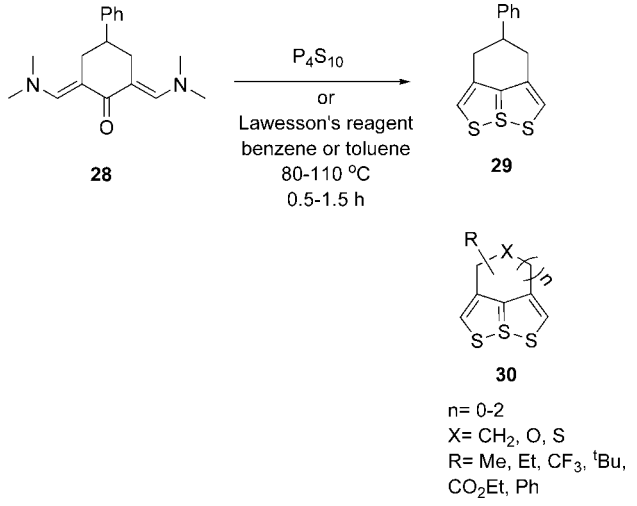


Replacement of carbonyl oxygens of ester and lactone groups with sulfur using P_4S_{10} has been demonstrated by

Scheme 9. Formation of Trithiapentalenes from 1,3,5-Triketones

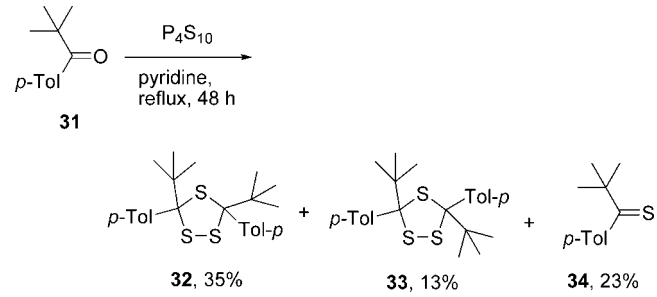


Scheme 10. Reaction of Dienamine with P_4S_{10}

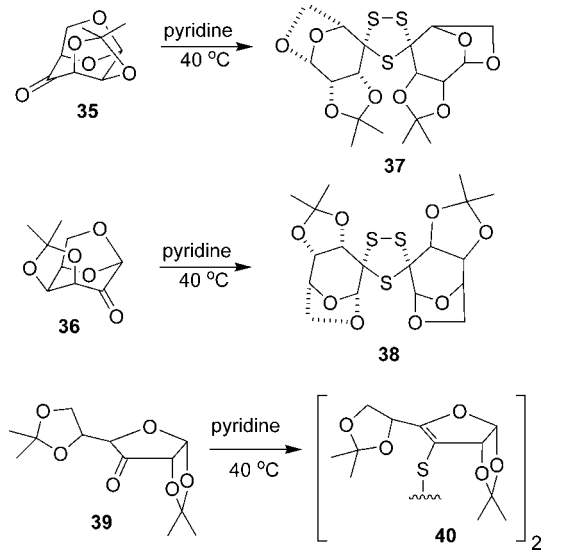


various examples. It looks that they are less reactive than amides, as the examples indicate that amide carbonyls could selectively be thionated in the presence of ester and/or lactone groups with P_4S_{10} (see the amide part). On the other hand, esters and lactones are reactive enough that they could be thionated in the presence of some simple functional groups such as alkylamines, halogens, nitro, and CN groups (Table 4). Although it appears that the general reaction solvents are toluene and xylene, aceto-

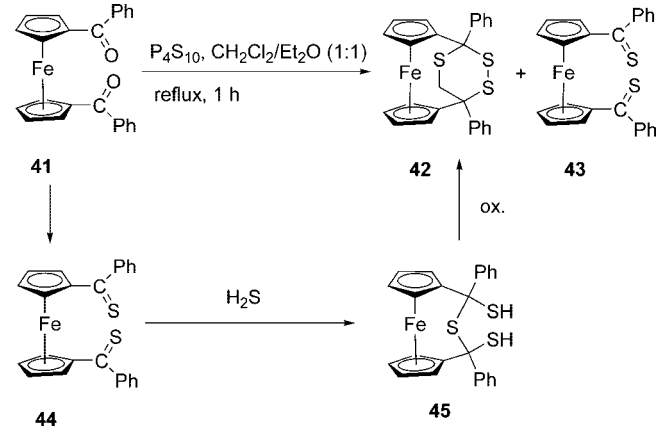
Scheme 11. Reaction of 31 with P_4S_{10}



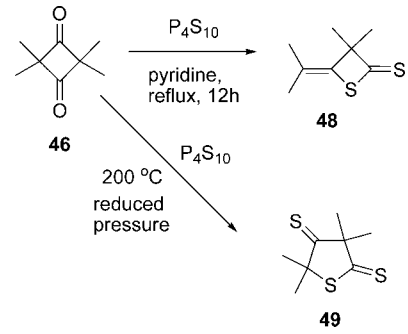
Scheme 12. Treatment of the Ketones 35, 36, and 39 with P_4S_{10}



Scheme 13. Thionation of Dibenzoferrocene 41 with P_4S_{10}

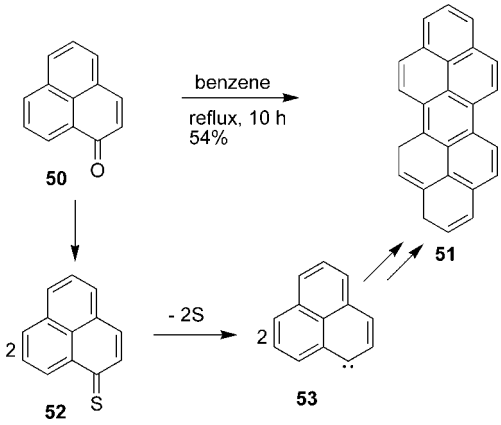


Scheme 14. Reaction of 46 with P_4S_{10}

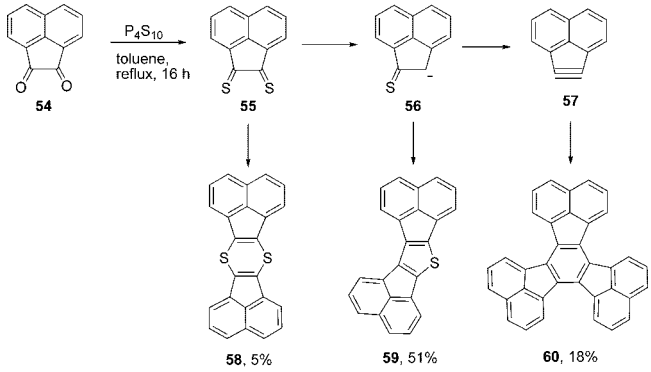


nitrile, diethyl ether, THF, benzene, dioxane, chloroform, and pyridine are also used. The reaction is generally

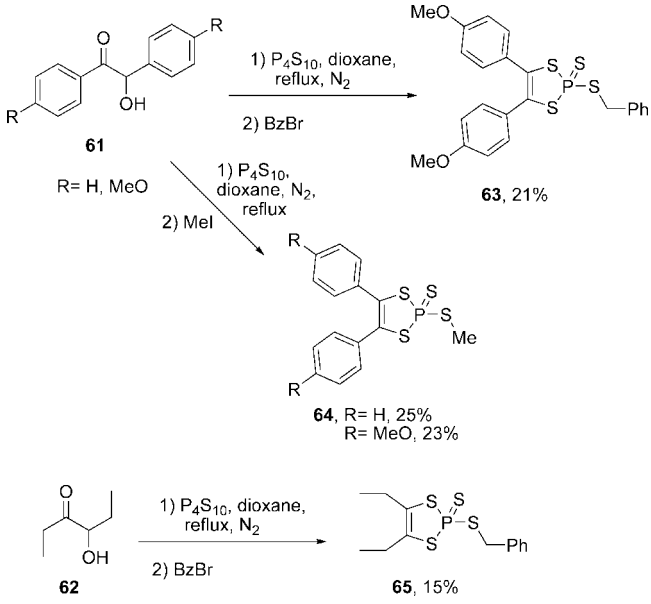
Scheme 15. Formation of Peropyrene 51



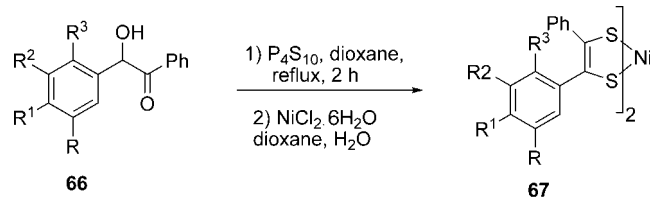
Scheme 16. Formation of the Coupling Products from 54



Scheme 17. Reactions of the α-Hydroxyketones with P_4S_{10}

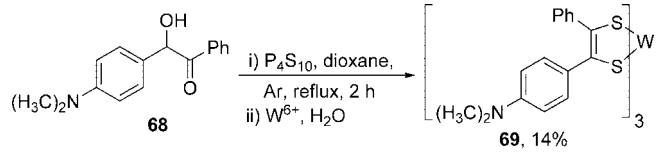


Scheme 18. Reaction of 66 with P_4S_{10}

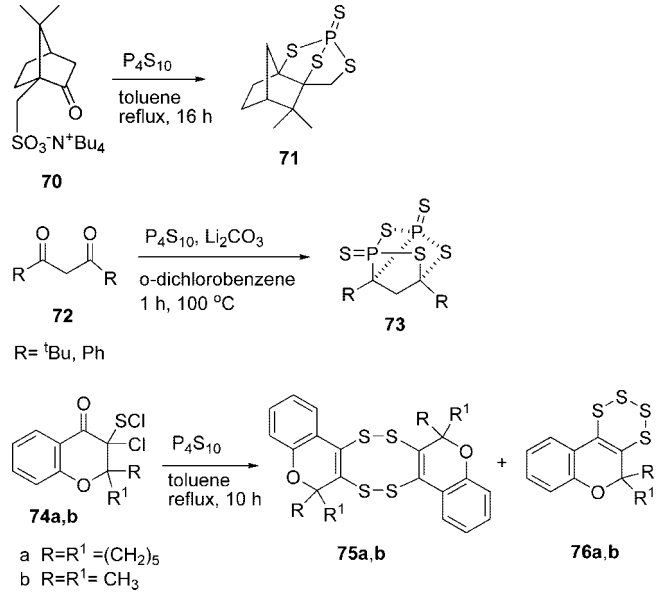


R= H, MeO
R^1 = H, Br
R^2= H, $(CH_3)_2N$, CH_3O, Me, Et, Cl, $(CH_3)_2CH$
R^3= H, Me

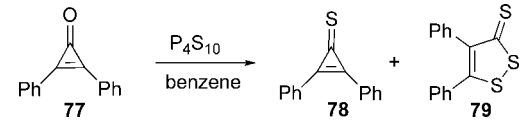
Scheme 19. Reaction of 68 with P_4S_{10}



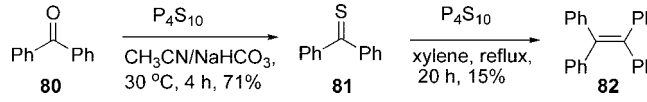
Scheme 20. Reaction of the Ketones 70, 72, and 74 with P_4S_{10}



Scheme 21. Reaction of Diphenylcyclopropenone with P_4S_{10}



Scheme 22. Synthesis of Tetraphenyl Ethylene

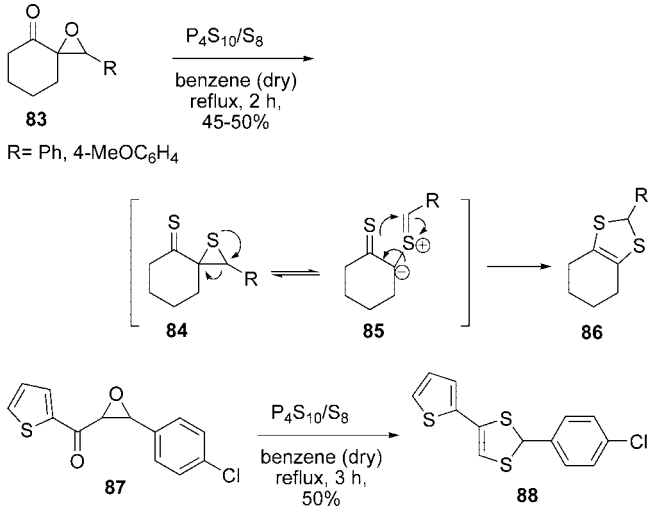


performed in refluxing solvents. There is no clear-cut indication that the thionation reaction should be conducted under an inert atmosphere. Some of the reactions are carried out using HMDO (hexamethyldisiloxane) (Table 4, entries 1−4, 14−18, 28, and 29, Table 5, entries 6 and 7), $NaHCO_3$ (Table 4, entry 26), S_8 and ZnO (Table 5, entries 1, 4, 5, and 7) along with P_4S_{10}.

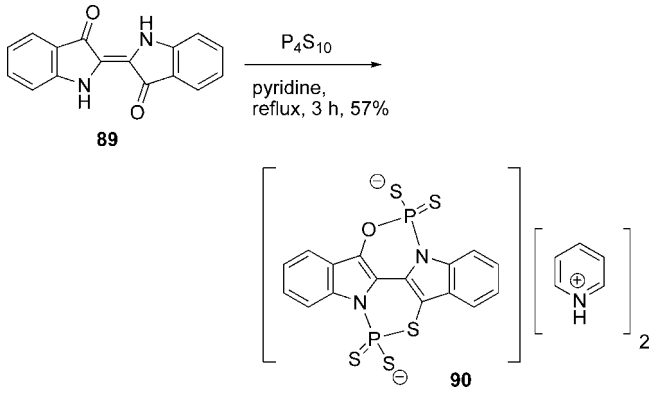
The synthesis of dithioesters from either carboxylic acids and alcohols or thiols using P_4S_{10} in usual thionation solvents was reported by various groups (Schemes 25−27). Treatment of the acids **91** and **94** with the alcohols **92** and **95** in the presence of $NaHCO_3$ and Ph_3SbO, respectively, produced the corresponding esters **93** and **96**, respectively (Scheme 25).[136,137] Using the same catalysis, Ph_3SbO, the reaction of acetic acid **97** with the olefins **98a−c** in benzene at 50 °C for 12 h gave the olefins **99a−c**.[138] Dithioesters **102** were also obtained only in the presence of P_4S_{10} through the reaction of the acids **100** with the alcohols or thiols **101** in toluene or CCl_4.[139]

The di-**106** and tri-**107** dithioesters were synthesized using the di- and trifunctional carboxylic acids **103** or **104** and

Scheme 23. Syntheses of the Dithioles 86 and 88



Scheme 24. Reaction of Indigo with P_4S_{10}



benzyl mercaptan **105** in refluxing toluene or dioxane, respectively (Scheme 26).[140]

It was reported that treatment of the carboxylic acids **110** with trialkyltetrathiophosphates **109**, which was obtained in bulk from alcohols **108** and P_4S_{10},[141,142] yielded the thiolocarboxylic esters **111** along with a small amount of the dithioesters **112** (Scheme 27).[143] Further reactions of the thiolocarboxylic esters with P_4S_{10} resulted in the complete transformation to the dithioesters.

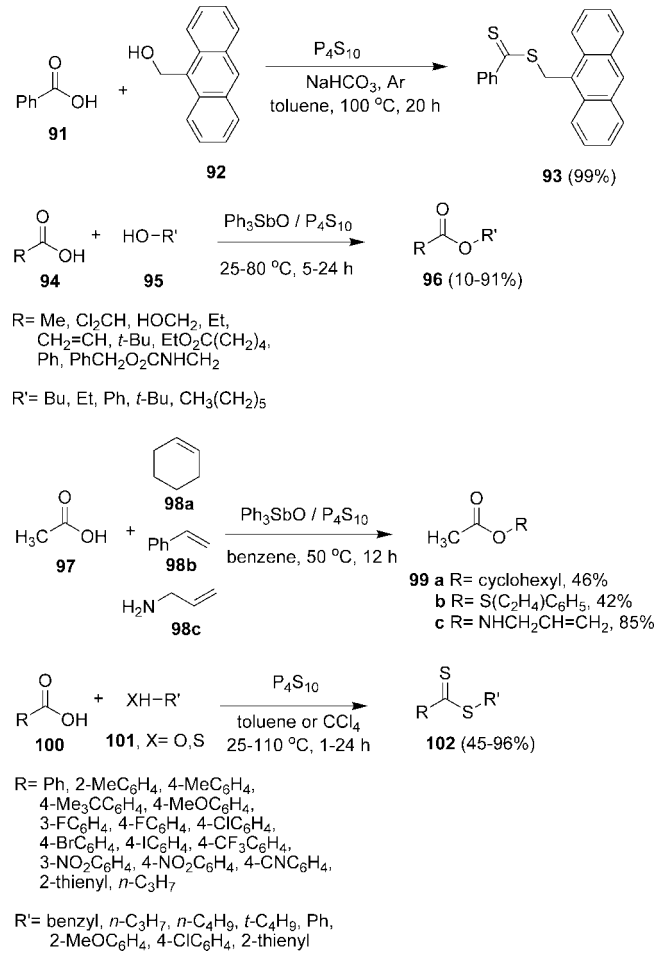
Thionoformate and dithioformate were synthesized with the reaction of P_4S_{10} with ethyl orthoformate and orthothioformate, respectively (Scheme 28).[144,145] The reaction of ethyl orthoformate **113** with P_4S_{10} at 95−150 °C gave three products: ethyl formate **114**, ethyl thionoformate **115**, and triethyl dithiophosphate **116**. Similar results were obtained on treatment of ethyl orthothioformate **117** with P_4S_{10}, which yielded ethyl dithioformate **118** and triethyltetrathiophosphate **119**.

The reaction of alkylaminocrotonates **120** with P_4S_{10} in benzene at 60 °C yielded thiaphosphetanes **121** in low yields, 1−4%, which were spontaneously rearranged to oxaphosphetanes **122** (Scheme 29).[146]

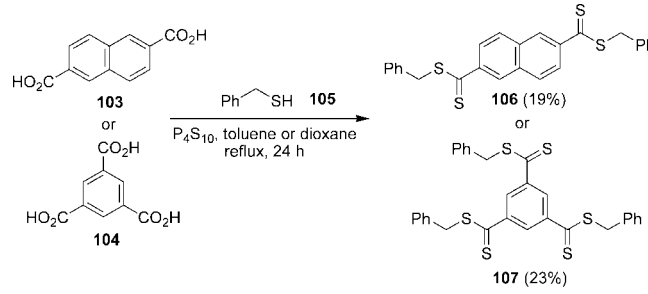
Benzoxanzinones **123** were transformed into benzothiazinthiones **126** in good yields on treatment with P_4S_{10} (Scheme 30).[93] The mechanism was suggested to involve initial thionation of the carbonyl group to give **124**, which was rearranged to **125** and then second thionation resulted in the formation of **126**.

Treatment of thienothiophene, having esters and amide groups ortho to each other, with P_4S_{10} in pyridine gave a

Scheme 25. Synthesis of Esters from Carboxylic Acids and Alcohols or Thiols



Scheme 26. Syntheses of di- and tri-Dithioesters



Scheme 27. Syntheses of Dithioester from Thiolocarboxylic Esters

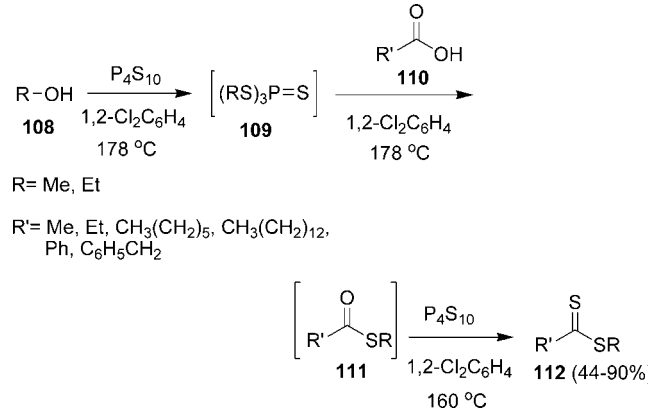


Table 4. Products of the Corresponding Esters and Lactones

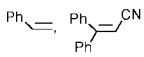
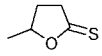
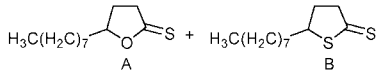
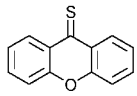
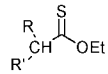
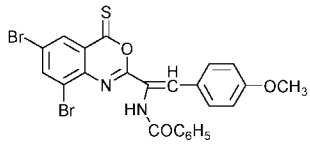
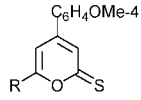
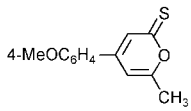
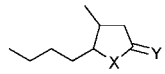
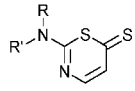
Entry	Product	Conditions	Yield (%)	ref
1	 R= Ph, 4-$NO_2C_6H_4$, Me, 1-naphtyl, *n*-hexyl,  R'= Me, Et, *i*-Pr, *t*-Bu, 2-naphtyl	HMDO, xylene, reflux, 4-18 h	21-87	66, 102
2		HMDO, MeCN or toluene, reflux, 1-5 h	78	102
3	 A B	HMDO, neat, MW (maximum 850 W)	74 Selectivity A= 86, B= 14	103
4	 n=3-5,14	HMDO, MeCN, or xylene, reflux, 0.5-4 h	65-86	66, 102
5	 R= Me, Ph, H R'= MeO, EtO, EtS	neat or diethyl ether, $NaHCO_3$, reflux, 6-24 h	14-60	48
6		THF, 30 °C, 3 h	75	48
7	 A) R= CF_3S, R'= H B) R= R'= CF_3S	toluene, reflux A= 14 d. B= 3 d.	A= 76, B= 64	104
8		xylene, reflux, 2 h	-	105
9	 R= 4-$MeOC_6H_4$, Me	benzene, dioxane or chloroform, reflux or sonication, 0.5-3 h	19-80	106, 107
10		benzene (dry), reflux, 4 h	84	108
11	 X= O, Y= S X= S, Y= O X= Y= S	-	-	109
12	 R= H, Ac R'= Me, Et, Ph, 2-ClC_6H_4	toluene (dry), 80 °C, 6 h	65-70	110

Table 4. Continued

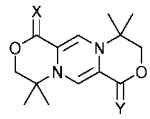
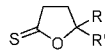
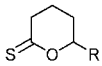
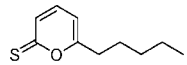
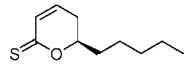
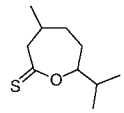
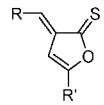
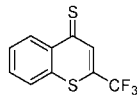
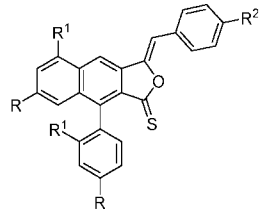
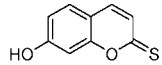
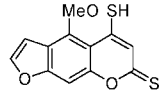
Entry	Product	Conditions	Yield (%)	ref
13	 X= S, Y= O X=Y= S	pyridine (dry), N_2, reflux, 12 h	-	111
14	 A R= H, R'= Me B R= Me, R'= hex-3-enyl	HMDO (hexamethyldisiloxane), CH_3CN, N_2, reflux, 3 h	A= 98 B= 84	112
15	 R= propyl, pentyl, heptyl pent-3-enyl, pent-2-enyl	HMDO, CH_3CN, N_2, reflux, 3 h	71-75	112
16		HMDO, CH_3CN, N_2, reflux, 3 h	97	112
17		HMDO, CH_3CN, N_2, reflux, 3 h	79	112
18		HMDO, CH_3CN, N_2, reflux, 3 h	85	112
19	 R= Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-MeC_6H_4 R'= Ph, 4-MeC_6H_4,4-$MeOC_6H_4$ 4-ClC_6H_4	xylene (dry), reflux, 6 h	50-80	113
20		toluene (dry), reflux, 1 h	66	114
21	 R= H, Me R^1= H, Cl R^2= H, NO_2	xylene, reflux, 5 h	~35	115
22		toluene, reflux, 8-10 h	60	116
23		toluene, reflux, 8-10 h	50	116

Table 4. Continued

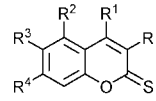
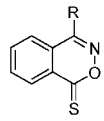
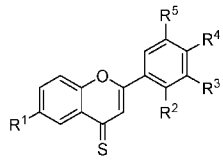
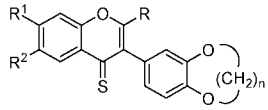
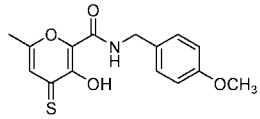
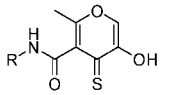
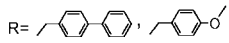
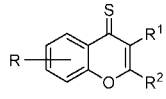
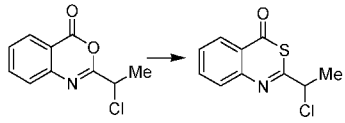
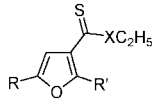
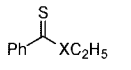
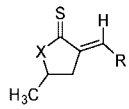
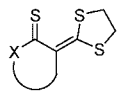
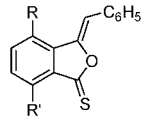
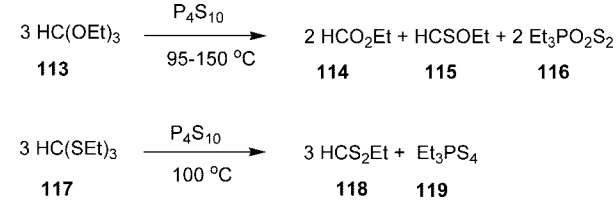
Entry	Product	Conditions	Yield (%)	ref
24	 R=R^1=R^2= R^3= H, R^4= OAc R= R^2= R^3= H, R^1=Me, R^4= OAc R= R^2= R^4= H, R^1= Me, R^3= OAc R^2= R^3= H, R^1= Me, R= Br, R^4= OAc R= R^2= R^3= H, R^1= CH_2CO_2Me, R^4= OAc	CH_3CN or dioxane, reflux, 2-3 h	50-75	117
25	 R=Ph, 4-MeC_6H_4, 3,4-$Me_2C_6H_3$, 4-$Me_2CHC_6H_4$	xylene, reflux, 8 h	52-63	118
26	 R^1= H, F, Cl, Br R^2= H, NO_2, I R^3= H, MeO, NO_2 R^4= H, Me, MeO, NO_2 R^5= H, NO_2	THF (dry), $NaHCO_3$, rt	70-85	119
27	 n= 1, 2 R= H, Me R^1= H, OH, MeO R^2= H, Propyl	pyridine (dry), reflux, 3- 3.5 h	74- 81	120
28		HMDO, benzene, reflux	61	121
29	 R= 	HMDO, benzene, reflux	16-18	121
30	 R= H, 6-Me, 7-MeO R^1= H, Cl, Br R^2= CF_3, $(CF_2)_2H$	toluene (dry), reflux, 4 h	49-93	122
31		xylene, reflux, 2 h	59	123
32	 X= O: R= Me, Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4; R^1= Me, Ph, 4-$MeOC_6H_4$, 2-Thienyl X=S: R= Me, Ph; R^1= Me, Ph	xylene (dry), reflux, 2-5 h	30-55	132

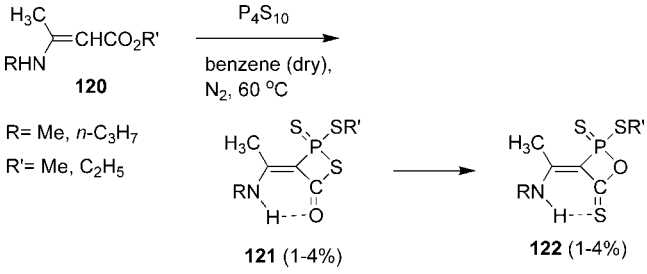
Table 4. Continued

Entry	Product	Conditions	Yield (%)	ref
33	 X= O, S	xylene (dry), reflux	-	133
34	 X= O, S R= Ph, 4-MeOC$_6$H$_4$	xylene (dry), reflux	-	134
35	 X= OCH_2CH_2, $OCH(CH_3)CH_2$, $SCH(CH_3)CH_2$, $OC(CH_3)_2CH_2$, SCH_2CH_2, $SC(CH_3)_2CH_2$, $O(CH_2)_2CH_2$, $S(CH_2)_2CH_2$, $OC(CH_3)$=CH, OC(Ph)=CH	xylene (dry), reflux	-	134
36	 A R= H, R^1= Cl B R= Cl, R^1= H	xylene (dry), reflux, 5 h	A= 73 B= 35	135

Scheme 28. Reaction of Orthoformate and Orthothioformate with P_4S_{10}



Scheme 29. Reaction of Alkylaminocrotonates with P_4S_{10}

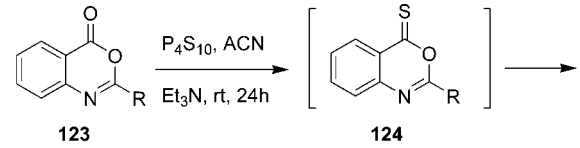


ring closure reaction (Scheme 31).[147] The reaction of **127** with P_4S_{10} in refluxing pyridine for 20 h yielded two compounds: the ring closure, **129**, and nonring-closure, **130**, products. On the other hand, the same reactions of **128** with P_4S_{10} gave only the ring closure products **129** and **131**.

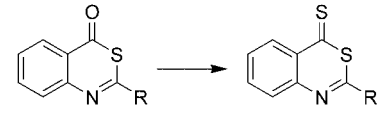
Dithiolactone **133** was obtained from the reaction of the dicarbonyl compound **132** with P_4S_{10} in refluxing dioxane for 4 h (Scheme 32).[148]

Dithiolethiones were synthesized from various starting materials, including thioacetals, having a carbonyl group at the 3-position (Table 6, entries 2, 3, 5, and 6). The reaction of diacylketene thioacetals **134** with P_4S_{10} in various solvents at room temperature gave dithiolethione **135** in moderate yield.[149] On the other hand, when the reaction was performed

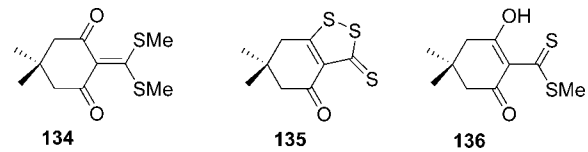
Scheme 30. Synthesis of Benzothiazinethiones from the Reaction of Benzoxazinones with P_4S_{10}



R= Me, Ph, $PhCH_2$, 4-$NO_2C_6H_4$



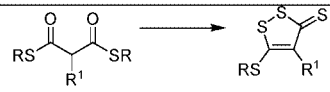
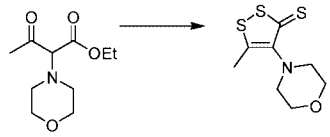
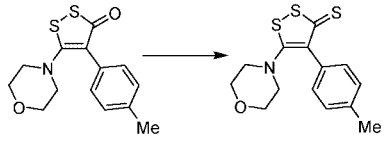
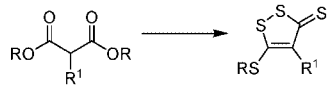
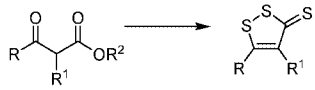
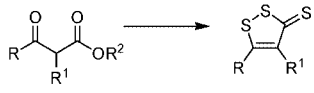
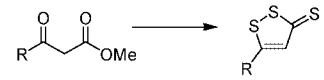
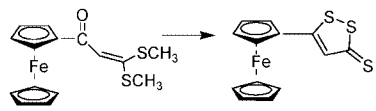
in a mixture of ACN−Et_3N (9:1) at −30 °C, the dithioester **136** was obtained in 44% yield.



1,2-Dithiol-3-thione **138** was obtained in 31% yield on treatment of 2-thioxo-1,3-thiazine-4-one **137** with P_4S_{10} in hot pyridine (Scheme 33).[159] On the other hand, when the reaction was performed in xylene in place of pyridine, with **137** or **139**, 1,3-thiazine-2,4-dithione **140** was obtained. No reaction took place when benzene or toluene was used as solvent. Moreover, the use of mixed solvents such as xylene/pyridine caused the formation of **140** in 60−80% yields.

The effect of the use of pyridine or xylene as solvent in the mechanism explained that pyridine, as a base, attacks at

Table 5. Formation of Dithiolethione

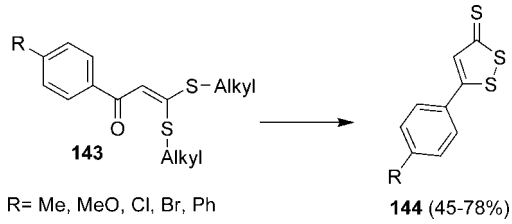
Entry	Product	Conditions	Yield (%)	ref
1	 R= Et, butyl, octyl R^1= H, benzyl	xylene, S_8, ZnO, N_2, reflux, 1.5 h	12-32	124
2		xylene, reflux, 15 min.	12	125
3		xylene, reflux, 15 min.	55	125
4	 R= Me, Et, Pr, butyl, octyl, $C_2H_5O(CH_2)_2$ R^1= H, Me, benzyl, Ph, Cl, MeO	xylene, S_8, 2-mercaptobenzothiazole (MBT), ZnO, N_2, reflux	5-35	126
5	 R= $CH_3(CH_2)_3$, $CH_3(CH_2)_{11}$, C_5H_9, C_6H_5, $(CH_3)_3C$, $C_6H_5CH_2$	xylene, S_8, MBT, ZnO, N_2, reflux	47-86	127
6	 R= Cl, Me, Ph, 4-BrPh, 4-MeOPh R^1= Cl, Me, Et, CF_3 R^2= Me, Et	HMDO, toluene (dry), reflux, 4 h	~30	128
7	 R= Me, Et, Ph, *t*-Bu, 1-adamantyl, ferrocenyl, -$(CH_2)_4$-, -$(CH_2)_3$-, -$(CH_2)_{3,5,6,15}$-, *n*-hexyl, 1-naphthyl, 4-$NO_2C_6H_4$, PhCH=CH-, Ph_2C=C(CN)-, -$(CH(CH_3)CH_2CH_2$-, pyrazin-2-yl R'= Me, Et, *i*-Pr, 2-naphthyl R^2= Me, Et	xylene, S_8, HMDO, reflux , 0.5-8 h	36-98	66, 102, 129
8	 R= $CHCF_2$, $(CF_2)_2H$, CF_3, C_4F_9	toluene, reflux	20-35	130
9		xylene, reflux, 30 min	40	131

hydrogen on the nitrogen, causing a ring-opening to produce **141**, reaction of which with P_4S_{10} gives **142**. Then the ring closure yields the product **138** (Scheme 34).

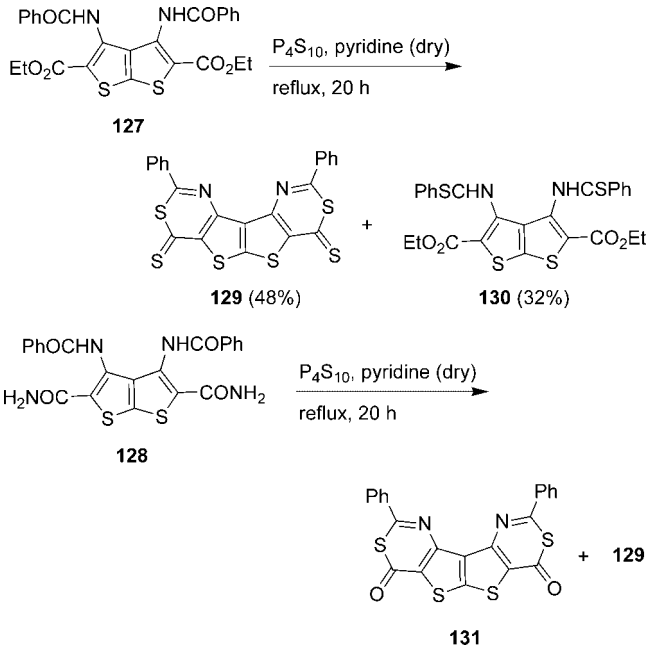
Aryldithiolethiones **144** were reported to be obtained from the reaction of 1-aryl-3,3-dialkylthio-2-propen-1-ones **143** with P_4S_{10}.[160] Similar results were obtained with β-oxoesters.[161]

Dithiolethione **146** was produced in 45% through the reaction of bis(2-carboxy-3-chlorophenyl)disulfur **145** with P_4S_{10} in refluxing xylene (Scheme 35).[162]

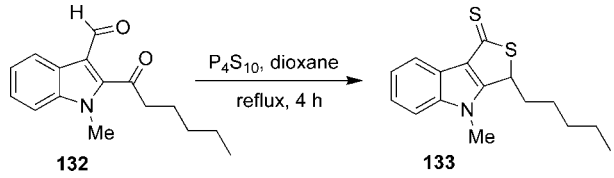
Interestingly, the reaction of the ester **147** with P_4S_{10} in different solvents such as xylene and pyridine gave different results (Scheme 36).[163] While the reaction of **147** with P_4S_{10} in refluxing xylene for 1.5 h yielded the dithiolactone **148**



Scheme 31. Reaction of Ortho Ester and Amide Groups with P_4S_{10}



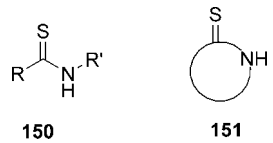
Scheme 32. Reaction of Dicarbonyl Compound with P_4S_{10}



in 25−30% yield, performing the same reaction in refluxing pyridine resulted in the formation of thionolactone **149** in 50−70% yield.

2.3. Amides and Lactams

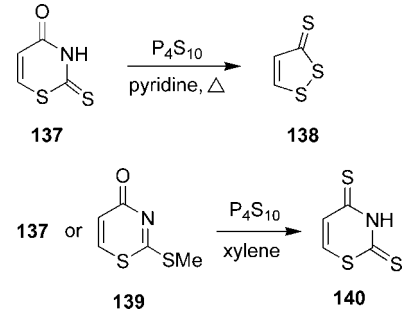
Amides and lactams can easily be converted to thioamides **150** and thiolactams **151** (Tables 7 and 8, respectively).



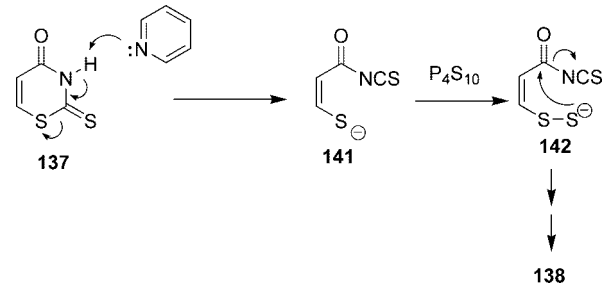
As they are among the most reactive groups, they could easily be thionated in the presence of various functional groups, such as ester, pyridine, Boc, amine, nitro, and cyano (Tables 7 and 8). The reaction was performed in various solvents, including toluene, xylene, benzene, THF, CH_2Cl_2, $CHCl_3$, pyridine, dioxane, hexamethylphosphoric triamide, acetonitrile, and dimethoxyethane, and the reaction temperature was changed from −20 °C to reflux. In some cases, thionation of amides and lactams was carried out in a basic medium using $NaHCO_3$, Na_2CO_3, Et_3N, KF, NaF, K_2S, and Dabco, although the reaction was generally conducted in neat solvent. Moreover, there are examples where catalysts such as hexamethyldisiloxane (Table 7, entries 1, 30, 31, and 35; Table 8, entry 1), silica gel 60 (Table 8, entries 36 and 43), and Al_2O_3 (Table 7, entries 21, 25, and 26; Table 8, entry 51) were employed. Surprisingly, in one example of thionation of some amide and lactams, P_4S_{10} was treated with *n*-BuLi prior to the addition of amide and lactams into the reaction medium (Table 7, entry 32; Table 8, entries 46−50, respectively).[224] It was concluded that P_4S_{10} was initially reacted with *n*-BuLi to form the complex **152**, the reaction of which with the lactams yields the thiolactams (Scheme 37).

Although there are examples which indicate that amides (Table 7, entry 27) and lactams (Table 8, entries 26 and 52)

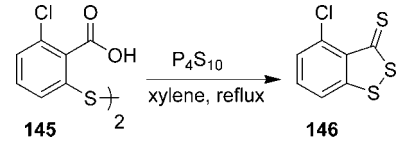
Scheme 33. Synthesis of 1,2-Dithiol-3-thione from 2-Thioxo-1,3-thiazine-4-one



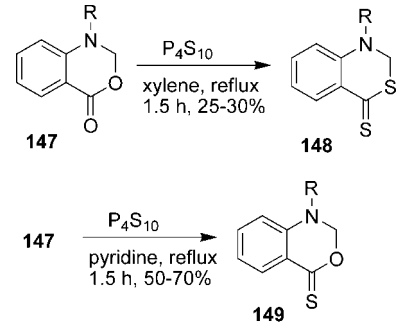
Scheme 34. Mechanism of Formation of 1,2-Dithiol-3-thione



Scheme 35. Reaction of 145 with P_4S_{10}

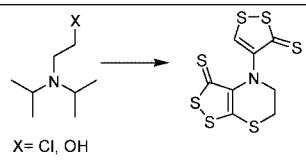
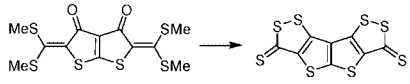
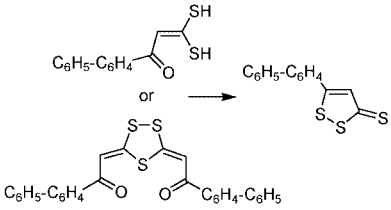
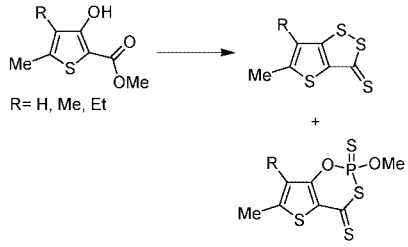
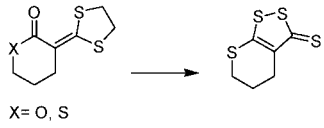
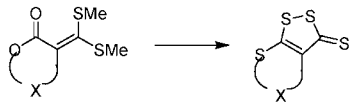
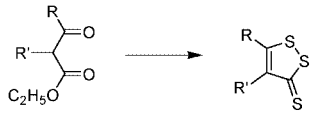


Scheme 36. Reaction of 147 with P_4S_{10}



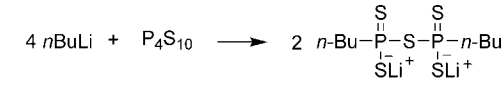
R= Me, Et, Ph, $C_6H_5CH_2$, 2-MeC_6H_4, 3-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$, 2-ClC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4

Table 6. Synthesis of Dithiolethione

Entry	Product	Reaction conditions	Yield (%)	ref
1	 X= Cl, OH	S_2Cl_2, then P_4S_{10}, THF, reflux, 5.5 h	40	150, 151
2		xylene, reflux	31	152
3		benzene or xylene, reflux, 4 h	76	153
4	 R= H, Me, Et	xylene (dry), reflux, 1 h	-	154, 155
5	 X= O, S	xylene , reflux, 15 min	-	134
6	 X= —(CH_2)-, —$CHCH_3CH_2$— —$C(CH_3)_2$-CH_2—, —$(CH_2)_2$— —CCH_3=CH—	xylene , reflux	15-28	134
7	 R= Me, Et, Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2-thienyl R'= -CO_2Et, CN, Cl	toluene, reflux , 1 h	37-70	156, 157
8		xylene, reflux, 6 h	75	158

could be thionated in the presence of cyano groups, there are also examples that the cyano groups could be converted to thioamides. Refluxing of acrylidenemalononitriles **153** with P_4S_{10} in toluene (dry) gave the corresponding thioamides **154a−c** along with a side product **155** derived only from **153a−c** (Scheme 38).[227]

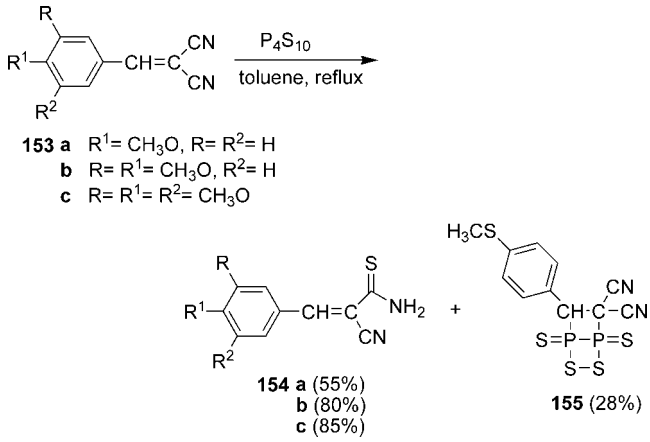
Scheme 37. Reaction of *n*-BuLi with P_4S_{10}



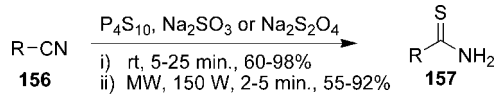
152

In another two examples, the nitriles **156** and **156a−e** were converted to the corresponding amides **157** and **157a−e**, respectively, under different conditions. While the reaction of the nitriles **156** with P_4S_{10} in the presence of sodium sulphite or sodium dithionite at room temperature produced

Scheme 38. Thionation of the Arylidenemalononitriles

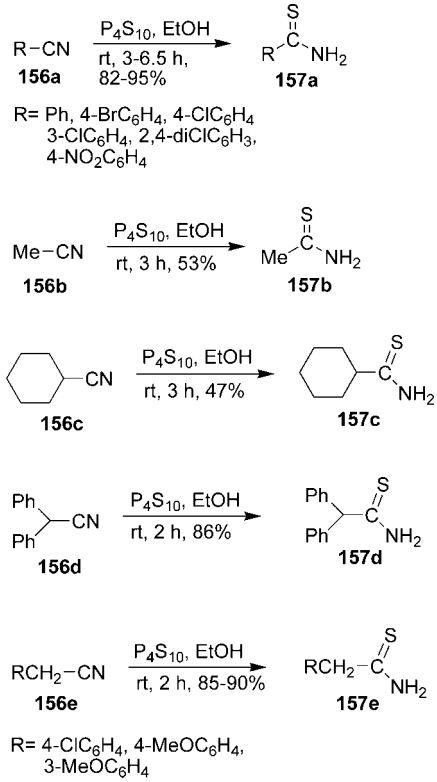


Scheme 39. Synthesis of Thioamides from Cyanides in the Presence of Na_2SO_3 or $Na_2S_2O_4$



R= CH_3, $NCCH_2$, EtO_2CCH_2, Ph, $NH_2(NH)CNH$, $C_6H_5CH_2$, 2-pyridyl, 3-pyridyl

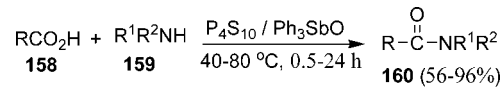
Scheme 40. Synthesis of Thioamides from Cyanides



the amides **157** in 5−25 min with 60−98% yield, performing the same reaction with a microwave resulted in 2−5 min with 55−92% yield (Scheme 39).[228] On the other hand, converting the nitriles **156a**−**e** to the corresponding amides **157a**−**e** with P_4S_{10} in ethanol at room temperature took between 2 and 6.5 h with 53−95% yield (Scheme 40).[229]

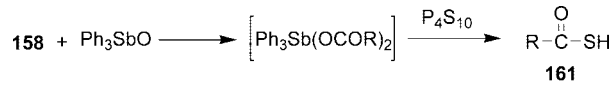
It looks as though the differences between the reaction conditions of thionation of amides and lactams in the presence cyanide, and converting a cyanide group to an amide are reaction temperatures, protic solvents, and inclusion of Na_2SO_3 or $Na_2S_2O_4$ in the reaction mixture. Thionations of amides and lactams, without affecting the cyanide groups, were performed in refluxing pyridine. On the other hand, a mild reaction condition such as room temperature is required to obtain thioamides from cyanides.

Scheme 41. Synthesis of Amides from Carboxylic Acids and Amines



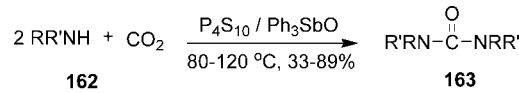
R= Me, Cl_2CH, CH_2CH, *t*-Bu, Ph
R^1= H, Et
R^2= *t*-Bu, Et, $HOCH_2CH_2$, Hexyl, CH_2=$CHCH_2$, Propyl, *t*-Bu, Ph

Scheme 42. Reaction of Carboxylic Acid with Ph_3SbO/P_4S_{10}



R= Me, Cl_2CH, CH_2CH, *t*-Bu, Ph

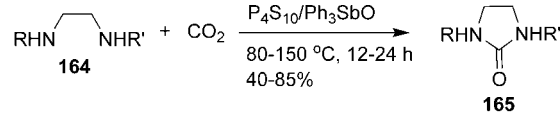
Scheme 43. Synthesis of Ureas from Amines and Carbon Dioxide



R= Bu, *i*-Bu, *t*-Bu, allyl, Ph, Me

R'= H, Me

Scheme 44. Synthesis of Cyclic Ureas



R= H, Me,Ph, $HOCH_2CH_2$, $HOCH(CH_3)CH_2$

R'= H, Me

Amides **160** were synthesized from carboxylic acids **158** and amines **159** in the presence of P_4S_{10} and triphenylstibine oxide (Ph_3SbO) (Scheme 41).[230] The method was also applied to the syntheses of some peptides, such as z-Gly-Gly-OEt, z-Phe-Leu-OEt, z-Leu-Phe-OMe, z-Ser-Gly-OEt, and z-Tyr-Gly-OEt, and to the preparation of diamides of adipic acid $(CH_2CH_2CO)_2(NHPr)_2$.

It was claimed that the combination of P_4S_{10} and Ph_3SbO leads to the formation of thiocarboxylic acid **161**, which could then react with the amine **159** to yield the amide **160** (Schemes 42 and 41).[230]

The same combination (P_4S_{10}/Ph_3SbO) was applied to the reactions of the amines **162** with carbon dioxide, which resulted in the formation 1,3-dialkylureas **163** (Scheme 43).[231] Moreover, when the diamines **164** were reacted with carbon dioxide, cyclic ureas **165** were obtained (Scheme 44).

Addition of part of P_4S_{10} was observed with the reactions of amide systems having reactive *ortho* amine groups. The reaction of the amides **166** with P_4S_{10} gave the addition products **168** through the intermediate **167**, which has an *o*-amino system (Scheme 45).[232] Similar results were observed with 2-amino-3-carbamoyltetrahydrobenzothiophene **169** and 2-aminobenzamide **170**, which gave the addition products tetrahydrobenzothiophenodiazaphosphinane-2-thion-4-one **171** and benzodiaza-

Table 7. Products of the Corresponding Amides with P_4S_{10}

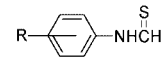
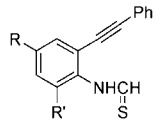
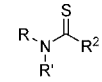
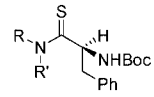
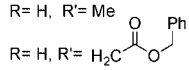
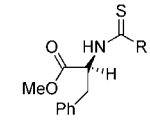
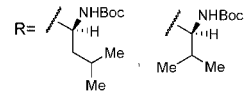
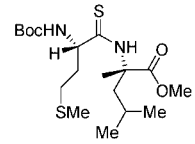
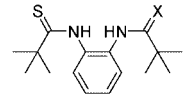
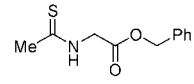
Entry	Product	Conditions	Yield (%)	Ref
1	 R= H, CH_3, Ph, pyridyl R'= NH_2, PhNH, $(CH_3)_2CN$, morpholino	with or without HMDO; CH_2Cl_2, $CHCl_3$, HMPA or benzene; rt, 80 °C or reflux, ; 0.33–18 h	49-100 (HPLC)	66
2		diethyl ether, reflux, 5 h	85	48
3	 R= H, 3-Cl, 4-Cl 4-CH_3, 4-CH_3O	base: $NaHCO_3$, Et_3N/HCO_2H, Et_3N, KF/HCO_2H, Et_3N/SO_2 or Na_2SO_3 CH_3CN, rt, 34 h	trace-95	164
4	 R= H, Cl, F R'= H, Cl	THF, reflux, 15 min	48-80	165
5	 R= R'= Me, R^2= H R= R'= H, R^2= Ph R=R'= Me, R^2= Ph R= R'=Me, R^2=4-$NO_2C_6H_4$	THF, Na_2CO_3, -20-25 °C, 2-18 h	90-91	166
6	 R= R'= H, R= H, R'= Me R= H, R'=  R= R'= $CH_2(CH_2)_2CH_2$	THF, Na_2CO_3, CF_3SO_3Me, 25 °C, 4-8 h	72-84	166
7	 R= 	THF, Na_2CO_3, CF_3SO_3Me, 25 °C, 4, 10 h	28, 84	166
8		THF, Na_2CO_3, CF_3SO_3Me, 25 °C, 2 h	72	166
9	 X= O, S	THF, Na_2CO_3, CF_3SO_3Me, 25 °C, 10 h	43, 80	166
10		THF, Na_2CO_3, 25 °C, 2.5 h	80	166

Table 7. Continued

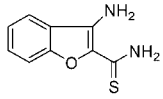
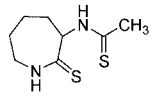
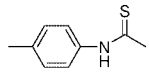
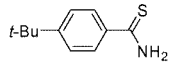
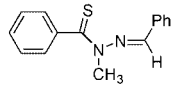
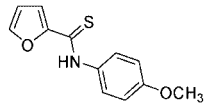
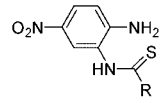
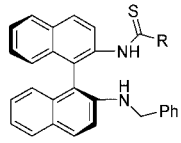
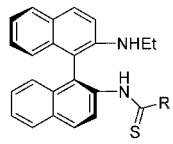
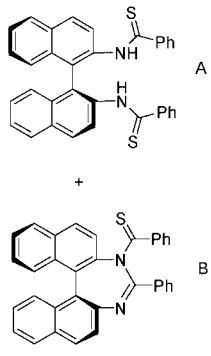
Entry	Product	Conditions	Yield (%)	Ref
11		pyridine (dry), reflux, 1 h	72	167
12		toluene, reflux, 20 h	41	168
13		toluene, reflux, 3 h	67	169
14		toluene, $NaHCO_3$, 90 °C, 1 h	49	170
15		pyridine, reflux, 3 h	90	171
16		dioxane, reflux, 1 h	62	172
17	 R= Et, 4-MeC_6H_4, 2-furyl, 4-$NO_2C_6H_4$, 4-$MeOC_6H_4$, 4-BrC_6H_4, pentyl, 2-thienyl	THF (dry), Na_2CO_3, 0 °C (3h), then rt (10 h)	59-96	173
18	 R= Me, Ph	pyridine, 120 °C, 10 h	R= Me, 76 R= Ph, 83	174
19	 R= Me, Ph	pyridine, 120 °C, 10 h	R= Me, 75 R= Ph, 65	174
20	 A + B	pyridine, 120 °C, 10 h	A= 70 B= 15	174

Table 7. Continued

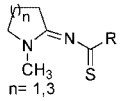
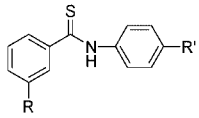
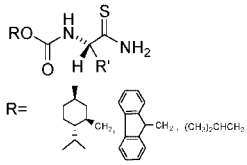
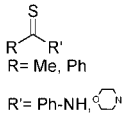
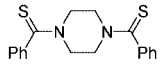
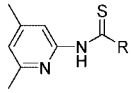
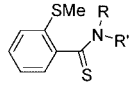
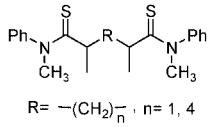
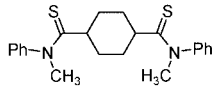
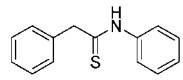
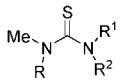
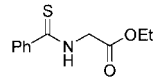
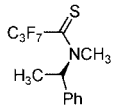
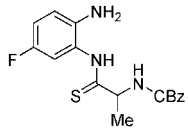
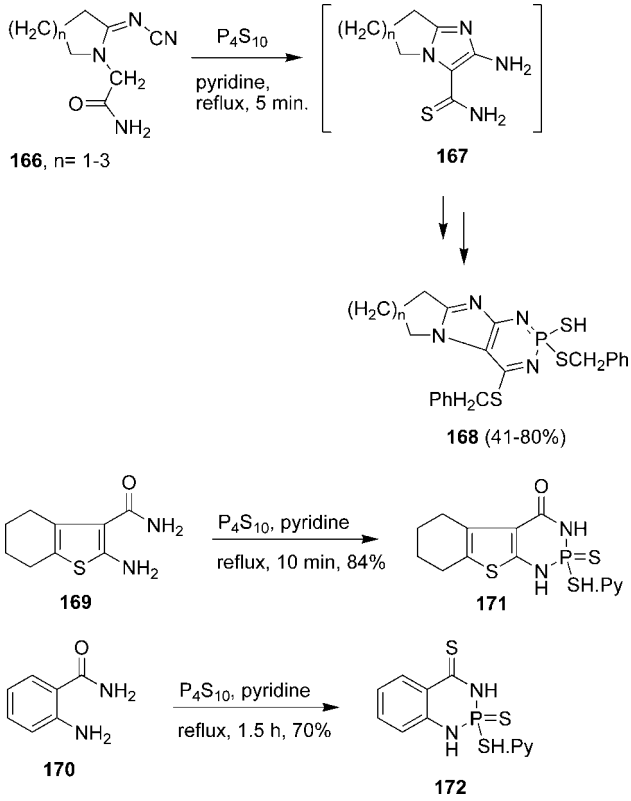
Entry	Product	Conditions	Yield (%)	Ref
21	 R= Me, Ph, hexyl, heptyl, nonyl R'= H, Ph, 4-ClC_6H_4	A= CH_3CN, reflux, 5-11 h B= CH_3CN, Al_2O_3, reflux, 5-11	A= 56-76 B= 79-88	175
22	 n= 1,3 R= Ph, 4-$MeOC_6H_4$	pyridine, reflux, 10 h	44-73	176
23	 R= H, Me, MeO, NO_2, Cl, Br R'= *i*-Pr, butyl, hexyl	pyridine, reflux, 10 h	5-45	177
24	 R'= *L*-ala, *D,L*-ala, *L*-phe, *D,L*-phe, *L*-val, *L*-leu, *L*-pro, gly	dimethoxyethane (dry), NaF, rt, 15 h	84-93	178
25	 R= Me, Ph R'= Ph-NH,	dioxane, Al_2O_3, reflux, 1 h	80-93	179
26		dioxane, Al_2O_3, reflux, morpholine, 1 h	85	179
27	 R= Ph, 3-FC_6H_4, 3-ClC_6H_4, 3-CNC_6H_4, 2-Furyl, 5-Br-2-furyl, 2-Thienyl, 2-Benzofuryl	pyridine (dry), reflux, 75 min	16-73	180
28	 A= R=H, R'= Me B= R= R'=Me	A xylene, K_2S, reflux, 2.5 h B benzene, reflux, 2 h	A= 57 B= 50	181
29	 R= Cl, Br	xylene (dry), steam-bath heating, 30 min	54, 67	182
30	 R= $-(CH_2)_n-$, n= 1, 4	HMDO, $CHCl_3$, reflux, 14 h	33-84	183
31		HMDO, $CHCl_3$, reflux, 3 h	84	183

Table 7. Continued

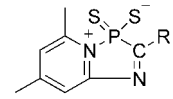
Entry	Product	Conditions	Yield (%)	Ref
32		THF (dry), *n*-BuLi, N_2, -10 → rt (1 h) → reflux,16 h	20	224
33	 R= Me, Ph R^1= Me, Ph, $C_6H_5CH_2$, $(CH_3)_2CH$ R^2= Me, Ph, $C_6H_5CH_2$ $(CH_3)_2CH$, *c*-C_6H_{11}	pyridine or benzene (dry), reflux, 2-24 h	6-78	241
34		benzene (dry), reflux, 2 h	~45	242
35		HMDO, toluene, 80 °C	92	250
36		THF (dry), Na_2CO_3, N_2, rt, overnight	65	216

Scheme 45. Addition of Part of P_4S_{10} to the Products Having *o*-Amino Groups



phosphorine-2,4-dithione **172**,[233−235] respectively, the structure of which were described by X-ray crystallography.[236]

A similar reaction, addition of part of P_4S_{10}, was reported as minor products of the reaction of *N*-(pyridine-2-yl)arylcarbomades with P_4S_{10} (Table 7, entry 27), which yielded **173**.[180]



R= Ph, 10%

R= 2-thienyl, 4%

173

An attempt to synthesize the corresponding thiolactam **176** from the lactam **174** in wet pyridine at 120 °C surprisingly gave **175** in 73% along with the desired product **176** as a minor product in 12%, which could also be converted to **175** by treatment with P_4S_{10} or H_2S (Scheme 46).[237] On the other hand, when the reaction was performed at 85 °C, the yields of **175** and **176** were changed to 5% and 79%, respectively. The thiolactam **175** was also synthesized from the corresponding lactam (Table 8, entry 54).

Scheme 46. Reaction of Lactam 174 with P_4S_{10}

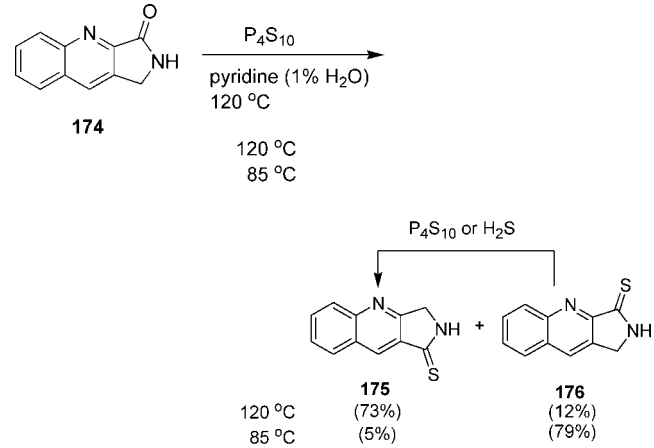


Table 8. Products of the Corresponding Lactams with P_4S_{10}

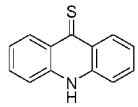
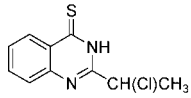
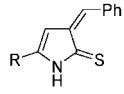
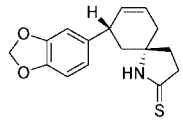
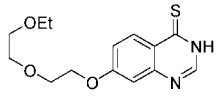
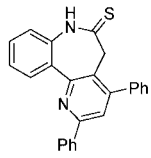
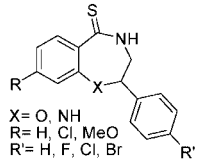
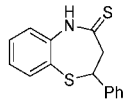
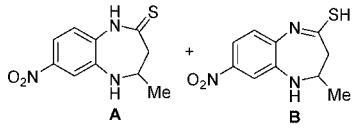
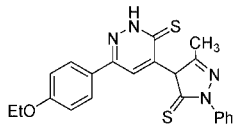
Entry	Product	Conditions	Yield (%)	Ref
1	 n= 1, 3	with or without HMDO; CH_2Cl_2, rt, 1- 4 h	69-100 (HPLC)	66
2	 n= 1, 3 R= H, Me, Bz	THF, Na_2CO_3, rt, 2,3 h	82-88	163
3		THF, Na_2CO_3, rt, 2,3 h	96	163
4		xylene, reflux, 12 h	58	123
5	 R= Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4	xylene, (dry), reflux, 6 h	50-68	113
6		toluene (dry) or benzene (dry), N_2, reflux, 3 h	80	184
7		pyridine, 110 °C	72	185
8		THF, $NaHCO_3$, N_2, reflux, 3 h	78	186
9	 X= O, NH R= H, Cl, MeO R'= H, F, Cl, Br	pyridine, reflux, 1.5 h	53-70	187
10		pyridine, reflux, 1.5 h	62	187
11	 A + B	pyridine, reflux, 1.5 h	A= 25 B= 50	188
12		xylene (dry), reflux, 6 h	69	189

Table 8. Continued

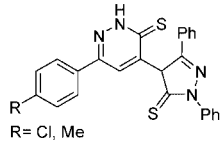
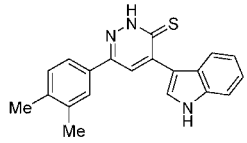
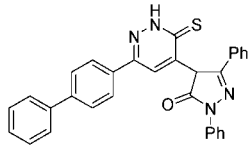
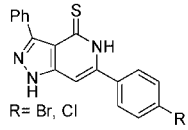
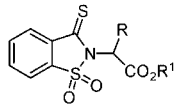
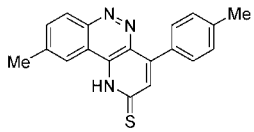
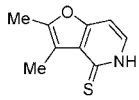
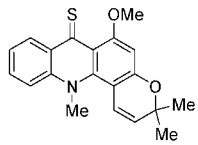
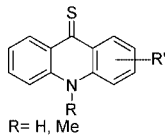
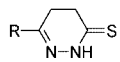
Entry	Product	Conditions	Yield (%)	Ref
13	 R= Cl, Me	xylene (dry), reflux, 6 h	62, 67	190
14		xylene (dry), reflux, 6 h	60	191
15		pyridine (dry), reflux, 3 h	30	192
16	 R= Br, Cl	pyridine (dry), reflux, 3 h	75, 78	193
17	 R= H, Me R^1= Me, Et	dioxane, reflux, 6-7 h	70-75	194, 195
18		pyridine (dry), reflux, 3 h	42	196
19		pyridine (dry), reflux, 5 h	56	197
20		HMPT, 140 °C, 1 h	45	198
21	 R= H, Me R'= H, 3-Me, 2-F, 6-Cl, 3-CF_3, 2-MeO,1,3-diMeO	HMPT, 115 °C, 2.5-18 h	70-99	198
22	 R= 4-Tolyl,β-naphthyl, 4-EtC_6H_4, 4-$tBuC_6H_4$, 4-$MeOC_6H_4$, 4-ClC_6H_4, 3,4-$diMeC_6H_3$, 2,5-$diMeC_6H_3$, 3,4-$diMeOC_6H_3$, 2-thienyl, 6-MeOnapthyl, *p*-biphenyl, 4-benzyl, 4-phenoxyphenyl	o-xylene (dry), reflux	-	199

Table 8. Continued

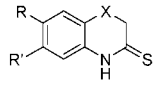
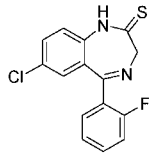
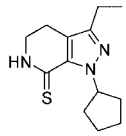
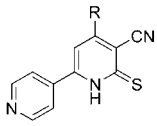
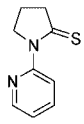
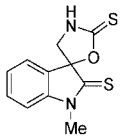
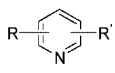
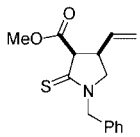
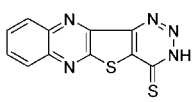
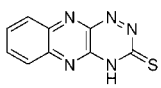
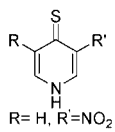
Entry	Product	Conditions	Yield (%)	Ref
23	 X=O, S R= H, Cl R'= H, Cl, Br, MeO	TEBA, dichloroethane, K_2CO_3, reflux, 15-20 min	90-93	200
24		pyridine, N_2, reflux, 1 h	66	201
25		dioxane (dry), reflux, 12 h	87	202
26	 R= Ph, 2-HOC_6H_4, 4-HOC_6H_4, 2,4-diHOC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2-furyl	pyridine, reflux, 8 h	58-69	203
27		THF (dry), $NaHCO_3$, reflux, 9 d	97	204
28		THF (dry), $NaHCO_3$, reflux, 24 h	16	205
29	 A R= 2-SH B R= 4-SH R'= H, 3,4-diiodo	pyridine, reflux, 1.5-2.5 h	A= 89 B= quant.	206, 207
30		THF	68	208
31		pyridine, reflux, 5 h	70	209
32		pyridine (dry), reflux, 4 h	82	210
33	 R= H, R'=NO_2 R= H, R'= NH_2 R= R'= NO_2 R= R'= NH_2	pyridine, reflux, 6 h	55-63	211

Table 8. Continued

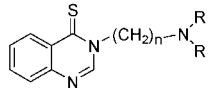
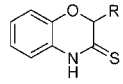
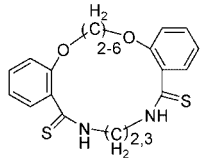
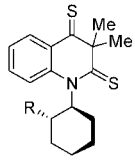
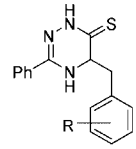
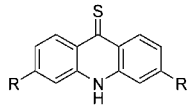
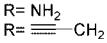
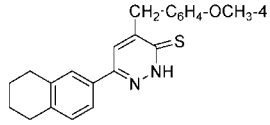
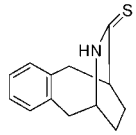
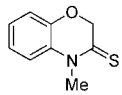
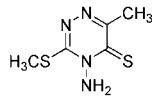
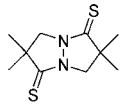
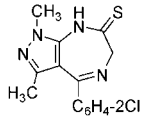
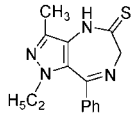
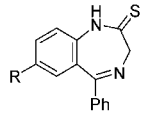
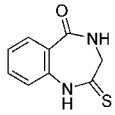
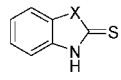
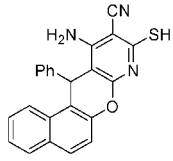
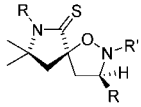
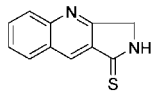
Entry	Product	Conditions	Yield (%)	Ref
34	 n= 2, 3 R= Et, Bu, Pr	xylene (dry), reflux, 4 h	~20	212
35	 R= H, Ph	CH_3CN, base (Et_3N, $NaHCO_3$, Dabco or Et_3NH^+ ^-OAc), rt, 24-48 h	20-94	213
36		A: P_4S_{10}, silica gel 60, MW (700 W), 30 min B: P_4S_{10}, pyridine, reflux, 6 h	A= 78-86 B= -	214
37	 R= Me, MeO, Cl	toluene, reflux, 24 h	4-27	215
38	 R= H, 4-Cl, 4-MeO	pyridine or toluene, reflux, 3 h	71-96	217
39	 A R= NH_2 B R= 	HMPT, 110-115 °C, 4 h	A= 39 B= 95	218
40		xylene, reflux, 6 h	-	219
41		pyridine, reflux, 2.5 h	74	220
42		THF (dry), $NaHCO_3$, rt, 3 h	82	221
43		silica gel 60, MW (900 w), 15 min	70	222

Table 8. Continued

Entry	Product	Conditions	Yield (%)	Ref
44	 A R=R'= Me B R=H, R'= Me	toluene, A: reflux, 4 h B: reflux, 8 h	A= 42 B= 21	223
45		toluene, reflux, 6h	37	223
46		THF (dry), *n*-BuLi, N_2, -10 → rt (1 h) → reflux,16 h	81	224
47		THF (dry), *n*-BuLi, N_2, -10 → rt (1 h) → reflux,16 h	65	224
48	 R= H, Cl	THF (dry), *n*-BuLi, N_2, -10 → rt (1 h) → reflux,16 h	65, 87	224
49		THF (dry), *n*-BuLi, N_2, -10 → rt (1 h) → reflux (16 h)	25	224
50	 n= 1, 2	THF (dry), *n*-BuLi, N_2, -10 → rt (1 h) → reflux,16 h	30, 37	224
51	 X= S, CH_2	dioxane, Al_2O_3, reflux, 1 h	62, 78	179
52		pyridine, reflux, 5 h	65	225
53	 **A** R= 3-$NO_2C_6H_4$, R'= Ph **B** R= 4-$CH_3OC_6H_4$, R'= Ph	pyridine (dry), reflux, 36 h	A= 40 B= 33	226
54		pyridine (1% aq.), 100 °C	90	235

The reaction of isatin **177** with P_4S_{10} in refluxing pyridine yielded **178** in 7%, rather than its corresponding thiolactam (Scheme 47).[238,101] On the other hand, when the reaction was performed at 85 °C for 30 min, the coupling product **179** was isolated together with indirubin **180**, and heating **177** at 85 °C for 5 min and leaving at room temperature for 2 days yielded another coupling product, **181**, in 90% yield.

Thiolactams **189**−**195** were reported to be obtained from the reaction of ω-amino acids **182**−**188** with P_4S_{10} in boiling toluene, the reaction time and the yields of which varied between 1 and 2 h and 38−91% (Table 9).[239]

Scheme 47. Reaction of Isatin with P_4S_{10}

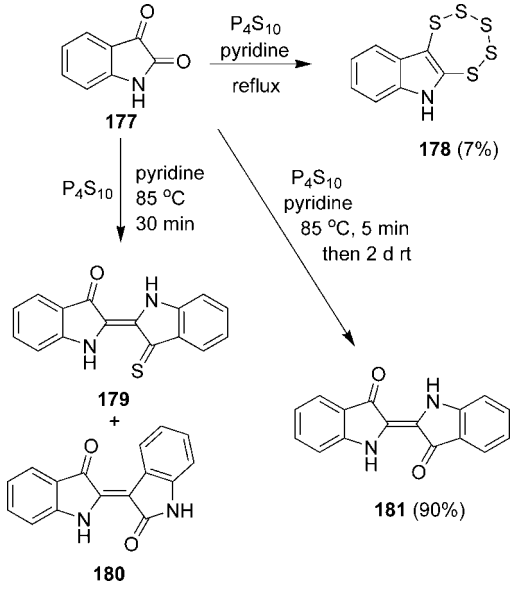


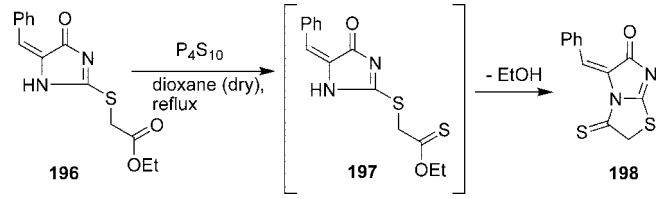
Table 9. Synthesis of Thiolactams from ω-Amino Acids

Aminoacids	Thiolactams
$H_2N(CH_2)_3CO_2H$ **182**	**189** (83%)
(±)$CH_3CH(NH_2)(CH_2)_2CO_2H$ **183**	**190** (78%)
(±)$NH_2CH_2CHCH_2CO_2H$ (4-ClC_6H_4) **184**	**191** (86%)
$H_2N(CH_2)_4CO_2H$ **185**	**192** (86%)
$H_2NCH_2CONHCH_2CO_2H$ **186**	**193** (86%)
H_2N–CO_2H **187**	**194** (70%)
$H_2N(CH_2)_5CO_2H$ **188**	**195** (45%)

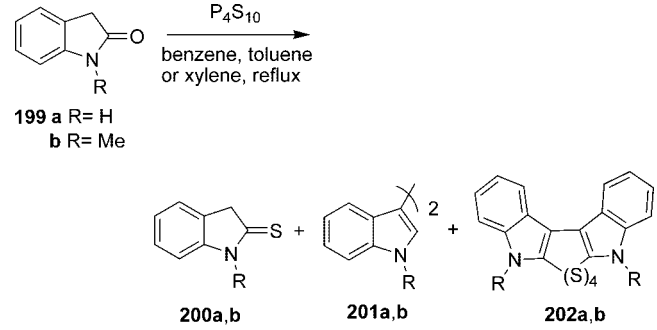
Treatment of the hydantoin **196** with P_4S_{10} in boiling dioxane gave imidazothiazole **198**, possibly through the thionoester **197**, which lost ethanol to yield **198** (Scheme 48).[240]

While the reaction of tetraalkyl ureas with P_4S_{10} smoothly gave the corresponding thioureas in moderate yields, the reaction of trialkyl urea resulted in side reactions giving such trans-acylated products and dithiophosphate (Table 7, entry 33).[241]

Scheme 48. Reaction of Hydantoin with P_4S_{10}



Scheme 49. Thionation of Indolin-2-one



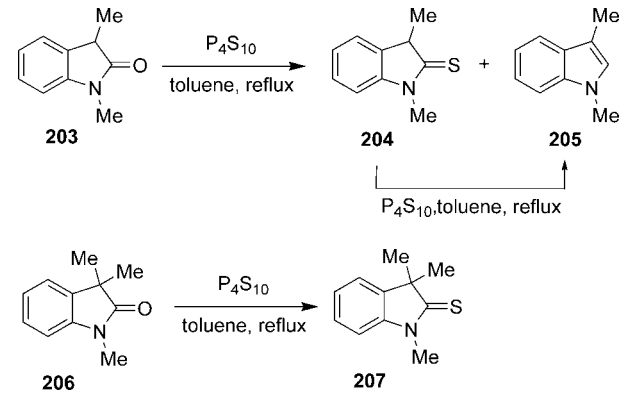
Although thionation of indolin-2-one **199a** with P_4S_{10} was carried out earlier,[243] an in-depth study indicated the formation of various side products (Scheme 49).[244,245] When **199a** was treated with P_4S_{10} in refluxing benzene for 2 h, indoline-2-thione **200a** was formed in 65% yield along with the side products **201a** and **202a**, as major and minor products, respectively. The amounts of the side products increased on performing the reaction in xylene, and the yield of **201a** became 45%. Thus, it was concluded that **200a** could be an intermediate for the formation **201a** and **202a**.

Similar treatment of 1-methylindonin-2-one **199b** with P_4S_{10} in xylene at 100 °C for 2 h yielded **200b** in 74% and the side products **201b** and **202b** as the minor products, which on the other hand surprisingly became major products in refluxing xylene. Heating **202b** in xylene did not result in any **201b**, which could be an indication that **202b** is not an intermediate for the formation of **201b**.

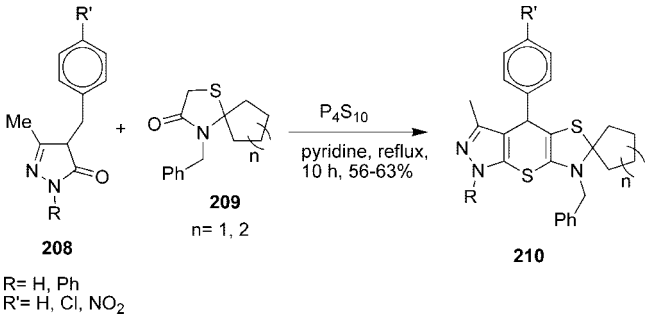
Thionation of 1,3-dimethylindolin-2-one **203** in boiling toluene for 2 h gave **204** in 60% yield and the desulfurized **205** as a minor product, which was also obtained by the reaction of **204** with P_4S_{10} (Scheme 50).[244−247] 1,3,3-Trimethylindoline-2-thione **207** was isolated as a sole product in 80% yield from the reaction of **206** with P_4S_{10}.

Reactions of two lactam groups, **208** and **209**, in the presence of P_4S_{10} in refluxing pyridine for 10 h gave thiopyrane ring **210** in 56−63% yields (Scheme 51).[248]

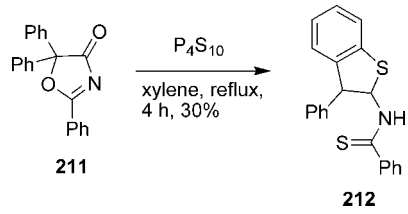
Scheme 50. Thionation of 3-Methyl- and 3,3′-Dimethylindolin-2-ones



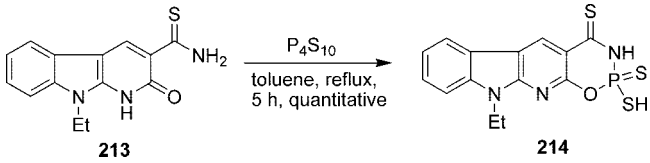
Scheme 51. Synthesis of Thiopyrane



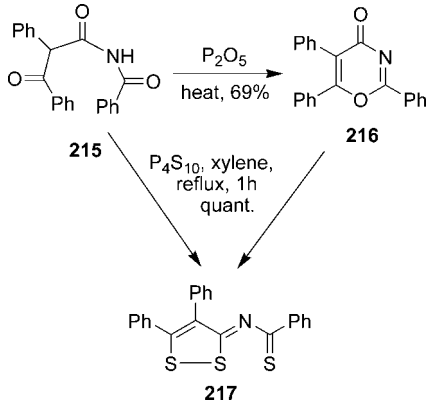
Scheme 52. Reaction of 211 with P_4S_{10}



Scheme 53. Reaction of 213 with P_4S_{10}



Scheme 54. Thionation of 215 and 216



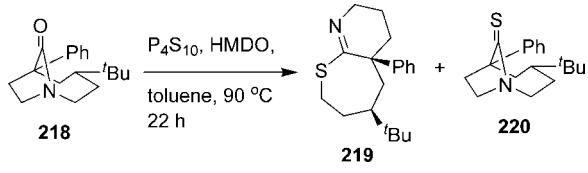
Subsequent ring-opening and then ring formation took place when oxazolinone **211** was refluxed in xylene, which yielded **212** in 30% yield (Scheme 52).[249]

Addition of part of P_4S_{10} was observed through the reaction of the thioamide **213** with P_4S_{10} in refluxing toluene for 5 h, which gave **214** in quantitative yield (Scheme 53).[251]

Thionation of diacylacetamide **215** or **216**, which was synthesized from **215** by treatment with P_2O_5, with P_4S_{10} in refluxing xylene for 1 h afforded quantitatively **217** (Scheme 54).[252]

An unusual rearrangement of the lactam **218** to **219** along with the expected product **220** was observed during the reaction of **218** with P_4S_{10} (Scheme 55).[253] As the rearrangement product **219** was obtained in 90% yield, **220** was reported to be in 5%. When the same reaction was repeated with LR, 70% overall yield of **219/220** was obtained with a ratio of 11:1, respectively.

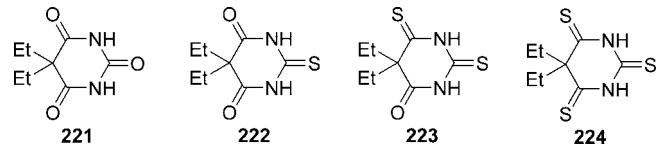
Scheme 55. An Unusual Rearrangement of 218



2.4. Imides

Replacement of carbonyl oxygens of imides with sulfur, even selectively (Table 10, entries 1, 6−8, 10, 15, 16, 19, and 20), is now a routine process (Table 10). It looks as though imide carbonyls are so reactive that even in the presence of functional groups such as amine (Table 10, entry 11) and esters (entries 6 and 7) such a conversion can successfully be achieved. The reaction can be performed at high temperature without any solvent (entry 1), under microwave irradiation using silica gel (entries 11−13) in shorter reaction time or in common solvents such as xylene, pyridine, dioxane, benzene, and acetonitrile. Although the reactions were generally carried out at refluxing solvent temperatures, there is an example of a reaction performed at room temperature (entry 17).

Thionation of phthalanil,[262] a phthalimide derivative 3,6-di-*p*-toluidino-*N*-tolylphthalimide (Table 10, entry 18), and phthalimide (entry 19) with P_4S_{10} goes back to the first half of the 20th century.[262−264] In this era, thionation of barbituric acid derivative **221** was reported to take place stepwise, replacing the imide oxygen by sulfur first.[265] When the reaction was performed in refluxing toluene, a mixture of thionated products **222** and **223** was obtained. On the other hand, in refluxing xylene a mixture of dithionated **223** and fully thionated **224** products was isolated.



It looks as though controlled thionation of various carbonyl groups in the presence of imide could be possible by using less P_4S_{10} and a shorter reaction time (Table 10, entries 8 and 9). While excess P_4S_{10} and a longer reaction time yielded full thionation of all carbonyl groups, less P_4S_{10} and shorter reaction time resulted in monothionation of the carbonyl moieties.

During thionation of **225** with P_4S_{10} in THF at 50 °C for 3 days, a rearrangement product **227** was obtained, the possible mechanism of which went through a ring-opening intermediate **226** (Scheme 56).[258]

Thionation of the oxo groups of **228**, having bulky isopropyl groups on the nitrogen atoms, with P_4S_{10} did not give the expected product; a disulfide product **229** was isolated (Scheme 57).[266]

It was reported that as the hindered thioimides (Table 10, entries 2−4) were prepared with P_4S_{10} in refluxing xylene, the less hindered thioimides **230**−**234** were synthesized using LR **566** from the corresponding imides.[256]

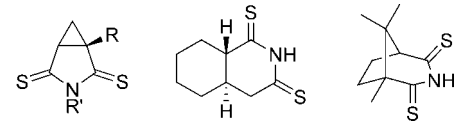


Table 10. Thionation Products of the Corresponding Imides

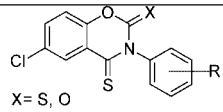
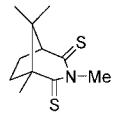
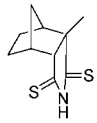
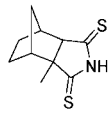
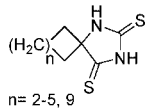
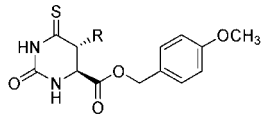
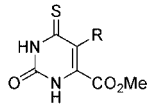
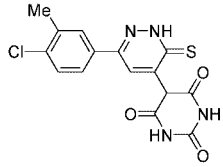
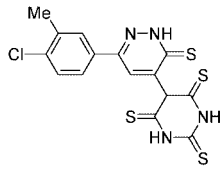
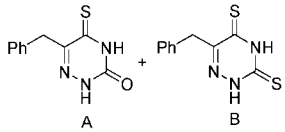
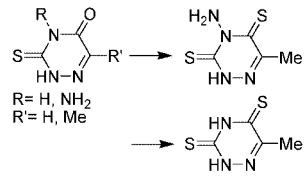
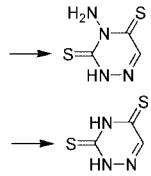
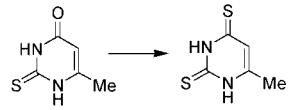
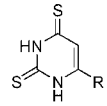
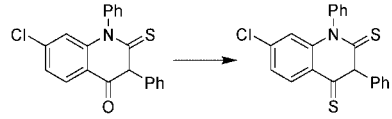
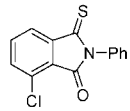
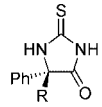
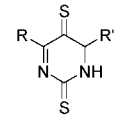
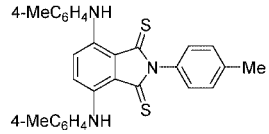
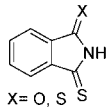
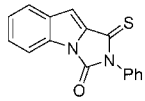
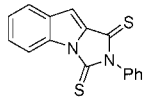
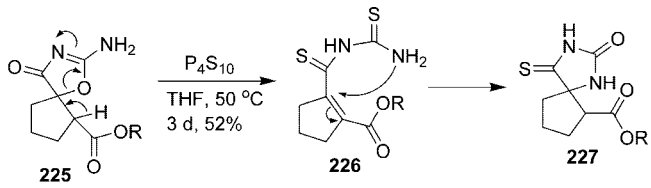
Entry	Product	Conditions	Yield (%)	Ref
1	 X= S, O R= H, 4-Me, 4-Cl 4-Br, 3,4-Cl_2, 3-Cl	Neat, 175-200 °C, 20 min	X= S, 28-47 X= O, 20-34	254
2		xylene, reflux, 12 h	93	256
3		xylene, reflux, 12 h	-	256
4		xylene, reflux, 12 h	93	256
5	 n= 2-5, 9	xylene, reflux, 5 h	-	257
6	 R= Me, Et, propyl	dioxane (dry), reflux, 2 h	16-21	258
7	 R= Me, Et, propyl	dioxane (dry), reflux, 2 h	69-85	258
8		0.01 mol starting material 0.02 mol P_4S_{10}, xylene (dry), reflux, 0.5 h	45	259
9		0.01 mol starting material 0.06 ol P_4S_{10}, xylene (dry), reflux, 6 h	48	259
10	 A B	pyridine (dry), reflux, 3 h	A= 37 B= 29	260
	 R= H, NH_2 R'= H, Me	Silica gel 60 (0.2-0.6 mm)		

Table 10. Continued

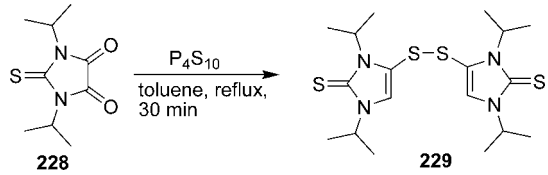
Entry	Product	Conditions	Yield (%)	Ref
11		M.W. (900 W), 20 min	60-80	222
12		Silica gel 60 (0.2-0.6 mm) M.W. (900 W), 10-15 min	40	222
13	 R= H, Me	Silica gel 60 (0.2-0.6 mm) M.W. (900 W), 20 min	65, 66	222
14		xylene, reflux, 2 h	92	261
15		xylene (dry), reflux, 5 h	80	135
16	 A R= Ph B R=c-C_6H_{11}	A= dioxane (dry), Al_2O_3, reflux, 6 h B= dioxane, reflux, 6.5 h	A= 65 B= 74	179
17	 R= Ph, 4-ClC_6H_4, 4-MeC_6H_4 R'= Ph, 4-ClC_6H_4, 4-ClC_6H_4	acetonitrile, Et_3N, rt, 24 h	33-60	93
18		benzene, aniline (trace), reflux, 4 h	50	262
19	 X= O, S	xylene (dry), reflux, 6 h	-	263
20		dioxane (dry), reflux, 8 h	~45	267
21		xylene (dry), reflux, 36 h	~75	267

Scheme 56. Rearrangement of 225 during Thionation with P_4S_{10}



R= 2-bromo-4-methoxybenzyl

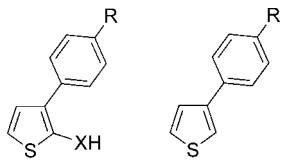
Scheme 57. Synthesis of the Unexpected Disulfide 229



2.5. Thiophenes

Synthesis of thiophenes, particularly from 1,4-diketones, is a well-known method (Table 11). Its possible mechanism, like the synthesis of thiophenes from 1,4-diketones using LR **566**,[278,279] involves initial thionation of the carbonyl groups **235** to 1,4-dithiones **236**, which is the usual reaction of P_4S_{10}. Its subsequent in situ cyclization and elimination of H_2S results in the formation of thiophene ring **237** (Scheme 58).

1,4-Dicarbonyls having different functional groups, such as aldehyde (Table 11, entry 12) and disodium succinate (entry 13), successfully produced the corresponding thiophene ring. In a later case, it was claimed that the use of red phosphorus during the reaction removes the formed −SH or −OH groups **238** to obtain **239**.[284] Otherwise, the yield goes drastically down from 95% to 98% to 55−60%.

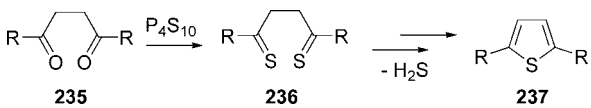


X= O or S

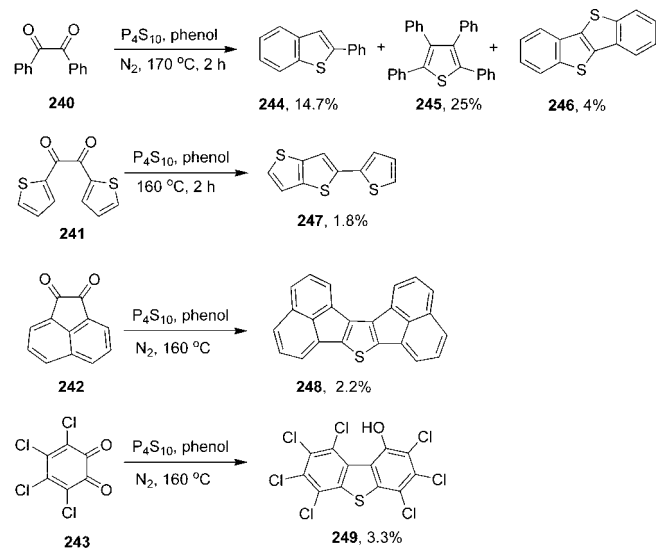
1,2-Diketones such as benzyl **240**, 2,2′-thienyl **241**, acenaphthenequinone **242**, and *o*-chloranil **243** were reported to give either fused or substituted thiophenes **244**−**249**, although in low yields, 1.8−25%, when reacted with P_4S_{10} in the presence of phenol at high temperatures 160−170 °C (Scheme 59).[285]

1,6-Dioxo compounds **250**, having 2,4-diene functionalities, yielded 2,5-disubstituted thiophenes **251** and **252** on reaction with P_4S_{10} (Scheme 60).[255] The mechanism was suggested to involve thionation of one of the carbonyl groups, and then Michael type addition yielded 2,5-disubstituted thiophenes. The second proposed mechanism involved an addition of sulfur to the four carbon unit between two carbonyl groups.

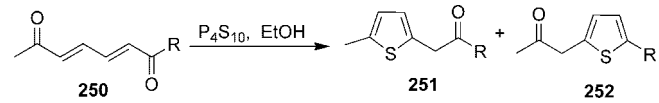
Scheme 58. General Scheme for the Synthesis of Thiophene from 1,4-Diketones



Scheme 59. Reactions of 1,2-Diketones with P_4S_{10}

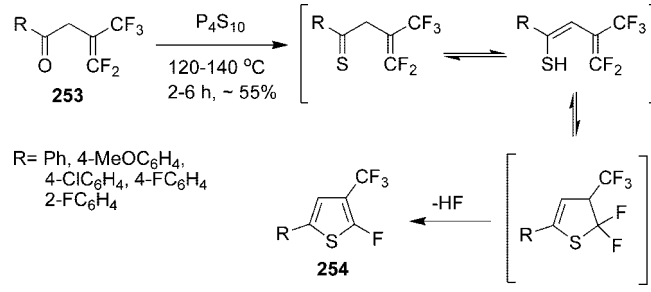


Scheme 60. Synthesis of 2,5-Disubstituted Thiophenes from 1,6-Dioxo-2,4-dienes



R= Me, Ph, EtO,
4-$MeO_2CC_6H_4$, 4-MeOPh

Scheme 61. Synthesis of Thiophenes Containing Trifluoromethyl and Fluorine



R= Ph, 4-$MeOC_6H_4$,
4-ClC_6H_4, 4-FC_6H_4
2-FC_6H_4

Thiophenes **254** containing trifluoromethyl and fluorine were prepared by treatment of α,β-unsaturated ketones **253**, prepared from hexafluoroacetone, with P_4S_{10} (Scheme 61).[286] It was suggested that the initial replacement of oxygen with sulfur at 120−140 °C was followed by an intramolecular 1,5-cyclization to yield **254**.

Thionation of *N*-phenylacetylthiobenzamides **255** with P_4S_{10} in boiling CS_2 unexpectedly resulted in the formation of thiophene rings **260** (Scheme 62).[287] A possible mechanism was reported in which, initially, the oxo group was converted to thione **256**, a tautomer from **257** was attached to the thione carbon of **256**, and then the H_2S elimination gave **258**. Intramolecular cyclization of **259**, which is a tautomer of **258**, yielded the thiophene **260** in 37−74% yields.

The reaction of γ-chloroketones **261** with P_4S_{10} in dimethylformamide (DMF) or dioxane at 90 °C gave the substituted thiophenes **262** in 65−77% yields (Scheme 63).[288]

In a similar manner, treatment of γ-hydroxycarbonyls **263** with P_4S_{10} in refluxing pyridine gave the fused thiophenes **264** in 38−64% yields (Scheme 64).[289] The reaction of a

Table 11. Synthesis of Thiophene Rings from the Corresponding Diketones unless Otherwise Stated

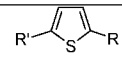
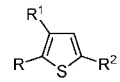
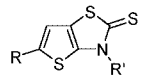
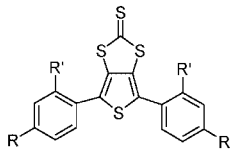
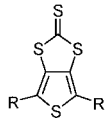
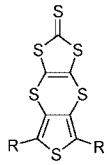
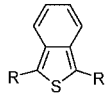
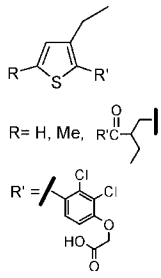
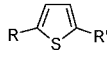
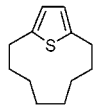
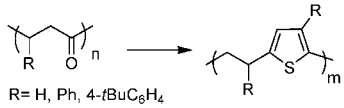
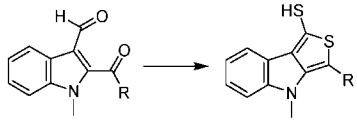
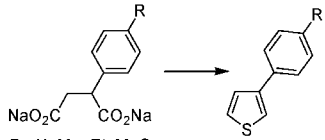
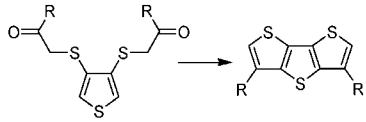
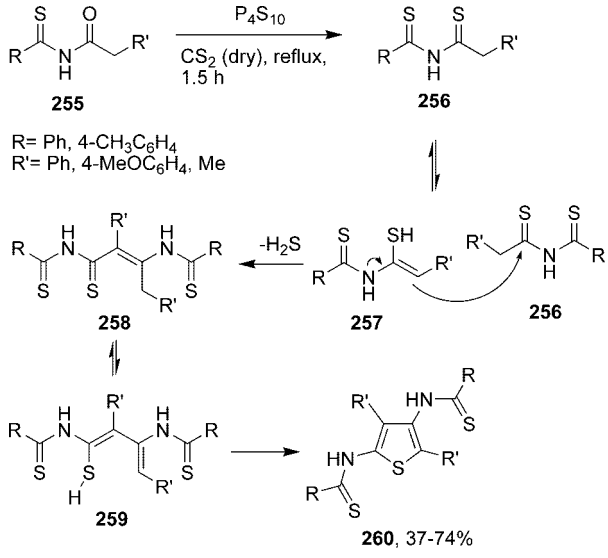
Entry	Product	Conditions	Yield (%)	Ref.
1	 R= R'= 2-thienyl R= 2-thienyl, R'= 3-thienyl	ether, $NaHCO_3$	70, 84	268
2	 R= R'= 2-thienyl, R^2= Me R= 2-thienyl, R'= 3-thienyl R^2= Me	ether, $NaHCO_3$	92, 90	268
3	 R= Ph, 4-MeC_6H_4, 2-thienyl, 4-BrC_6H_4 R'= Ph, 4-MeC_6H_4, 4-ClC_6H_4, $C_6H_4CH_2$	xylene, reflux, 4 h	79-89	269
4	 R= R' = H R= H, R'= MeO R= MeO, R'= H R= R'= MeO	dioxane, $NaHCO_3$, N_2, 100 °C, 1.5 h	57-86	270
5	 R= 2-thienyl	dioxane, $NaHCO_3$, N_2, 100 °C, ~1.5 h	70	271
6	 R= Me, Ph, *t*-butyl, 2-thienyl	dioxane (dry), $NaHCO_3$,90 °C, 1- 2 h	35-77	271, 272
7	 R= 2-thienyl	THF, $NaHCO_3$, or ACN, $NaHCO_3$, 4 h, 30 °C	52	273, 274
8	 R= H, Me, R' =	THF, reflux, 1 h	11-12	275
9	 R= 5-cyanothien-2-yl R'= 5-(1-piperidinyl)thiophene-2-yl	THF, Na_2CO_3	-	276

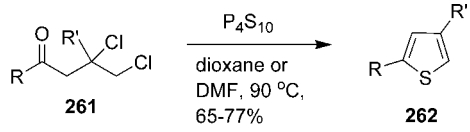
Table 11. Continued

Entry	Product	Conditions	Yield (%)	Ref.
10		neat, 100 °C, 3 h	trace	277
11	 R= H, Ph, 4-*t*BuC$_6$H$_4$	chlorobenzene, 135 °C, 24 h	-	280
12	 R= *p*-MeOC$_6$H$_4$	dioxane, reflux, 1 h	51	281
13	 R= H, Me, Et, MeO F, Cl	red phosphorus, 18-crown-6, benzyltriethylammonium chloride, solvents: *o*-dichlorobenzene, chlorobenzene, 1,1,2,2-tetrachloroethane or xylene, heat, 6-12 h	10-98	282-284
14	 R= Ph, 4-MeOC$_6$H$_4$, 4-BrC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$	A: toluene, N_2, P_4S_{10}, reflux, ~ 3 h B: toluene, P_4S_{10}, pTSA, reflux, ~ 3 h	A: 50-58 B: 51-75	A: 297, 298 B: 418

Scheme 62. Synthesis of Thiophenes from *N*-Phenylacetylthiobenzamides

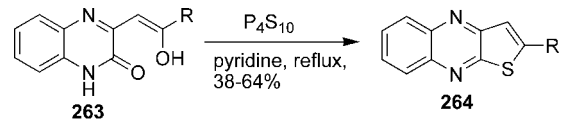


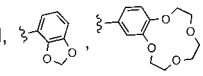
Scheme 63. Thiophenes from γ-Chloroketones



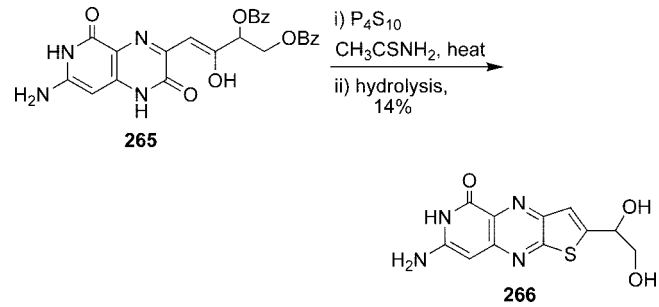
R= cyclohexyl, cyclopentyl, 1-chlorocyclohexyl, 1-chlorocyclopentyl, 4-chlorocyclohexyl
R'= H, Me

Scheme 64. Thiophenes from γ-Hydroxycarbonyls

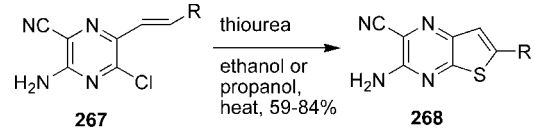


R= 2-thienyl, 

Scheme 65. Synthesis of Fused Thiophene from γ-Hydroxycarbonyl

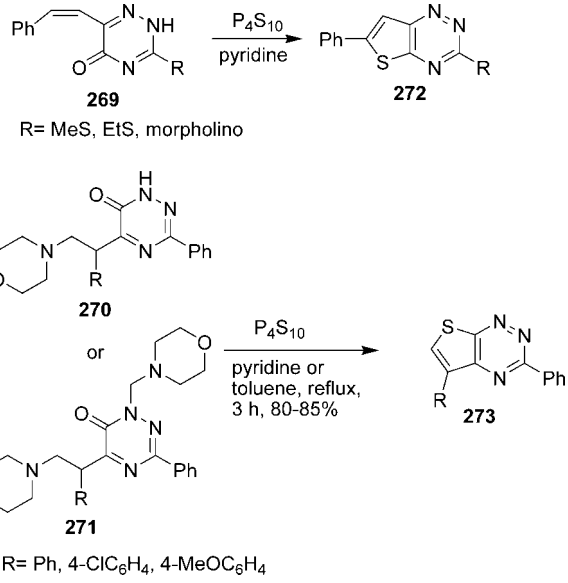


Scheme 66. Synthesis of Fused Thiophenes from Chloropropenylpyrazine

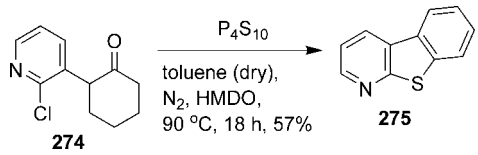


R= Me, 2-thienyl, CH(CH$_3$)$_2$, C=CHPh, Ph, 4-CH$_3$OC$_6$H$_4$

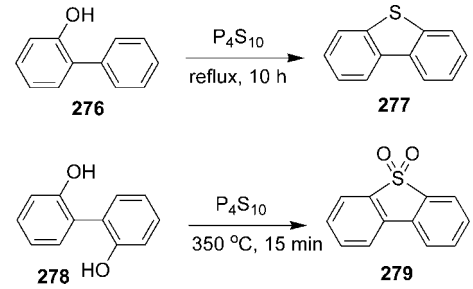
Scheme 67. Synthesis of Fused Thiophenes to 1,2,4-Triazines



Scheme 68. Synthesis of Fused Thiophene from α-(2-Chloropyridyl)ketone



Scheme 69. Synthesis of Diphenyl Sulfide and Dibenzothiophene *S*,*S*-Dioxide



more complex γ-hydroxycarbonyl **265** with P_4S_{10} in thioacetamide gave a similar product, fused thiophene **266** (Scheme 65).[290,291] Its yield was reported to be 14%, after deprotection. Alternatively, such fused thiophene systems **268** were synthesized by the reaction of chloropropenylpyrazine **267** with thiourea (Scheme 66).[292]

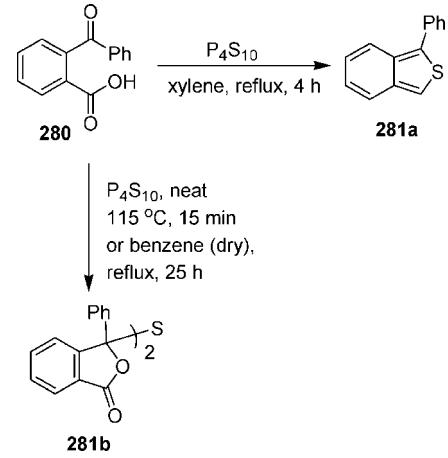
Thiophenes fused to 1,2,4-triazines **272** and **273** were obtained from the reaction of both α,β-unsaturated carbonyls **269**[293] and Mannic bases **270** and **271**,[217] respectively (Scheme 67).

During the synthesis of thioketones from α-(2-haloaryl)ketones, using P_4S_{10} as a thionation reagent, fused thiophene **275**, directly obtained as the 2-halophenyl group, was replaced by 2-chloropyridyl **274** (Scheme 68).[45]

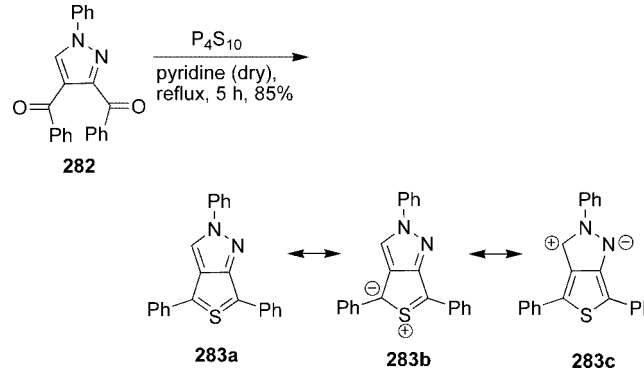
Refluxing a mixture of 2-hydroxydiphenyl **276** and P_4S_{10} for 10 h produced diphenylene sulfide **277** (Scheme 69).[294] Following a similar methodology, 2,2′-dihydroxydiphenyl **278** was heated with P_4S_{10} at 350 °C for 15 min in CO_2 in an autoclave, which yielded dibenzothiophene *S*,*S*-dioxide **279**.

Treatment of 2-benzoylbenzoic acid **280** with P_4S_{10} in refluxing xylene for 4 h produced the thiophene **281a**,

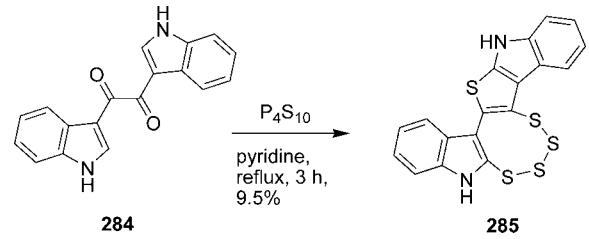
Scheme 70. Reaction of 2-Benzoylbenzoic Acid with P_4S_{10}



Scheme 71. Reaction of 3,4-Dibenzoylpyrazole with P_4S_{10}



Scheme 72. Reaction of 1,2-Diketone with P_4S_{10}



whereas either refluxing the same compound in benzene (dry) for 25 h or heating the mixture neat at 115 °C for 15 min gave the dimer **282b** (Scheme 70).[295]

Thienopyrazole **283** was obtained in 85% yield on treatment of 3,4-dibenzoylpyrazole **282**, which is a 1,4-diketone, with P_4S_{10} in refluxing dry pyridine for 5 h, and the resonance structures are depicted as **283a**−**c** (Scheme 71).[296]

An interesting thiophene derivative **285** was isolated, although in low yield, 9.5%, by the reaction of 1,2-diketone **284**, having two indole moieties, with P_4S_{10} in refluxing pyridine. The structure of **285** was confirmed by X-ray crystallography (Scheme 72).[101]

2.6. Thiazolines, Thiazoles, and Thiazines

The reaction of 1-amide-4-hydroxyl and 1-amide-4-carbonyl systems (Tables 12 and 13, respectively) yielded thiazoline and thiazole heterocyclics. Similar results were obtained on treatment of the 1-amide-4-halogene system with P_4S_{10}. The reaction of γ-chloro and γ-bromo amides **286** and **287** with P_4S_{10} in pyridine at 100 °C for 2 h and neat at 145−150 °C (1 h) and 120 °C (2 h), respectively, gave the corresponding thiazoles **288** and **289** (Scheme 73).[303,305]

Table 12. Synthesis of the Thiazolines and Thiazoles from 1-Amide-4-hydroxyl

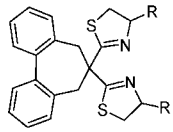
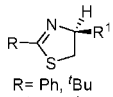
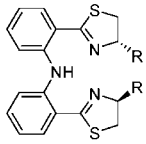
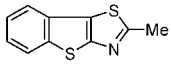
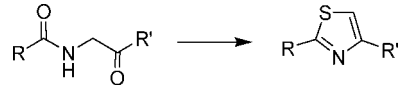
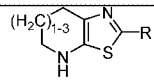
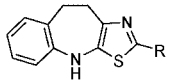
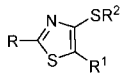
Entry	Product	Conditions	Yield (%)	Ref.
1	 R= $(CH_3)_2CHCH_2$, $(CH_3)_2CH$, $PhCH_2$, Ph	toluene (dry), Et_3N, reflux, 4 h	50-81	299
2	 R= Ph, ^{t}Bu R^1= Bn, ^{i}Pr	CH_2Cl_2, reflux, 40 h	59-96	300
3	 R= Ph, $PhCH_2$, $(CH_3)_2CH$, $(CH_3)_2CHCH_2$, $(CH_3)_3C$	pyridine (dry), reflux, 22 h	47-82	301
4		neat, 120 °C, 5 min	69	302

Table 13. Synthesis of the Thiazoles from 1-Amide-4-carbonyl



Entry	Product	Condition	Yield (%)	Ref.
1	 R= CO_2Me, $C_6H_5CH=CH$, Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$, 4-MeC_6H_4, 4-$MeO_2CC_6H_4$, 4-CNC_6H_4, 4-$NO_2C_6H_4$, 2-NH_2-3-MeC_6H_3, 4-$MeCSNHC_6H_4$, 2-thienyl, 2,3-di$MeOC_6H_3CH=CH$, 2-quinolyl, 1-Me-triazol-4-yl, 5-benzimidazolyl, 4-$MeOC_6H_4CH_2CH_2$	pyridine, 100 °C, 5,7 h	13-90	303, 167
2	 R= Me, Ph	pyridine, 100 °C, 5 h	50, 74	168
3	 R= Me, Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$, 2-furyl, 2-thienyl R'= Ph, 4-FC_6H_4, 4-$MeOC_6H_4$, 2-thienyl R^2= Et, $C_6H_5CH_2$, Ph, 4-ClC_6H_4, 4-MeC_6H_4	chlorobenzene, 100 °C, 2 h	50–69	304

Arylthiazoles **291** were obtained on treatment of *N*,*N*-diformylaminomethyl aryl ketones **290** with P_4S_{10} in $CHCl_3$ at 60 °C for 45−60 min (Scheme 74).[306]

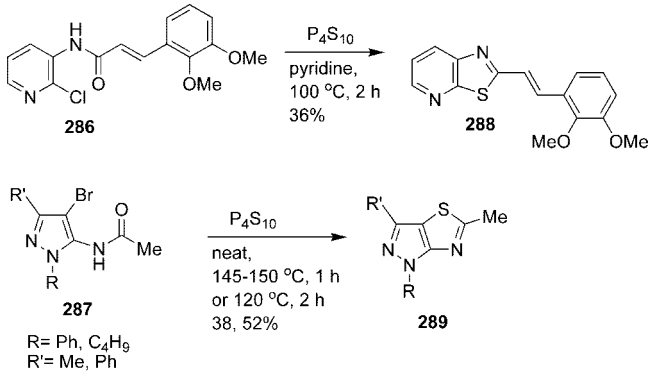
The reaction of the benzamidodiethoxypropionate **292** with a mixture of P_4S_{10}/S in xylene or CS_2 gave a mixture of the thiazoles **293** and **294** (Scheme 75).[307]

Tris(thiazoline)s **296** were successfully synthesized with treatment of tris(β-hydroxamide)s **295** with P_4S_{10} in refluxing toluene in the presence of Et_3N (Scheme 76).[308]

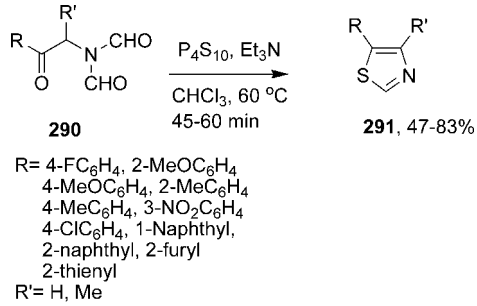
An interesting reaction of *N*-aroylaziridines **297** and **298** with P_4S_{10} in refluxing toluene for 3 h resulted in the formation of the thiazoline ring **301** and **302** in 70−77% yield (Scheme 77).[309] The possible mechanism was suggested to involve the intermediate aziridine-1-thione **299** and **300**, which was rearranged to the thiazolines **301** and **302**.

Treatment of oxazolines **303** with P_4S_{10} in refluxing CH_2Cl_2 for a prolonged time, 140 h, was reported to produce the thiazolines **304** in 32−49% yields (Scheme 78).[300]

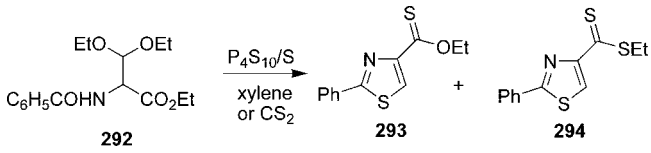
Scheme 73. Synthesis of Thiazoles from γ-Haloamides



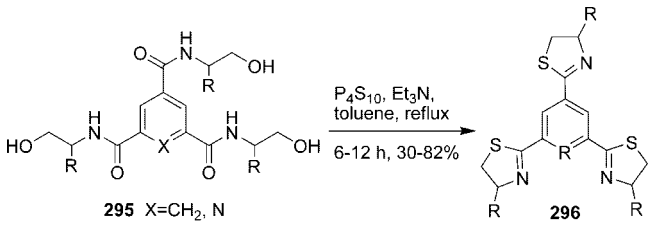
Scheme 74. Synthesis of Thiazoles from *N*,*N*-Diformylaminomethyl Aryl Ketones



Scheme 75. Reaction of 292 with P_4S_{10}



Scheme 76. Synthesis of Tris(thiazoline)s



R= Me, *i*-Pr, *i*-Bu, Bn

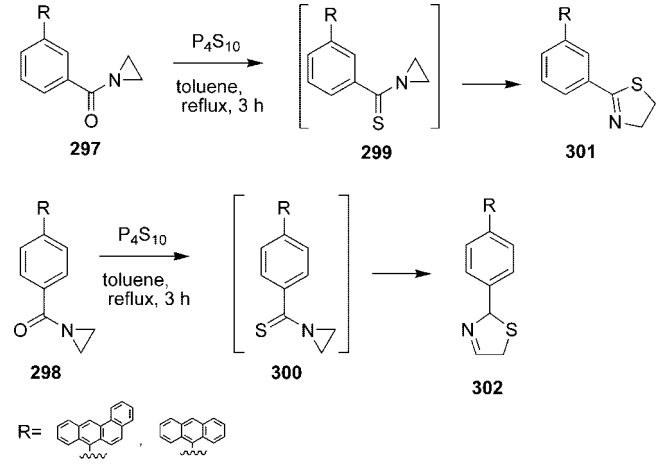
The synthesis of fused benzo-1,4-thiazines **307** was reported to be achieved by the reaction of benzyl arylimines **305** with P_4S_{10} in boiling xylene or toluene, the reaction mechanism of which was suggested to involve thionation of the carbonyl group **306** followed by a cyclization process (Scheme 79).[310]

2.7. Dithiazoles

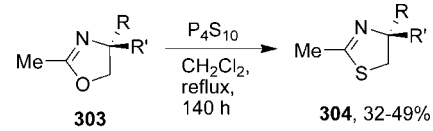
Synthesis of the dithiazole **309** by treatment of oxathiazine *S*-oxides **308** with P_4S_{10} in refluxing toluene for 1 h was reported, although it was indicated that using LR **566** gave a slightly higher yield (Scheme 80).[311]

Treatment of P_4S_{10} with chlorine was explained to give a mixture of products, such as sulfur chloride and phosphorus pentachloride (Scheme 81).[312] Application of a similar method, that is addition of chlorine to a mixture of P_4S_{10} and 4-chloroaniline **310** in acetic anhydride at 75 °C, led to the formation of benzothiazathiolium chloride **311**, which was reported to be in good yield (Scheme 82).

Scheme 77. Synthesis of Thiazoles from *N*-Aroylaziridines



Scheme 78. Reaction of Oxazolines with P_4S_{10}



R= H, Et
R'= H, Bn, *i*Pr

2.8. Thiadiazoles

Thiadiazoles were obtained by the reaction of 1,4-diamides with P_4S_{10} (Table 14). The reaction was in general conducted in boiling xylene and toluene.

A report indicated that treatment of the 1,4-diamide **312**, having an ester functional group, with P_4S_{10} in pyridine at 80 °C gave a low yield of the thiadiazole **313**, around 30%, and no product was obtained if more than 0.01 mol of starting material was used (Scheme 83).[317] On the other hand, when the 1,4-diamide **312** was first reacted with LR **566** in a refluxing solvent mixture of toluene (dry)/pyridine (dry) for 4 h and then subsequently reacted with P_4S_{10} in pyridine for 4 h at 80 °C, successful transformation to the thiadiazole **313** was achieved. The crude product was hydrolyzed to the hydroxyphenylthiadiazole **314** in 52−90% yields.

An interesting synthesis of the thiadiazoles **317** from the reaction of the hydrazides **315** with the triethylorthoformates **316** using P_4S_{10} in alumina (P_4S_{10}/Al_2O_3) under microwave irradiation was disclosed (Scheme 84).[318]

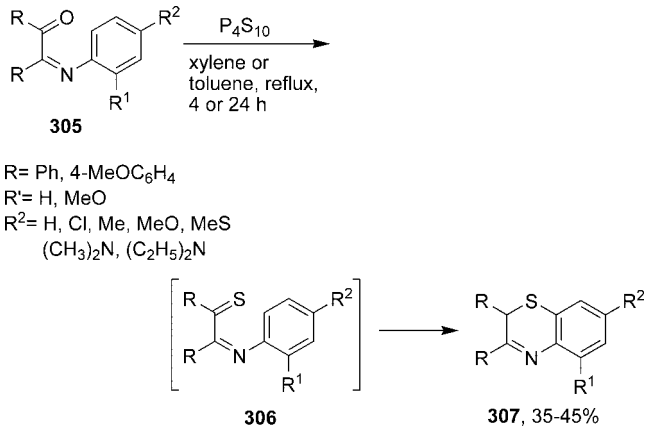
2.9. Imidazolines and Pyrimidines

Reactions of diamines with nitriles in the presence of P_4S_{10} were reported to yield imidazolines. Treatment of ethylenediamine **318** with arylaminoacetonitriles **319** in the presence of a catalytic amount of P_4S_{10} at 80−120 °C gave the imidazolines **320** in 72−88% yields (Scheme 85).[319]

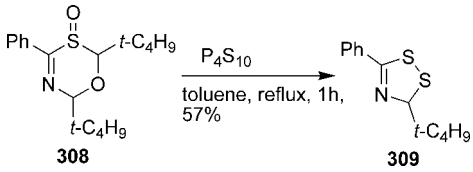
By employment of a similar methodology, compounds having diimidazoline and dipyrimidine moieties were synthesized (Scheme 86).[320] Alkanedinitriles **321** were reacted with ethylenediamine **318** and propylenediamine **322** in toluene (dry) at 90 °C for 10 h to obtain dimidazolines **323** and dipyrimidines **324**, respectively, in the presence of a catalytic amount of P_4S_{10}. Similar results were reported to be obtained when LR, S_8, or $Na_2S\cdot 9H_2O$ was used in place of P_4S_{10}.

The reaction mechanism was suggested to take place with an initial attack of amine to P_4S_{10}, followed by an attack

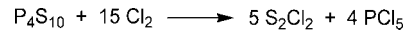
Scheme 79. Synthesis of Fused Benzo-1,4-thiazines



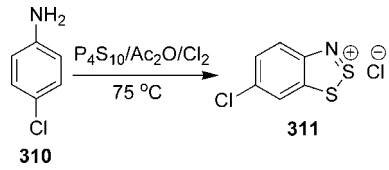
Scheme 80. Synthesis of Dithiazole



Scheme 81. Reaction of P_4S_{10} with Chlorine

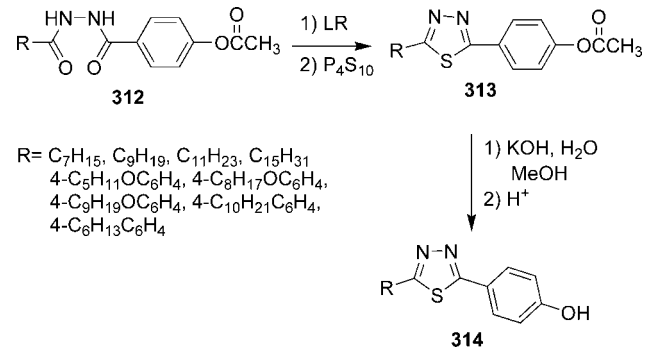


Scheme 82. Synthesis of Dithiazole with a Mixture of P_4S_{10} and Chlorine

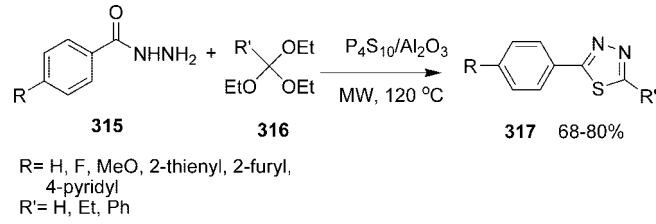


from the thiol to the nitrile. Then a series of rearrangements led to the formation of imidazolines and pyrimidines (Scheme 87).

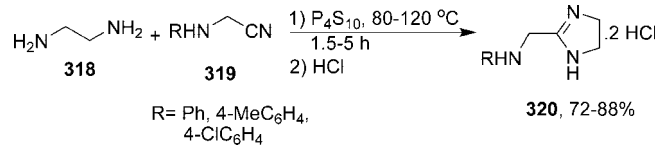
Scheme 83. Reaction of 1,4-Diamide with LR and Then with P_4S_{10}



Scheme 84. Synthesis of Thiadiazoles with P_4S_{10}/Al_2O_3

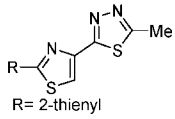
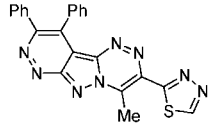
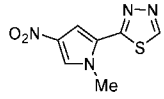
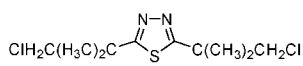


Scheme 85. Synthesis of Imidazolines 320

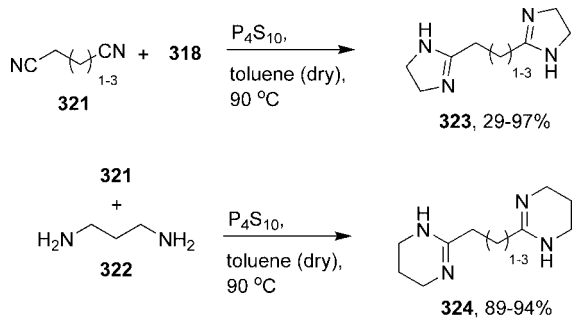


Imidazolines **327** and **328** were synthesized by microwave irradiation of a mixture of nitriles **325** and **326**, ethylenediamine **318**, and P_4S_{10} (Scheme 88).[321] Irradiation (720 W) was performed for 1.25−20 min, which produced a high yield of the imidazolines, 86−98%.

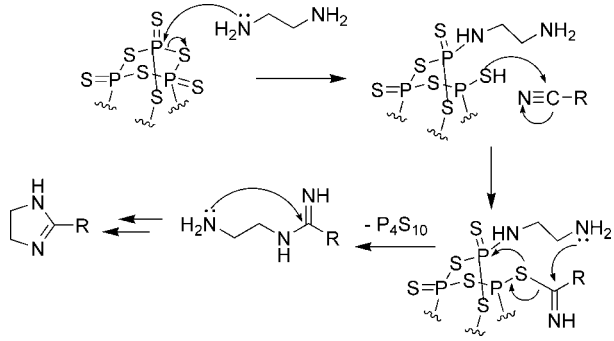
Table 14. Synthesis of Thiadiazoles from the Corresponding 1,4-Diamides

Entry	Product	Conditions	Yield (%)	Ref.
1	 R= 2-thienyl	neat, 140-150 °C, 2 h	56	313
2		xylene, reflux, 45 min	66	314
3		xylene, reflux, 45 min	40	315
4	 R= 5-methyl-4-oxazolyl 4-methyl-5-oxazolyl	xylene, reflux, 45 min	60, 62	316
5		xylene, reflux, 4 h	31	223

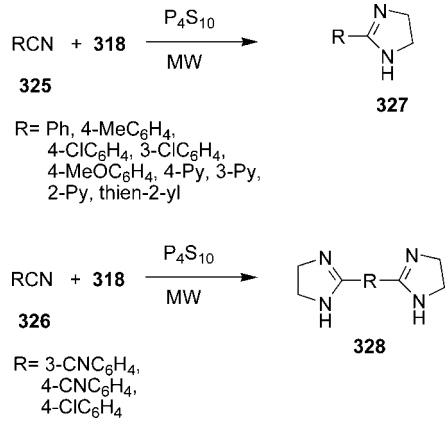
Scheme 86. Synthesis of Diimidazolines and Dipyrimidines



Scheme 87. Possible Reaction Mechanism of Formation of Imidazoline (and Pyrimidine)



Scheme 88. Synthesis of Imidazolines by Microwave Irradiation



2.10. Alcohols

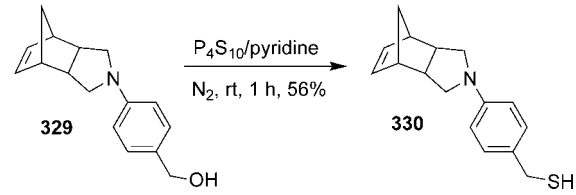
Conversion of hydroxyl groups to thiols does not look very successful, although there are examples indicating that such a conversion could be performed, particularly with phenolic hydroxyl groups. The compound **329**, having hydroxyl moeity, was stirred with P_4S_{10} in pyridine for 1 h at room temperature to obtain thiol **330** in 56% yield (Scheme 89).[334]

Similar reaction of hydroxyl cinnolines **331**−**335** with P_4S_{10} in boiling pyridine, toluene, or quinoline yielded the corresponding thiols **336**−**343** (Scheme 90).[335]

The usual product obtained on reaction of P_4S_{10} with alkylalcohols is dialkyldithiophosphoric acid, which forms at various temperatures and with various solvents, including pyridine, toluene, benzene, CS_2, and dichloromethane (Table 15). Moreover, some reactions were conducted as neat (entries 1 and 4) and under microwave irradiation (entry 11).

A report indicated that further reactions of dialkyldithiophosphoric acids with P_4S_{10} lead to the formation of trialkyl phosphorotetrathioates.[336] It was explained that treatment of alcohols **344** with P_4S_{10} initially gives the usual product, the dialkyldithiophosphoric acid **345**, to which further addition of P_4S_{10} and conducting the reaction at elevated temperatures, such as 105−230 °C, result in the formation of the phosphorotetrathioates **346** (Scheme 91).

Scheme 89. Conversion of Hydroxyl Group to Thiol



Scheme 90. Reaction of Hydroxy Cinnolines with P_4S_{10}

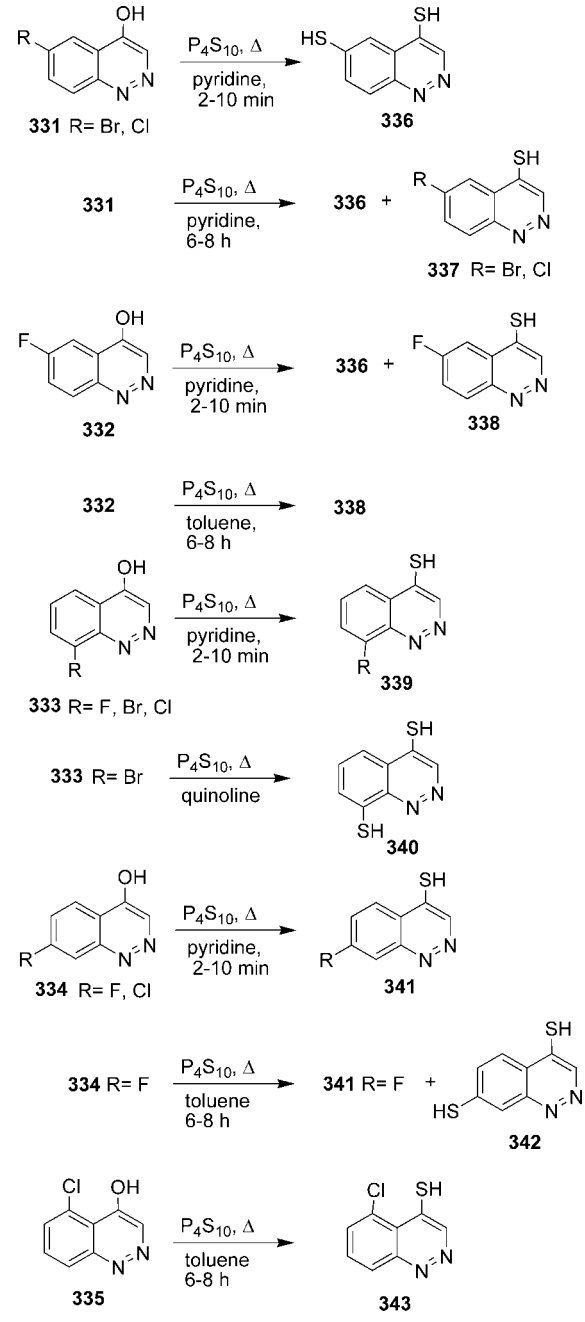
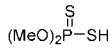
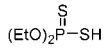
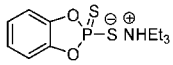
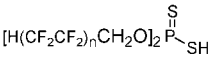
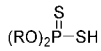
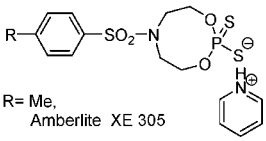
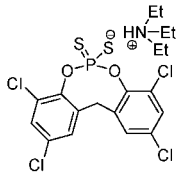
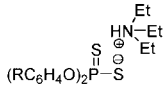
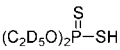
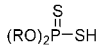
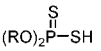
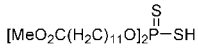
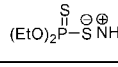
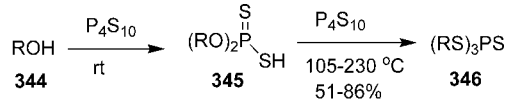


Table 15. Dialkyldithiophosphoric Acids from the Reactions of the Corresponding Alcohols/Diols with P_4S_{10}

Entry	Product	Conditions	Yield (%)	Ref.
1		neat, 24°C, 7 h	78	322
2		benzene, 85-90 °C, 8 h	-	323
3		toluene (dry), $(Et)_3N$, 80-95°C, 30 min	51	324
4	 n= 1, 2	neat, 150-170 °C, 45 h	99	325
5	 R= (±)-(Et)(Me)CH, *s*-(-)-(Et)(Me)$CHCH_2$, *l*-(-)-Menthyl, *d*-(+)-bornyl	benzene (dry), rt	-	326
6	 R= Me, Amberlite XE 305	pyridine, 105 °C, 3, 24 h	85	327
7		$(Et)_3N$	-	328
8	 R= 2-Me, 3-Me, 4-Me	toluene, $(Et)_3N$, 50 °C, 5-7 min	98-quantitative	329
9		benzene, reflux, 2 h	-	330
10	 R= *d*-borneol, *l*-menthol	toluene, reflux, 2 h	38, 89	331
11	 R= butyl, pentyl, hexyl, heptyl, octyl, nonyl	MW, 3 min	89-96	332
12		CS_2, CH_2Cl_2, N_2, reflux, 48 h	98	333
13		Al_2O_3/NH_4OAc, MW, 1 min	75–93	343

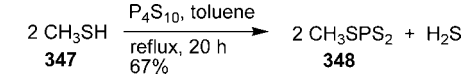
Scheme 91. Formation of Phosphorotetrathioates



R= n-$C_{1\text{-}10}H_{3\text{-}21}$

The reaction of methyl mercaptan **347** with P_4S_{10} in refluxing toluene for 20 h gave methyl phosphenotrithioate **348** in 67% yield (Scheme 92).[337]

Scheme 92. Synthesis of Methyl Phosphenotrithioate



Displacement of halogens with thiol was reported to take place on reaction of halogen- substituted nitrogen heterocycles and phenyl with P_4S_{10} (Table 16).[338,339] Although most of the conversions were performed in refluxing pyridine, in a few cases the reactions were carried out in refluxing

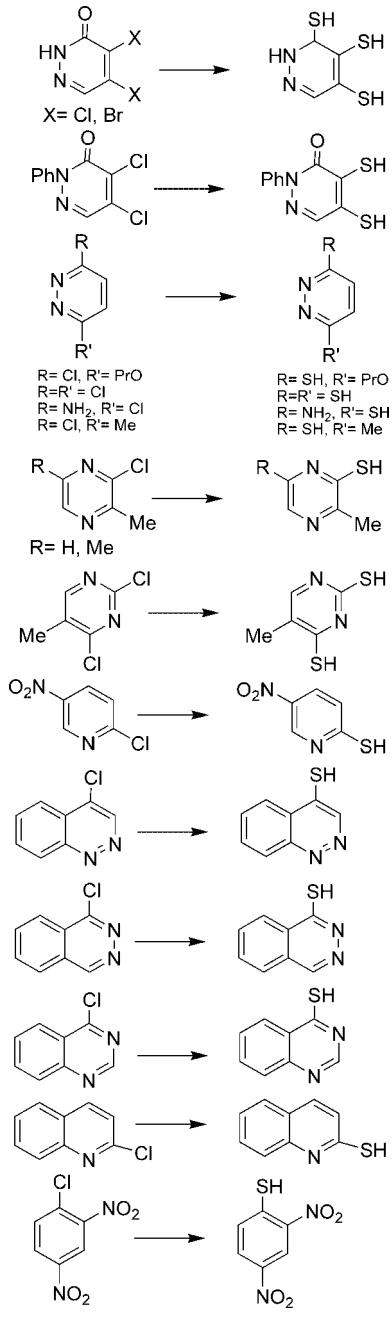
toluene, and the reaction time and the yields were varied in the ranges 2−4 h and 18−95%, respectively.

The reaction of the alcohols **349a**−**b** and **352**, having an acetylene moiety next to the hydroxyl group, with P_4S_{10} resulted in the rearrangement to yield α,β-unsaturated thioketones **351** and **353** (Scheme 93).[340] The reaction was performed in toluene at room temperature for 6 h. Although the reaction mechanism has not been fully explained, it was assumed that the intermediate **350** could be involved in the rearrangement.

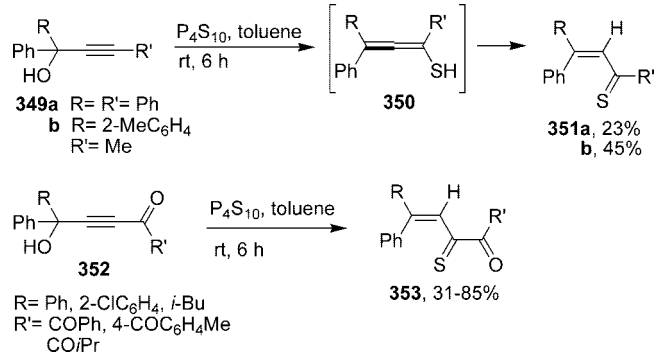
Treatment of the dithiols **354** with P_4S_{10} in boiling o-$C_6H_4Cl_2$ for 10−40 min yielded the metaphosphorotrithioic esters **355** and **356** in 40−60% yields (Scheme 94).[341]

The reactions of the coumarins **357** and **358** and the furocoumarins **359** and **360**, having hydroxyl groups, with P_4S_{10} in boiling toluene (dry) yielded various products (Scheme 95).[116] While the 4-hydroxycoumarine **357** gave

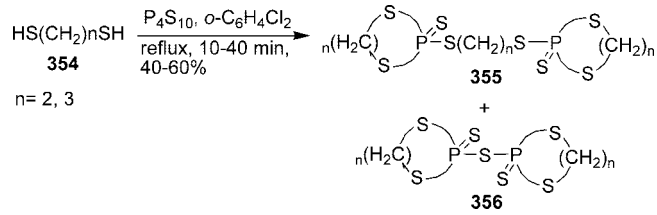
Table 16. Displacement of Halogens with Thiols



Scheme 93. Reaction of Acetylenic Alcohols with P_4S_{10}



Scheme 94. Reaction of Dithiols with P_4S_{10}

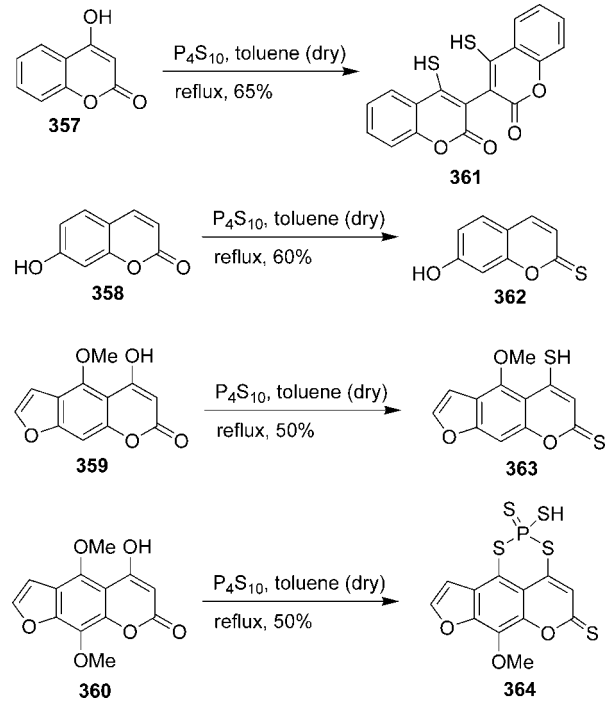


the dimer **361**, the 7-hydroxycoumarine **358** yielded only thiolactone **362**, the hydroxyl group of which did not react with P_4S_{10}. On the other hand, the reaction of furocoumarine **359** with P_4S_{10} resulted in the thionation of the hydroxyl and carbonyl groups, to give **363**. Surprisingly, the similar compound **360** produced the organophosphorus **364.**

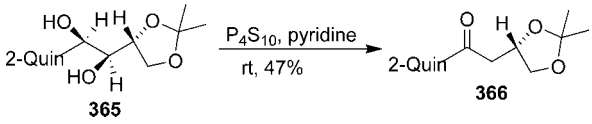
An interesting reaction of the diol acetal **365** with P_4S_{10} was reported to produce the keto acetal **366** in moderate yield, 47% (Scheme 96).[342]

Addition of chlorine to the suspension of P_4S_{10} and hydroxylmethylphthalimide **367** in CCl_4 at room temperature yielded *N*-chloromethylphthalimide **368** (Scheme 97).[312] The reaction that took place by addition of chlorine

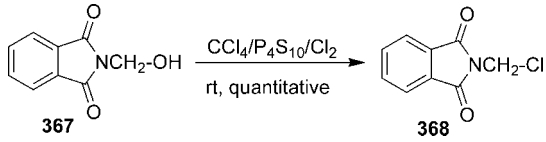
Scheme 95. Reactions of Coumarines with P_4S_{10}



Scheme 96. Reaction of Diol Acetal with P_4S_{10}



Scheme 97. Replacement of the Hydroxy Group by Chlorine with the Mixture of P_4S_{10} and Chlorine



to P_4S_{10} was explained in Scheme 97, which could be the reason for transformation of the hydroxyl group to chlorine.

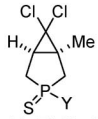
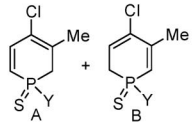
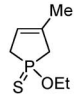
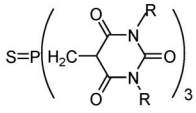
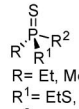
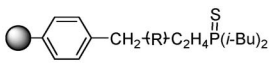
2.11. P═O to P═S

Conversion of the oxo group of phosphorus (P═O) to the thio (P═S) can be carried out using P_4S_{10} (Table 17). Reports in the literature indicate that such a conversion can even selectively be accomplished with a sterically hindered phosphoryl oxide and in the presence of imide groups (Table 17, entry 6). Such a transformation was also achieved without affecting the lactam moiety.[349]

Although the reaction was in general performed in refluxing benzene and toluene (entries 3−6), there are examples where the reaction was carried out in CH_2Cl_2 at room temperature (entries 3 and 4) and under microwave irradiation (entries 1 and 2).

The reaction of compound **369** having phosphoryl oxide and ester groups with P_4S_{10} at room temperature resulted in the replacement of the oxo group of the phosphorus with thiol, yielding **370** along with **371** and **372**, which had sulfur atoms

Table 17. Conversion of P═O Groups of the Corresponding Compounds to P═S

Entry	Product	Conditions	Yield (%)	Ref.
1	 R= Me, Et, Pr, *i*-Pr, hexyl R'= Me, Et, Pr, *i*-Pr,hexyl	HMDO, MW (900 W), 4-8 min	88-92	344
2	 R= Me, Pr, Ph R'= C_6H_{11}, C_8H_{15}, C_8H_{17} $C_{12}H_{23}$, 2-naphthyl	HMDO, MW (900 W), 6-10 min	82-89	344
3	 Y= Et, Ph, EtO	benzene, N_2, reflux, 20 h Y= EtO; CH_2Cl_2, N_2, rt, 5 d.	53-76	345
4	 Y= Et, Ph, EtO	benzene, N_2, reflux, 20 h Y= EtO; CH_2Cl_2, N_2, rt, 5 d.	Y= Et, 42, A= 77, B= 23 Y= Ph, 73, A= 75, B= 25 Y= EtO, 56, A= 74, B= 26	345
5		benzene, rt, 5 d.	84	345
6	 R= allylisocyanuratomethyl	toluene, reflux, Ar, 8 h	31	346
7	 R= Et, Me R^1= EtS, Pr R^2= EtO, *i*-PrO, Ph	$(Me)_2NH$, 120 °C, 2 h	12–61	347
8	 R= O-$(CH_2)_6$-, S-$(C_2H_4O)_2$-, S	DMA, 120 °C, 15 h	-	348

in the ring rather than having exchange of carbonyl oxo with thione (Scheme 98).[349] Further reaction of **372** with P_4S_{10} at 100 °C gave three products, including exchange of the oxygen atoms of phosphor and carbonyl groups with sulfur, **373** and **375**, respectively, and the dehydration product **374**.

Thionation of tetraalkylphosphorodiamidous acids **376** with P_4S_{10} in the presence of triethylamine for 1.5 h at room temperature was claimed to produce the intermediate **377**, to which was added in situ the alkyl halides **378** to obtain **379** (Scheme 99).[350]

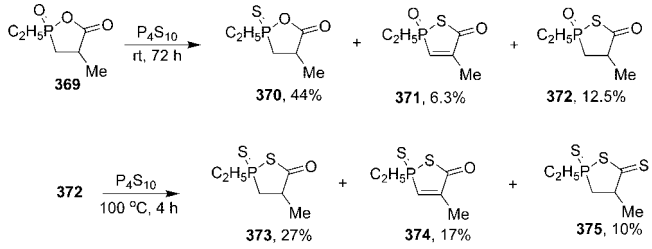
The reaction of triethylphosphite **380** with P_4S_{10} in benzene for 1 h thionated the phosphorus to yield **381** in 44% yield (Scheme 100).[350] A similar reaction was performed for **382**, this time in xylene at 100 °C for 20 min, which also gave thionation at phosphorus; **383** was obtained in 60% yield.

2.12. Reduction

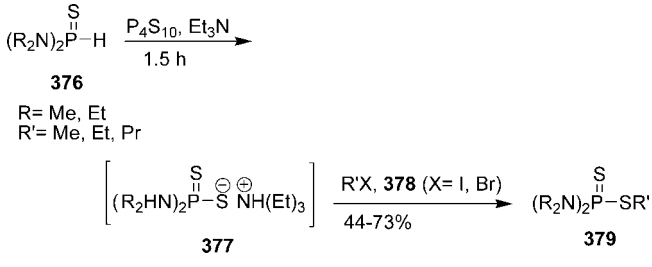
Reduction of particular sulfoxides **384** to sulphides **385** using P_4S_{10} as a reducing agent is a well established methodology (Scheme 101, Table 18).[351−353]

It was reported that the reaction of an S═O group with P_4S_{10} is faster than the reaction between C═O and P_4S_{10} (Table 18, entry 4). The reduction mechanism was suggested to involve a Wittig-like intermediate **387**, which was supposed to form through the reaction of **386** with sulfoxide **384** (Scheme 102).[351,352] Thiosulfoxide forms along with oxygenated P_4S_{10} **389**. Production of 100% of a stoichiometric amount of elemental sulfur was considered to be evidence of loss of sulfur from thiosulfoxide **388** to form sulphide **385** (Scheme 103).

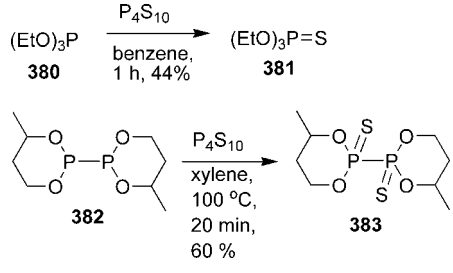
Scheme 98. Reaction of P═O with P_4S_{10} in the Presence of a Lactone Group



Scheme 99. Thionation of Phosphorodiamidous Acids with P_4S_{10}

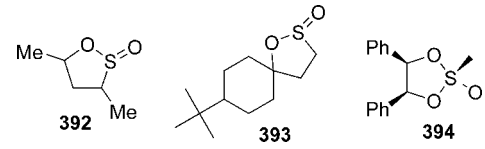


Scheme 100. Reaction of 380 and 382 with P_4S_{10}



It appears that, in the presence of ester, amide, nitro, and halogen, such a reduction can selectively be achieved.[354] In addition to sulfoxides, the sulfilimines **390** can in a similar fashion be reduced to the sulphides **391** (Scheme 104).[355]

As the amino, hydroxyl, or cyano groups are more reactive toward P_4S_{10}, if those groups are present in the molecule, such a reduction is not expected to take place.[351] In contrast to sulfoxides, sulfones, sulfinates **392** and **393**, and sulfites **394** were reported to be not reactive toward P_4S_{10}.[351,354]



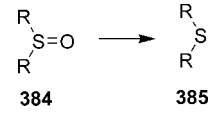
The same group reported that the selenoxides **395** could successfully be reduced to selenides **396** even faster than sulfoxides (Scheme 105).[351] The faster reaction rate was attributed to the longer and more polar Se−O bond. On the other hand, attempts to reduce selenoxides with P_4Se_{10} to selenides were unsuccessful.[351]

Reduction of the sulfines **397** to the thiones **398** was successfully achieved, although thiophosphoryl bromide ($PSBr_3$) was reported to give even better yields (Scheme 106).[356] The reaction was performed in CH_2Cl_2 at room temperature for 2 h to yield the thiones in 58−94% yields.

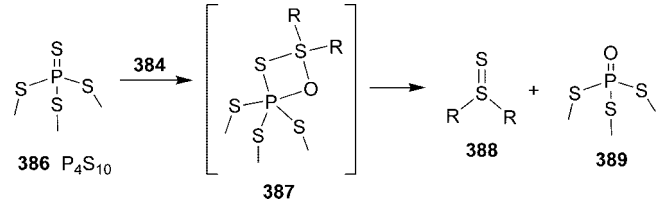
Deoxygenation of the benzoyl oxygen of 1,2-dicarbonyls **399** was reported to be successful on reaction with P_4S_{10} in refluxing pyridine for 2 h to afford **400** (Scheme 107).[357]

Treatment of sulfonic acids **401** with P_4S_{10} was claimed to result in the reduction to the corresponding polysulfides **402**, which was, without isolation, reacted with $LiAlH_4$ or $NaBH_4$ to obtain the thiols **403** (Scheme 108).[358]

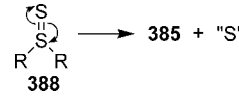
Scheme 101. General Reaction of Reduction of Sulfoxides to Sulfides



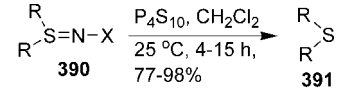
Scheme 102. Reaction Mechanism of Sulfoxide with P_4S_{10}



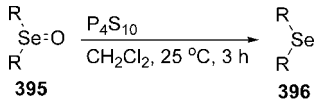
Scheme 103. Decomposition of Thiosulfoxide to Sulfide



Scheme 104. Reduction of Sulfilimines to Sulfides

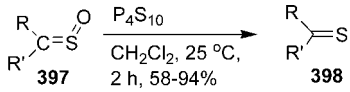


Scheme 105. Reduction of Selenoxides to Selenides with P_4S_{10}



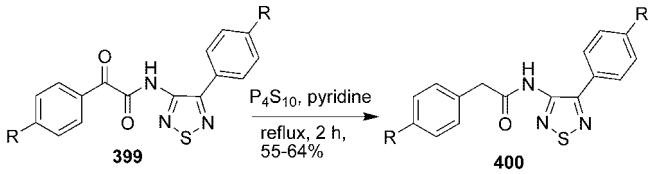
R= Ph, $C_6H_5CH_2$

Scheme 106. Reduction of Sulfines to Thiones



R= Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$(Me)_2NC_6H_4$, 2,4,6-*tri*-MeC_6H_2
R'= Ph, 4-MeC_6H_4,4-$MeOC_6H_4$, 4-$(Me)_2NC_6H_4$, PhS, 2,4,6,-*tri*-MeC_6H_2S

Scheme 107. Deoxygenation of the Benzoyl Oxygen of 1,2-Dicarbonyl

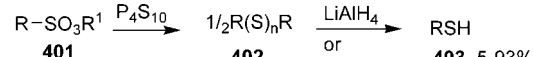


R= NO_2, Cl, Br

2.13. Nucleotides, Purines, and Pyrimidines

Replacement of oxo groups of nucleotides, purines, and pyrimidines with thione using P_4S_{10} has wide application to obtain their sulfur analogues (Table 19). Although the reaction was, in general, conducted in refluxing pyridine, in some reactions, tetralin (entry 7), dioxane (entries 14 and 15), and diglyme in the presence of $NaHCO_3$ (entries 12 and 13) were also used. Particularly, when the nucleotides were thionated, the hydroxyl groups were protected by acetyl (entries 1 and 2) or benzyl (entries 10 and 15) groups.

Scheme 108. Reduction of Sulfonic Acids to Polysulfides



n=2.9 ~3.3
R= Ph, 4-MeC_6H_4, 4-ClC_6H_4, 2,4-MeC_6H_3, $C_{10}H_7$, 3-$NO_2C_6H_4$, $CH_3(CH_2)_4$, $CH_3(CH_2)_{11}$
R^1= H, Na^+, NH_2, $CH_3(CH_2)_3CH_2$, $C_6H_5CH_2SC(=NH_2^+)NH_2$

Possibly, due to steric hindrance and resonance reasons, the amino groups on the molecules do not react with P_4S_{10} first (entries 1, 2, 11, and 21). Also, the presence of other functional groups such as esters does not alter the reaction (entries 1, 2, 13, 24, and 25). Moreover, a selective thionation of only one oxo group is possible (entries 5, 8−10, 12, 13, 15−17, 20, and 24). The reaction of xanthine **404** with P_4S_{10} was reported to result in a selective thionation to yield **405** rather than **406**, which was proved by comparing the UV measurements (Scheme 109).[373]

An extensive study on the thionation of the purines **407**−**410** and **415** revealed that, contrary to results obtained with the purine, where R = H (Table 19, entry 5), thionation of **407**, where R = Me, with P_4S_{10} gave fully thionated product **411** along with a trace of **414** (Scheme 110). Interestingly, attempts at the thionation of **408** did not yield any product while compound **409** yielded the fully thionated compound **411** smoothly. Contrary to the result obtained with **407**, thionation of the purine **410**, where R = Ph, with P_4S_{10} gave selectively thionated product **412**. It was indicated that when the same reaction was performed, this time with a specially purified P_4S_{10}, again a selectively thionated product **413**, but on the other oxo group, was obtained. Extension of the study to purine **415**, which has three oxo groups, gave **416** as the major and **417** as the minor products (Scheme 111).[374]

The reaction of the purine **418**, as either its iodide or the *p*-toluenesulphonate form, with P_4S_{10} was reported to yield **419**, which had two thione groups (Scheme 112).[375]

Table 18. Production of Sulfides from the Corresponding Sulfoxides unless Otherwise Stated

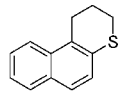
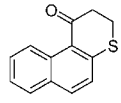
Entry	Product	Conditions	Yield (%)	Ref.
1	 R= Me, *n*-C_4H_9, *s*-C_4H_9, *t*-C_4H_9, $C_6H_5CH_2$, Ph, 4-$CH_3C_6H_4$, 4-ClC_6H_4, 4-$MeOC_6H_4$	CH_2Cl_2, 25 °C, 4 h	42-100	351, 352
2	 n= 1, 2	CH_2Cl_2, 25 °C	31,50	351, 352
3		CH_2Cl_2, 25 °C, 4 h	78	351, 352
4		CH_2Cl_2, 25 °C, 4 h	60	351, 352
5	 R= R'= Me, $C_6H_5CH_2$, Ph,4-MeC_6H_4, R= Me, R'= $C_6H_5CH_2$ R= Me, R'= Ph R= Me, R'= propyl R= Ph, R'= $C_6H_5CH_2$	CS_2, 0 °C, 10 min	quantitative	353

Table 19. Thionation of the Nucleotides

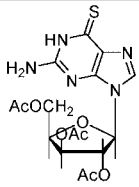
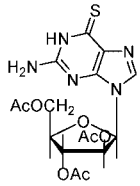
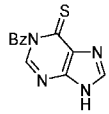
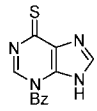
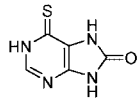
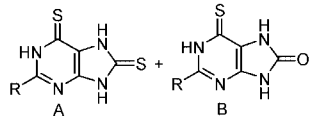
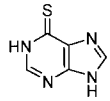
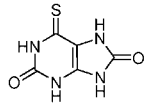
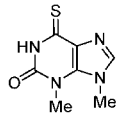
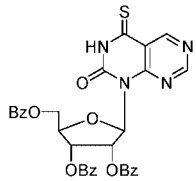
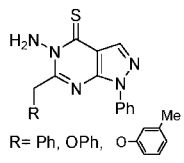
Entry	Product	Conditions	Yield (%)	Ref.
1		pyridine, 80 °C	64	359
2		pyridine, reflux	80	359
3		pyridine, reflux, 5 h	51	360
4		pyridine, reflux, 5 h	62	360
5		pyridine, reflux, 6 h	74	361
6	 R=Me, H	pyridine, reflux, 4 h	A= 52% B= trace	362, 363
7		tetralin, 190-200 °C, 5 h	54	364
8		pyridine, reflux, 11 h	-	365
9		pyridine (dry), reflux, 4 h	70	366
10		pyridine (dry), reflux, 12 h	73	367
11	 R= Ph, OPh,	pyridine (dry), reflux, 16 h	59-67	368

Table 19. Continued

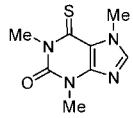
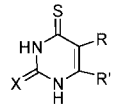
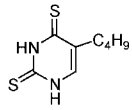
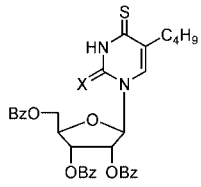
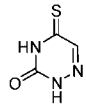
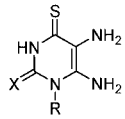
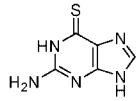
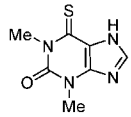
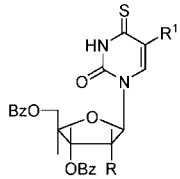
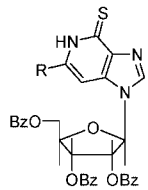
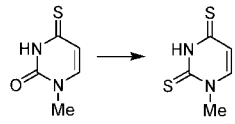
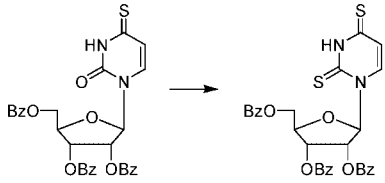
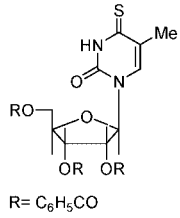
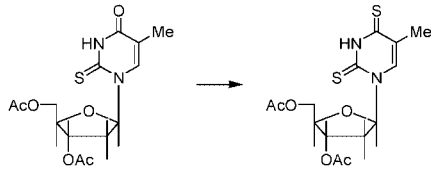
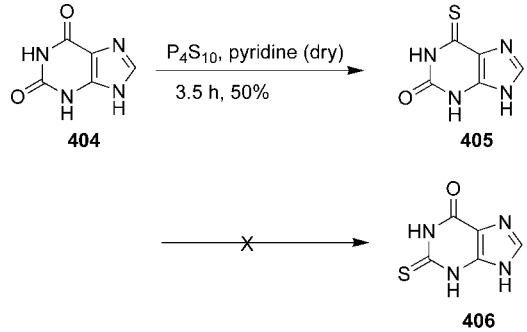
Entry	Product	Conditions	Yield (%)	Ref.
12		diglyme, $NaHCO_3$, 110 °C, 5 h	90	369
13	 X O, S R= H, Me, F, Cl, Br, $CH_2CO_2CH_3$, $CH_2CO_2C_2H_5$ R'= H, Me, $CO_2C_4H_9$-*n*	diglyme, $NaHCO_3$, 110 °C, 1-3 h	90-99	369
14		dioxane, reflux, 2 h	72	370
15	 X= O, S	dioxane (dry), reflux, 1.5 h	85	370
16		pyridine, reflux, 3 h	98	371
17	 X= O, S R= H, Me	pyridine, reflux, 2.5, 4 h	60–87	372
18		Sulfolane, 170-180 °C, 4 h	66	379
19		pyridine (dry), reflux, 8 h	94	380
20	 R= H, OBz R^1= H, Me	pyridine, H_2O, reflux, 4-7 h	72- 87	381
21	 R= H, NH_2	pyridine, H_2O, reflux, 4-6 h	50, 90	382

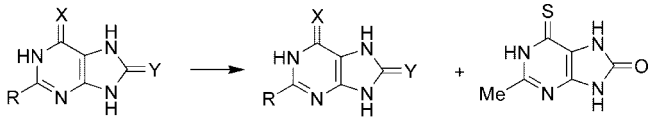
Table 19. Continued

Entry	Product	Conditions	Yield (%)	Ref.
22		tetralin, 180 °C, 4 h	23	383
23		tetralin, 165 °C, 1.5 h	50-60	383, 384
24	 R= C_6H_5CO	pyridine, reflux	38	384
25		pyridine, reflux, 4 h	~ 60	384

Scheme 109. Selective Thionation of Xanthine



Scheme 110. Thionation of the Purines 407−410

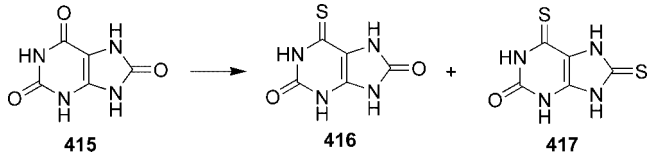


407 R= Me, X= Y= O
408 R= Me, X=S, Y= O
409 R= Me, X= O, Y= S
410 R= Ph, X= O, Y= O

411 R= Me, X= Y= S
412 R= Ph, X=O, Y= S
413 R= Ph, X= S, Y= O

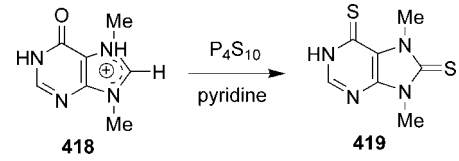
414, trace

Scheme 111. Thionation of the Purine 415

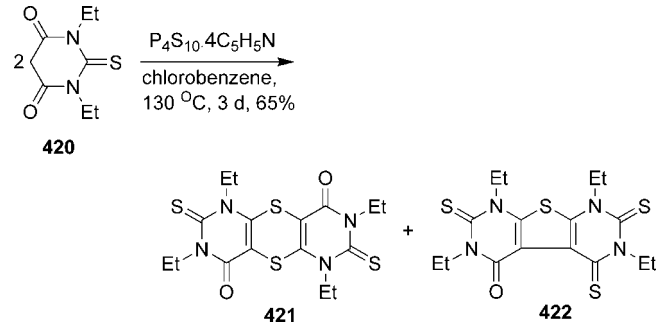


Dimers **421** and **422** having dithiino and thiophene moieties, respectively, were obtained on treatment of the thiobarbituric acid derivative **420** with a P_4S_{10}−pyridine complex (Scheme 113).[376] The reaction was conducted in chlorobenzene for 3 days at 130 °C to yield 65% of a mixture of the products **421** and **422**, which were characterized by extensive spectroscopic studies.

Scheme 112. Thionation of the Purine 418



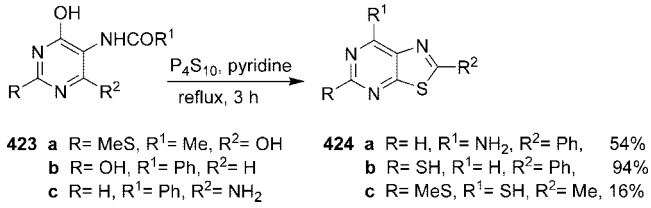
Scheme 113. Synthesis of Dithiinodipyrimidine 421 and Dipyrimidine-thiophene 422 Derivatives



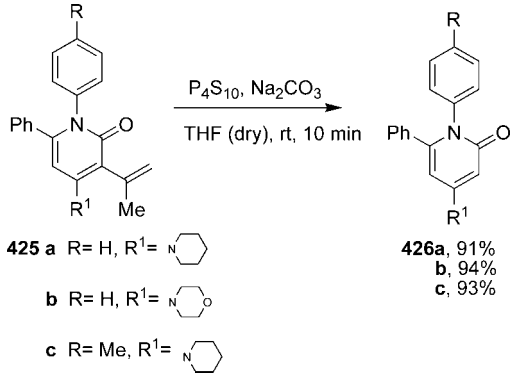
The synthesis of the thiazolopyrimidines **424a−c** was performed by the reaction of the pyrimidines **423a−c** with P_4S_{10} in refluxing pyridine for 3 h (Scheme 114).[377]

Treatment of the vinylpyrimidinones **425a−c** with P_4S_{10} in the presence of Na_2CO_3 in THF (dry) at room temperature for 10 min yielded the pyrimidinones **426a−c** in good yields, 91−94% (Scheme 115).[378]

Scheme 114. Synthesis of Thiazolopyrimidines



Scheme 115. Synthesis of Pyrimidinones



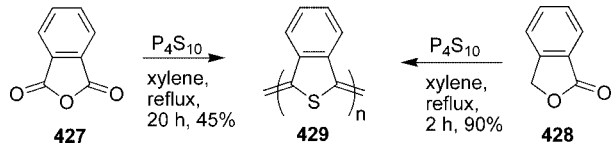
2.14. Miscellaneous

The synthesis of poly(isothianaphthene) (PITN) **429** from phthalic anhydrate **427** and phthalide **428**, using P_4S_{10}, was reported, and the mechanism was extensively studied (Scheme 116).[385−389] The reactions of both phthalide anhydride and phthalide with the P_4S_{10} in refluxing xylene for 20 h gave the same product, PITN.

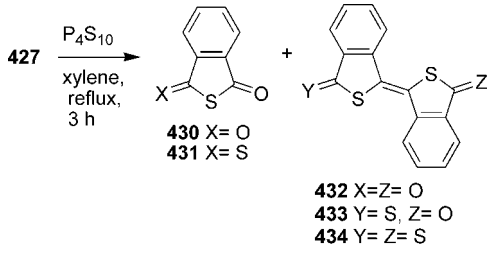
When the reaction time was kept shorter, such as 3 h, polymerization did not take place; instead thiophthalic anhydrides **430** and **431** and the dimers **432**−**434** were obtained along with a trace amount of PITN (Scheme 117).[386] The polymerization of thiophthalic anhydride under the same conditions demonstrated a higher yield of PITN.

The mechanism of the polymerization of phthalic anhydride was depicted in Scheme 118.[386] The initial step, similar to ester reactions, is thionation of the carbonyl group, **435**, which is isomerized to the more stable thiophthalic anhydride **430**. Then, thionation of **430** gives dithiophthalic anhydride **431**, further thionation or dimerization of which yields trithiophthalic anhydride **436** or dithiodimer **432**, respectively. The reaction of **432** with P_4S_{10} produces tetrathio-dimer **434** and subsequently PITN

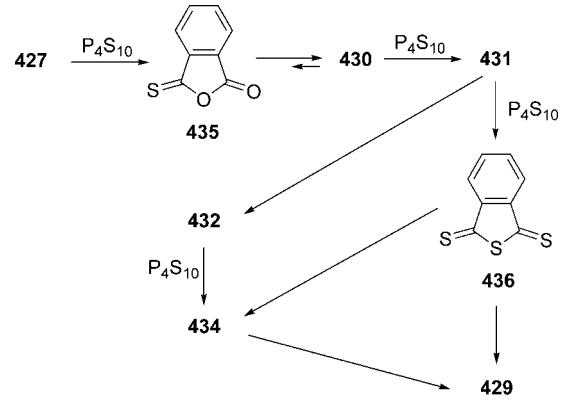
Scheme 116. Synthesis of PITN



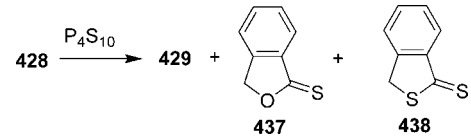
Scheme 117. Reaction of 427 with P_4S_{10} in a Shorter Reaction Time



Scheme 118. Mechanism of the Polymerization of Phthalic Anhydride



Scheme 119. Reaction of 428 with P_4S_{10} in a Shorter Reaction Time



429. At the same time, **436** can either yield the polymer PITN or first forms the dimer **434** and then polymerizes to yield PITN.

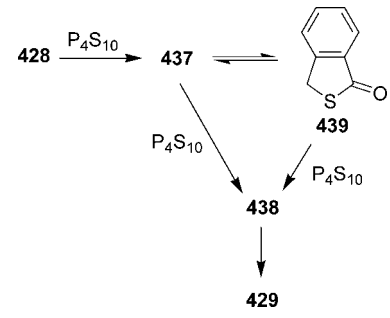
Similar to the case of phthalic anhydride, the reaction time for the polymerization of phthalide **428** was kept shorter. PITN was obtained only in 9%, and the major product was reported to be thiophthalide **437** along with a small amount of dithiophthalide **438** (Scheme 119).[386]

The mechanism of the polymerization of **428** was explained to involve initial thionation of the carbonyl group to form **437**, which can izomerize to **439** (Scheme 120). Reactions of both isomers **437** and **439** with P_4S_{10} yield the dithiophthalide **438**, the polymerization of which produces the polymer PITN.

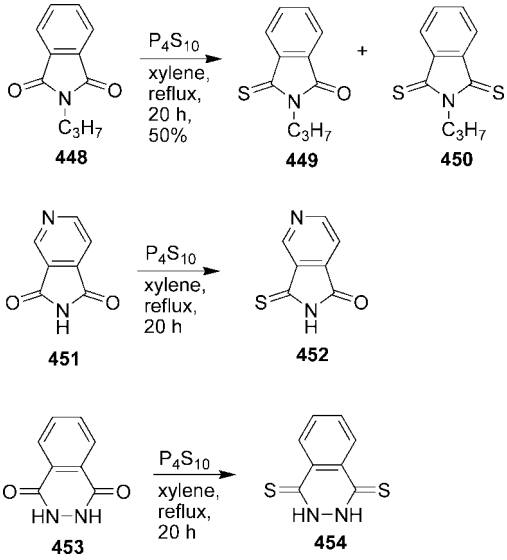
Applying the method developed for the synthesis of PITN, using P_4S_{10}, various analogues, **440**, **441**,[390] **442**,[389] **443**−**445**,[390] and **446**,[391] along with the aza-analogue **447**,[389] were synthesized. Contrary to the synthesis of polyisoindole **447** from phthalimide, attempts to polymerize *N*-propylphthalimide **448**, 3,4-pyridinedicarboximide **451**, and phthalhydrazide **453** gave their corresponding thionated products **449**, **450**, **452**, and **454**, respectively (Scheme 121).[389]

The synthesis of dithiophthalide **438** was performed with the reaction of 1,2-phthaldehyde **455** with P_4S_{10} (Scheme 122).[387] Its various analogues **456** were reported to be synthesized as potential chain stoppers.[386,392] Thionation of the phthalid **457** with P_4S_{10} exclusively produced exchange

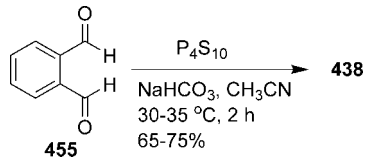
Scheme 120. Polymerization Mechanism of Phthalide



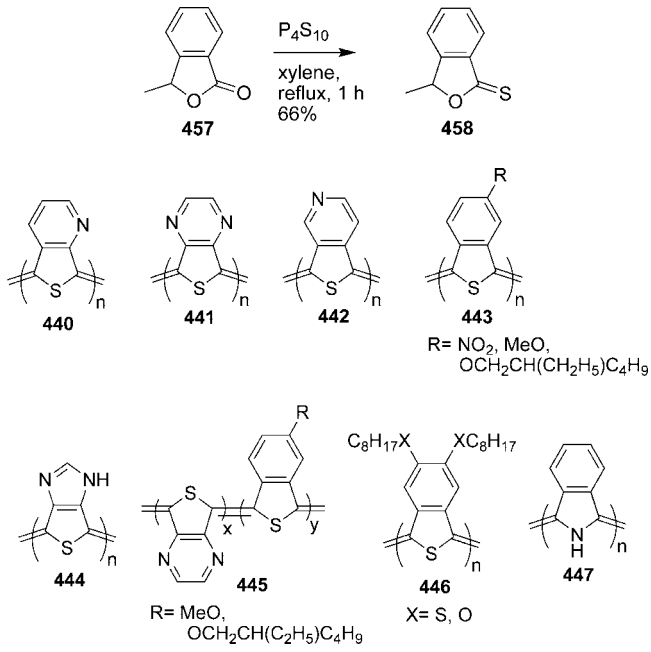
Scheme 121. Thionation of 448, 451, and 453 with P_4S_{10}



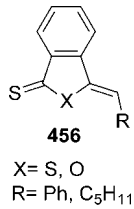
Scheme 122. Reaction of 1,2-Phthaldehyde with P_4S_{10}



Scheme 123. Thionation of Phthalid 457 with P_4S_{10}

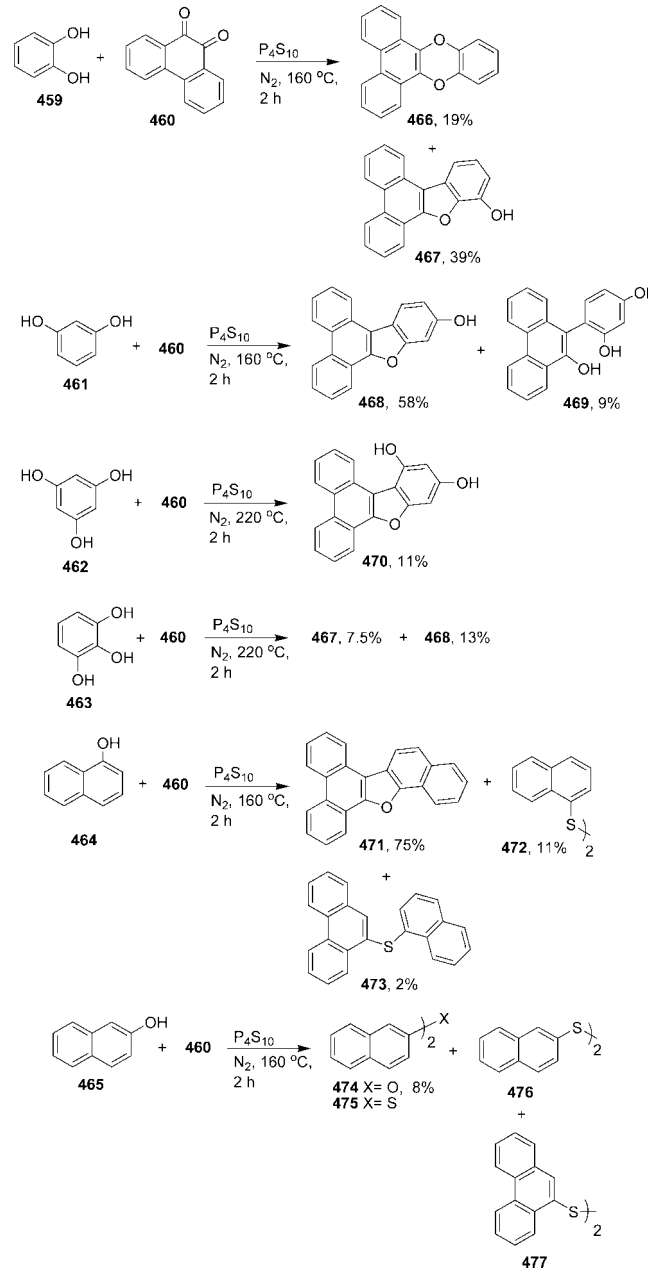


of carboxylic oxygen with sulfur to yield **458** (Scheme 123).[393]



Phenanthrene-9,10-quinone **460** was reacted with various arylalcohols such as catechol **459**, resorcinol **461**, phloroglucinol **462**, pyrogallol **463**, 1-naphthol **464**, and 2-naphthol **465** in the presence of P_4S_{10} (Scheme 124).[285] The reactions were performed at 160 and 220 °C for 2 h, which yielded the dioxin **466**, the furans **467**, **468**, **470**, and **471**, the disulfides **472**, **476**, and **477**, the sulfides **473** and **475**, the ether **474**, and the alcohol **469**.

Scheme 124. Reaction of Aryl Alcohols with 460

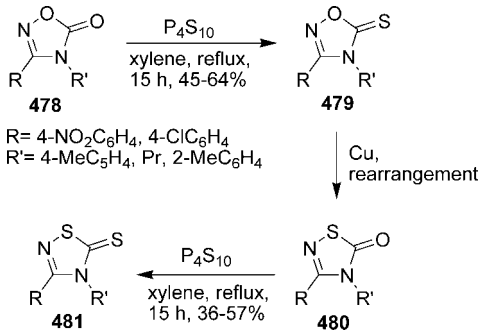


Oxadiazolethiones **479** were synthesized through the reactions of oxadiazoleones **478** with P_4S_{10} in refluxing xylene, which were obtained in 45−64% yields (Scheme 125).[394] The products were subjected to rearrangement to obtain the thiadiazoleones **480**, reaction of which with P_4S_{10} under the same conditions yielded the thiadiazolethiones **481**.

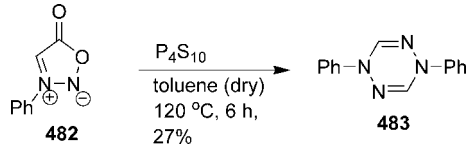
Treatment of *N*-phenylsydnone **482** with P_4S_{10} in dry toluene in a sealed tube at 120 °C for 6 h gave 1,4-diphenyltetrazine **483** in 27% yield (Scheme 126).[395]

The same reaction was repeated by a separate group; that is, syndone **482** was reacted with P_4S_{10}, and even in a different solvent such as CH_2Cl_2 at room temperature, the tetrazine **483** was also obtained.[396] On the other hand, when

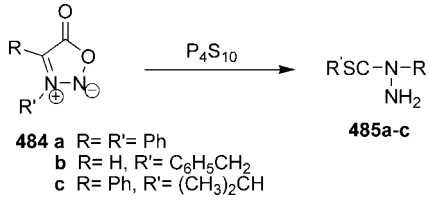
Scheme 125. Synthesis of Oxadiazolethiones



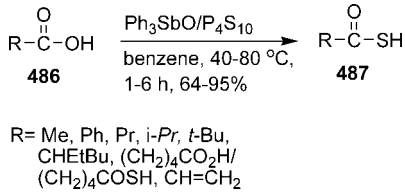
Scheme 126. Reaction of *N*-Phenylsydnone with P_4S_{10}



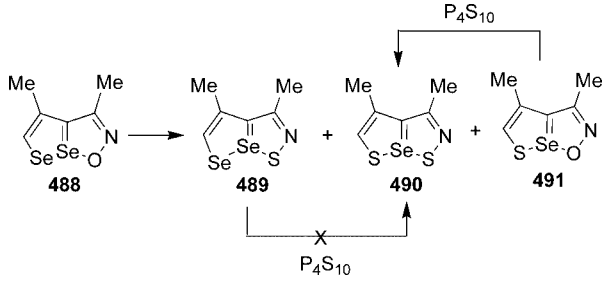
Scheme 127. Reaction of Sydnones with P_4S_{10}



Scheme 128. Synthesis of Thiocarboxylic Acids



Scheme 129. Reaction of Oxadiselenaazapentalene with P_4S_{10}

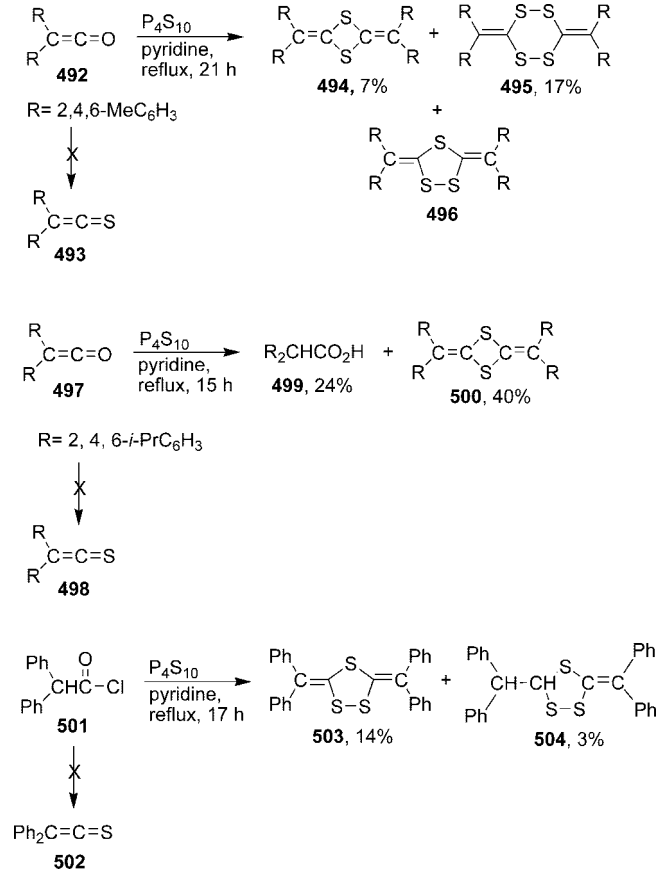


the syndones **484a**−**c**, having different groups, were reacted with P_4S_{10} in various solvents such as benzene, CH_2Cl_2, and CS_2, *N*-thioacylhydrazines **485a**−**c** were obtained instead (Scheme 127).

The carboxylic acids **486** were converted into thiocarboxylic acids **487** using triphenylstibine oxide/P_4S_{10} as catalyst. The reaction was performed in benzene at 40−80 °C for 1−6 h, which gave 64−95% yields (Scheme 128).[138]

The reaction of oxadiselenaazapentalene **488** with P_4S_{10} in boiling benzene yielded three products, **489**, **490**, and **491** (Scheme 129).[397] It was explained that while treatment of **491** with P_4S_{10} produced **490**, the reaction of **489** did not give **490**, which was interpreted as the reaction sequence following the order **488** → **491** → **490**.

Scheme 130. Reactions of Ketenes with P_4S_{10}



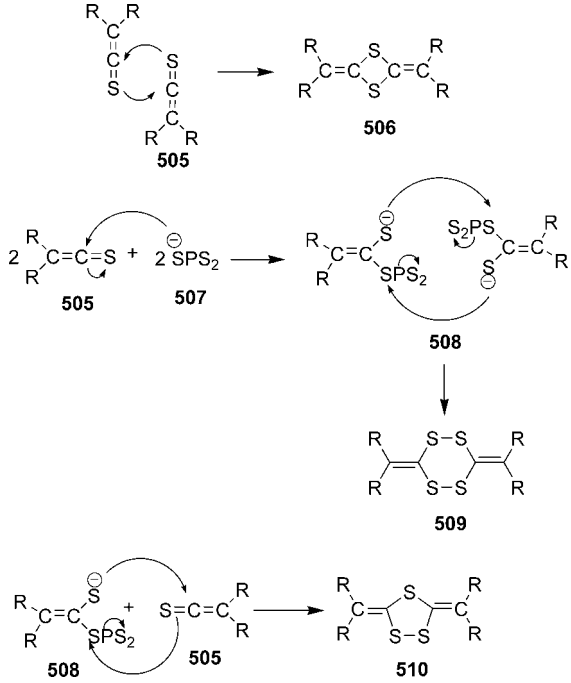
Attempts to synthesize the thioketenes **493**, **498**, and **502** from the ketenes **492** and **497** and diphenylacetyl chloride **501**, respectively, resulted in the formation of various dimers (Scheme 130).[398] The reaction was conducted in refluxing pyridine between 15 and 17 h. As dimesityl ketene **492** gave three dimmers of **494**−**496**, ditipyl ketene **497** yielded only one **500** along with the carboxylic acid **499**, and from diphenylacetyl chloride **501**, two dimers **503** and **504** were obtained. The mechanism was suggested that the thioketenes **505** formed in situ either react with each other to form **506** or react with the anion **507**, produced from P_4S_{10}, to give **508**. It then reacts with itself to yield **509** or reacts with the thioketene **505** to give the dimer **510** (Scheme 131).

Similar results were obtained in an attempt to synthesize the thioketene **514**, having trifluoromethylsulphanyl groups.[104] The reactions of the acetyl chloride **511**, the carboxylic acid **512**, and the ketene **513** with P_4S_{10} in refluxing toluene resulted in the formation of the dimers **515** and **516**, which were suggested to form through the intermediate thioketene **514** (Scheme 132).

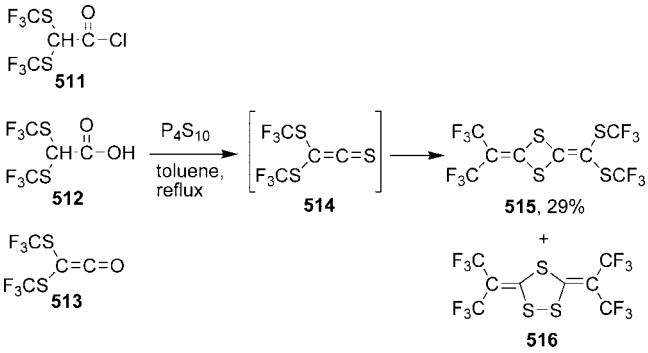
A ring-opening of the oxadiazino moiety **517** was observed when reacted with P_4S_{10} in refluxing pyridine for 1 h (Scheme 133).[399] One thione group and one oxo group were formed in the product **518**, the reaction of which with H_2SO_4 gave the thiadiazino ring **519**.

The reactions of the alkylamine **520** with P_4S_{10}, in different ratios, were investigated.[400−402] The reactions were conducted between 2, 6, and 12 molar ratios of dibutylamine **520** and one mole of P_4S_{10} (Scheme 134). While 2 mol of the amine **520** gave the thioic acid **521** along with **522**, 6 mole ratios yielded **523**, triethylamine **524**, and H_2S **525**. Finally, 12 mol of the amine produced **526** along with **524** and **525**. It could

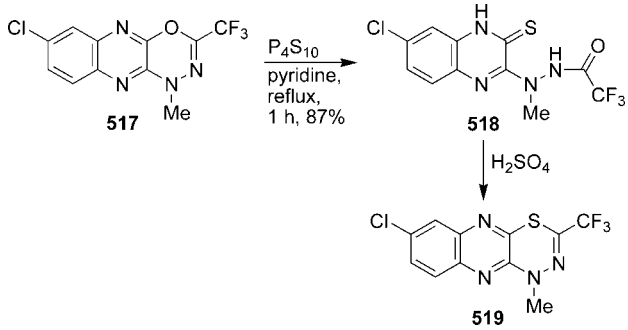
Scheme 131. Mechanism for the Formation of the Dimers from Thioketenes



Scheme 132. Attempt To Synthesize Fluoronated Thioketenes



Scheme 133. Reaction of Oxadiazino Group with P_4S_{10}



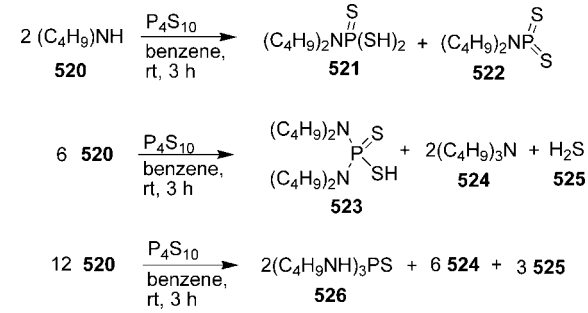
be concluded that the molar ratio for amine is effective for the formation of different products.

Hexamethyldisilazane, $(Me_3Si)_2NH$, was reacted with P_4S_{10} in different stoichiometric ratios to give $SP(NHSiMe_3)_x(SSiMe_3)_{3-x}$, where $x = 0-3$, along with a linear trimer $(Me_3SiNH)P(S)[(\mu\text{-}NH)P(S)(Me_3SiNH)P(S)][(\mu\text{-}NH)P(S)(NHSiMe_3)_2]_2$.[403]

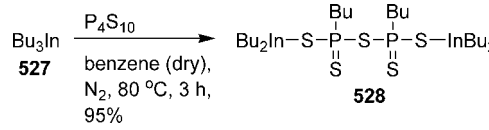
Treatment of tributylindium **527** with P_4S_{10} in benzene at 80 °C for 3 h gave **528** in 95% yield (Scheme 135).[404]

Heating P_4S_{10} with alkyl halides such as octyl bromide and butyl chloride did not give any product.[405] On the other hand, introduction of Lewis acid, $AlCl_3$, resulted in the formation of products. Thus, reactions of primary and secondary alkyl halides **529** with P_4S_{10} in the presence of $AlCl_3$ in CS_2 at 40−50 °C for 30 min gave the products **530** and **531** (Scheme 136).

Scheme 134. Reaction of Alkylamine with P_4S_{10}



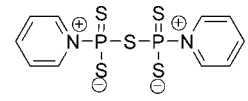
Scheme 135. Reaction of Tributylindium with P_4S_{10}



Scheme 136. Reaction of Alkyl Halides with P_4S_{10}

When the alkyl halides and the Lewis acid were changed to alkyl bromide and $AlBr_3$, respectively, different products, $(RS)_2P(S)Br$ and $RSP(S)Br_2$, were obtained.[406]

The use of pyridine as a solvent in reactions of P_4S_{10} is well-known, and it was reported that pyridine as a base attacks at P_4S_{10} to form the zwitterionic species **11a**.[16−18]



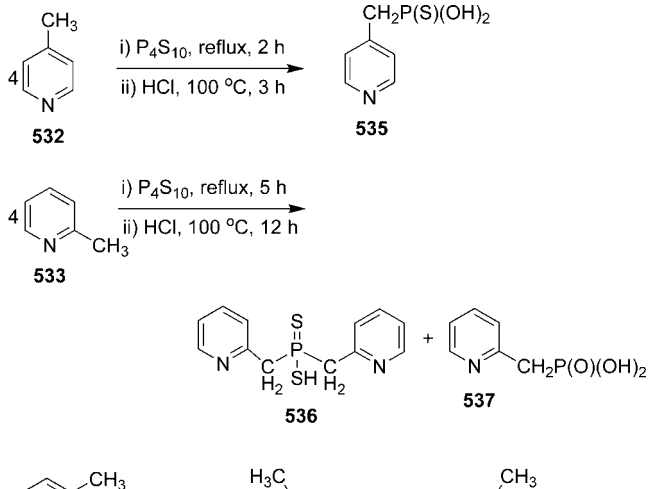
The reaction of 2-, 3-, and 4-methylpyridines **532**−**534** with P_4S_{10} indicated that, different from the case of 2- and 4-methylpyridines, only 3-methylpyridine, similar to unsubstituted pyridine, produces zwitterionic product **11b** (Scheme 137).[16] On the other hand, the pyridines **532** and **533**, after the hydrolysis, yielded the products **535**−**537**, having carbon−phosphorus bonds. Surprisingly, a similar result was obtained when pyridine **538** itself was subjected to the same reaction sequence: (i) reflux with P_4S_{10} and (ii) hydrolysis, which produced the product **539**, having a carbon−phosphorus bond (Scheme 138).

Reaction of the enamine **540** with P_4S_{10} in pyridine gave the heterocycle diazaphosphorinethione **541**, which had part of P_4S_{10} (Scheme 139).[407]

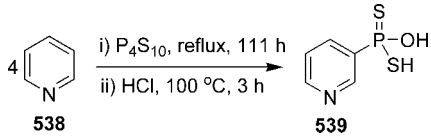
Treatment of diethyl oxomalonate **542** with P_4S_{10} yielded thioxomalonate **543** through a selective thionation of the oxo group (Scheme 140).[408] It was trapped *in situ* with cyclopentadiene **544**, 2,3-dimethylbuta-1,3-diene **545**, and anthracene **546** to obtain the corresponding adducts **547**, **548**, and **549**, respectively.

Surprisingly, fused dithiins **551** as major and thiophenes **552** as minor products were obtained as a result of the

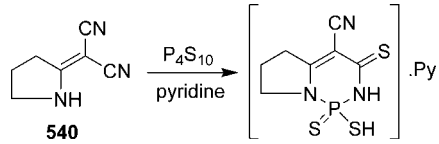
Scheme 137. Reaction of 2-, 3-, and 4-Methylpyridines with P_4S_{10}



Scheme 138. Reaction of Pyridine with P_4S_{10}



Scheme 139. Reaction of Enamine with P_4S_{10}



reaction of 1,8-diketones **550** with either P_4S_{10} or LR **566** in refluxing toluene (Scheme 141).[409−416] Computational chemistry studies suggested that its mechanism follows two paths after an initial thionation of the carbonyl groups: (i) an attack from sulfur to the thione, leading to a six-membered dithiin ring **553**, and (ii) the reaction of two thione rings, eliminating H_2S, resulting in the formation of a nine-membered ring **554**, rearrangement of which leads to a second six-membered ring **555** (Scheme 142).[417] The thiophene heterocycle **552** forms from the dithiin **551** by its rearrangement through **556**, which eliminates elemental sulfur to yield **552**.

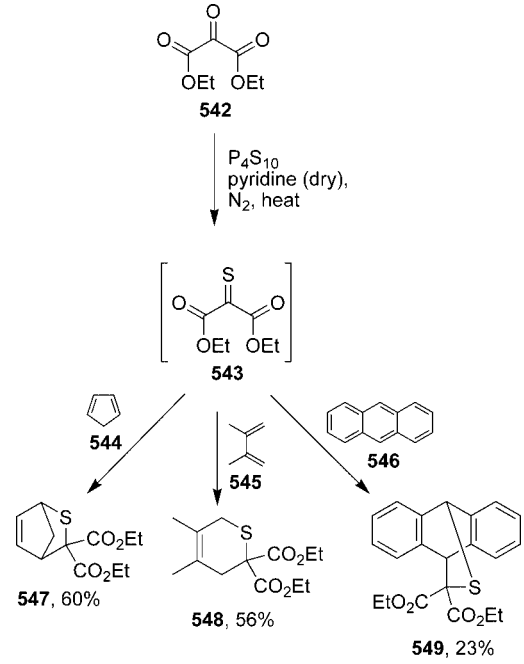
An in-depth study of the reactions of the 1,8-diketones **557** with P_4S_{10} in refluxing toluene or dioxane and with or without *p*TSA or $NaHCO_3$ surprisingly yielded the vinylene analogue **558** of ethylenedioxythiphene (EDOT) along with dithienothiophene (DTT) **559** (Table 11, entry 14) in 51−75% yield (Scheme 143).[418]

The reaction of benzyl monoarylimines **560** with P_4S_{10} in refluxing toluene yielded the indoles **563**, possibly through the intermediates **561** and **562** (Scheme 144).[310]

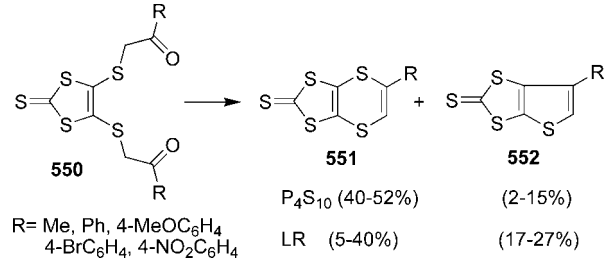
Stilbene **565** was obtained, although in low yield, 5%, on treatment of benzaldehyde **564** with P_4S_{10} in refluxing xylene for 20 h (Scheme 145).[98]

An important application of P_4S_{10} could be counted as the synthesis of LR **566**, which is the product of the reaction of P_4S_{10} with anisole.[278] LR has now been the most used

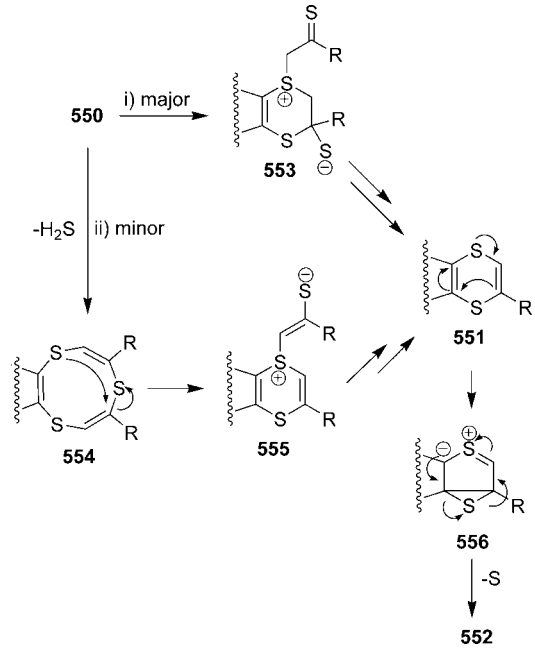
Scheme 140. Reaction of Oxomalonate with P_4S_{10}



Scheme 141. Reaction of 1,8-Diketones with P_4S_{10} and LR

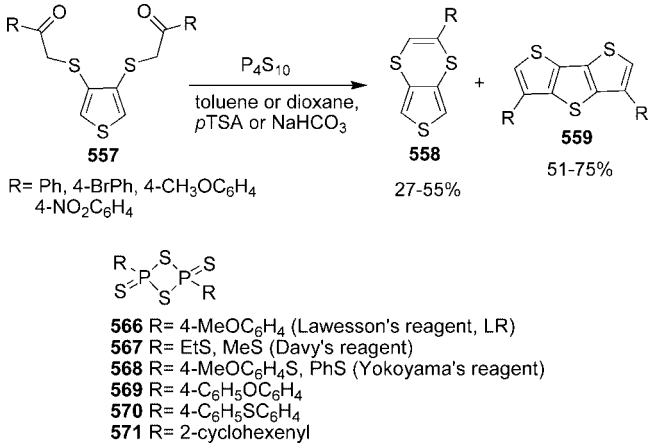


Scheme 142. Possible Reaction Mechanism of Formation of Dithiin and Thiophene



sulfurizing agent of organic compounds. In a similar fashion, P_4S_{10} was extensively used for the preparation of analogues of LR such as **567**,[419] **568**,[420] **569**,[421,422] **570**,[422] **571**,[423,424] **572**,[425] **573**−**576**,[426] **577**, **578**,[427] **579**,[428] and **580**.[429]

Scheme 143. Synthesis of the Vinylene Analogue of EDOT



Thionation of multiwalled carbon nanotubes using P_4S_{10} in refluxing toluene was reported that the sulfur content bonded to nanotubes was 0.6%, which was confirmed by TEM.[430] Attachment of vertically aligned single walled carbon nanotubes onto a silicon substrate was achieved through a thioester linkage, which was formed by the reaction of carboxylic acid and −OH moieties, respectively, with P_4S_{10}.[431]

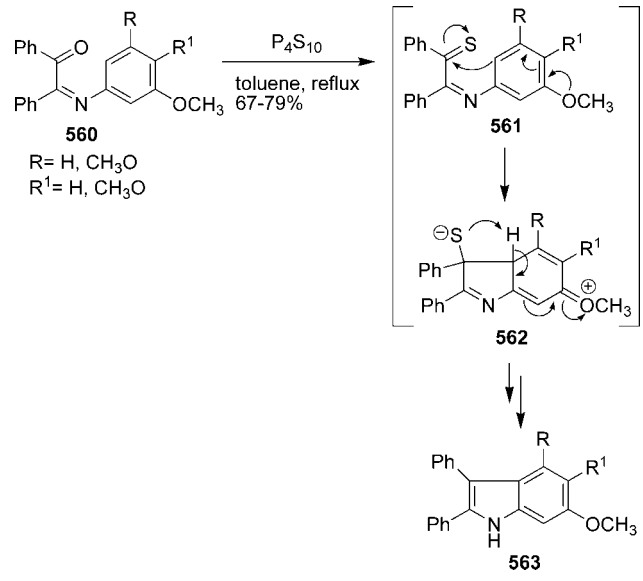
Modifications of cellulose, β-cyclodextrin, and starch in terms of introducing sulfur atoms were achieved by their reactions with P_4S_{10} in the absence or presence of dimethyl formamide.[432] The resultant products were reported to have about 2−22% sulfur and about 1−10% phosphorus contents.

Reactions of disulfides **581** with P_4S_{10} were reported to produce tetrathiolothionophosphates **582** (Scheme 146).[433] The reaction was conducted in dry toluene at 100−110 °C for 1 h, and the yield varied between 7 and 38%.[433,434] Further studies revealed that the use of ultrasonic irradiation[435] and iodine[436] improved the yields, and reaction conditions, such as lower temperature and shorter reaction time, were required.

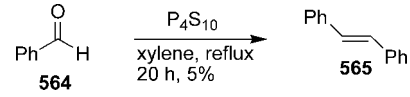
Treatment of the thioacetals **583** with P_4S_{10} at 100−140 °C for around 3 h gave **584** and **585** in 86−93 and 8−9% yields, respectively (Scheme 147).[433]

Treatment of alkoxy- **586** and alkylthiotrimethylsilanes **587** with P_4S_{10} yielded *s*-trimethylsilyl esters of dithio- and

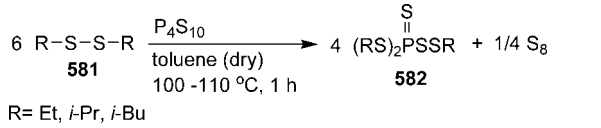
Scheme 144. Synthesis of Fused Indoles



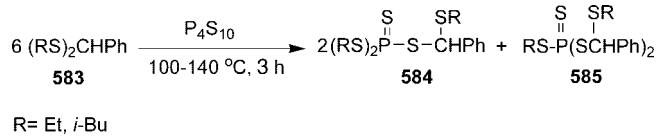
Scheme 145. Synthesis of Stilbene

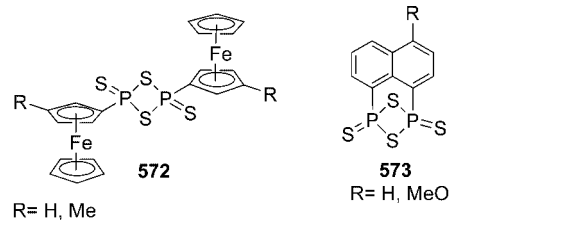


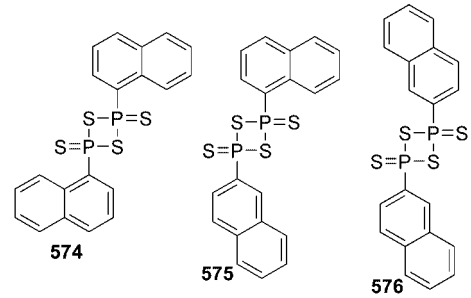
Scheme 146. Reaction of P_4S_{10} with Disulfides

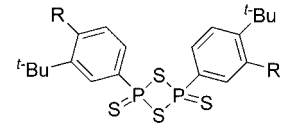


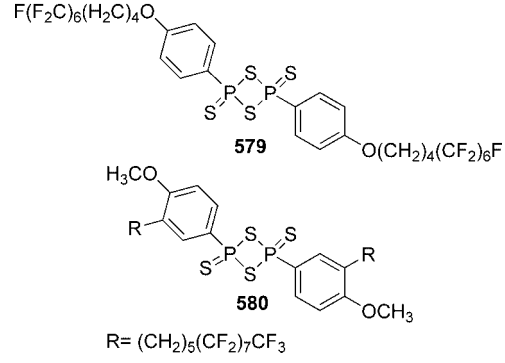
Scheme 147. Reaction of P_4S_{10} with Thioacetals







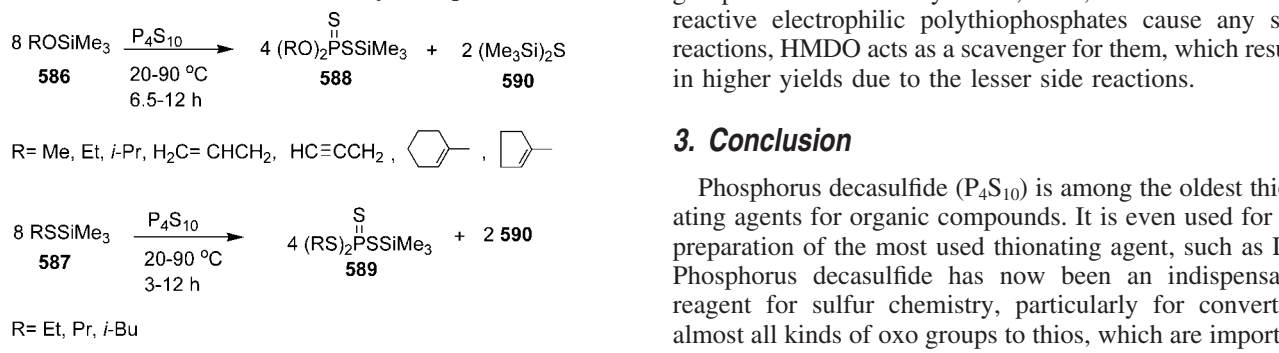




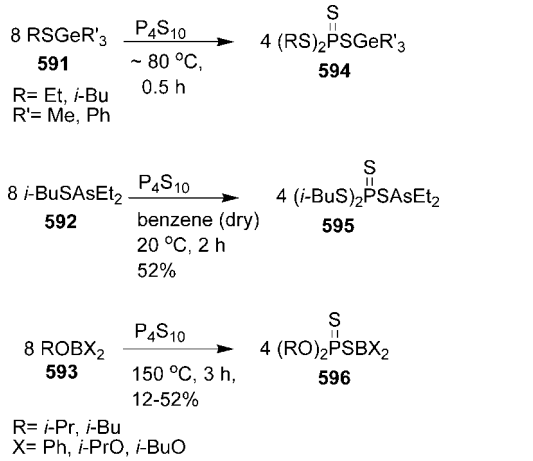
tetrathiophosphoric acids **588** and **589**, respectively, along with bis(trimethylsilyl)sulfide **590** (Scheme 148).[437−440]

A similar reaction of organogermanium **591**,[441,442] organothiarsenic **592**,[442,443] and organoborates **593**[444,445] with P_4S_{10} produced the esters **594**, **595**, and **596**, respectively (Scheme 149).

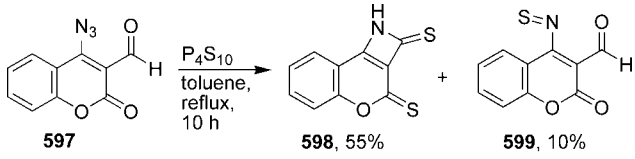
Scheme 148. Reaction of P_4S_{10} with Silyl Compounds



Scheme 149. Reaction of Organogermanium, Organothiarsenic, and Organoborates with P_4S_{10}



Scheme 150. Reaction of Coumarine 597 with P_4S_{10}



Reaction of benzyl chloride with P_4S_{10} in the presence of K_2CO_3 in acetonitrile (dry) at 60−70 °C for 2 h gave tribenzyltetrathiophosphate $(PhCH_2S)_3P{=}S$.[446,447]

Treatment of coumarine **597**, having an azido and a carboxaldehyde at 4- and 3-carbons, respectively, with P_4S_{10} in refluxing toluene resulted in the formation of two unusual products, **598** and **599** (Scheme 150).[448]

2.15. P_4S_{10} vs Lawesson's Reagent (LR)

Unfortunately, there is no clear-cut mechanism for understanding the difference between the two well-known thionating reagents, P_4S_{10} and LR. On the other hand, although both reagents are widely used in organic syntheses, considering the number of papers appearing each year, it looks as though LR is more popular among chemists. There is a general conclusion that LR is superior over P_4S_{10}, particularly in terms of obtaining better yields. On the other hand, this view may change with the recent developments, which indicate that the use of hexamethyldisiloxane (HMDO) together with P_4S_{10} gives superior or comparable yields to those obtained with LR.[66,102,129] This mixture is now called "Curphey reagent".[253] It has been claimed that this method has the advantage of easily removing the reagent-derived byproducts. Detailed experimental and NMR studies revealed that during the reaction initially P_4S_{10} converts the carbonyl groups into thiocarbonyls and, then, before the formed reactive electrophilic polythiophosphates cause any side reactions, HMDO acts as a scavenger for them, which results in higher yields due to the lesser side reactions.

3. Conclusion

Phosphorus decasulfide (P_4S_{10}) is among the oldest thionating agents for organic compounds. It is even used for the preparation of the most used thionating agent, such as LR. Phosphorus decasulfide 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 for use as end products in material, medicinal, etc. chemistry. Moreover, phosphorus decasulfide is widely applied for the synthesis of almost all kinds of heterocyclic compounds incorporating sulfur atom(s). Its range varies from thiophene to thiazoline, thiazole, thiazine, dithiazole, thiadiazole, pyrimidine, and imidazoline. It finds widespread application in thionation reactions of nucleosides, purines, and pyrimidines. Reduction of sulfoxides to sulfides could be concluded as another useful reaction of phosphorus pentasulfide.

Like LR, phosphorus decasulfide is a reagent that can make surprises by giving unexpected reactions, the results of which lead chemists to new methodologies and reactions. Depending on our experience and the literature survey, it could be to the synthetic chemists' benefit to try both reagents, P_4S_{10} and LR, in their syntheses to obtain the best results and surprising products.

4. Acknowledgments

We thank Tubitak for supporting this work (TBAG 108T941).

5. References

(1) Cowley, A. H. *J. Chem. Educ.* **1964**, *41*, 530.
(2) Marggraf, A. S. *Misc. Berolin.* **1740**, *6*, 54.
(3) Berzelius, J. *Liebigs Ann. Chem.* **1843**, *46*, 251.
(4) Berzelius, J. *Poggendorffs Ann. Phys. Chem.* **1843**, *59*, 539.
(5) Kekule, A. *Liebigs Ann. Chem.* **1854**, *90*, 309.
(6) Carius, L. *Liebigs Ann. Chem.* **1859**, *112*, 190.
(7) Fletcher, J. H.; Hamilton, J. C.; Hechenbleikner, I.; Hoegberg, E. I.; Sertl, B. J.; Cassaday, J. T. *J. Am. Chem. Soc.* **1950**, *72*, 2461.
(8) Hofmann, A. W.; Gabriel, S. *Ber.* **1892**, *25*, 1578.
(9) Hoffman, H.; Becke-Goehring, M. Phosphorus Sulfides. In *Topics in Phosphorus Chemistry*; Griffith, E. J., Grayson, M., Eds.; John Wiley and Sons: New York, 1976; Vol. 6, p 193.
(10) Demarcq, M. C. *J. Chem. Soc., Dalton Trans.* **1990**, 35.
(11) Demarcq, M. C. *J. Ind. Eng. Chem. Res.* **1991**, *30*, 1906.
(12) Andrews, L.; Reynolds, G. G.; Mielke, Z.; McCluskey, M. *Inorg. Chem.* **1990**, *29*, 5222.
(13) Retuert, P. J.; Fluck, E.; Riffel, H.; Hess, H. *Z. Anorg. Allg. Chem.* **1985**, *521*, 153.
(14) Roesky, H. W.; Noltmeyer, M.; Sheldrick, G. M. *Z. Naturforsch.* **1986**, *41B*, 803.
(15) Flanagan, S.; Luten, H. A.; Rees, W. S., Jr. *Inorg. Chem.* **1998**, *37*, 6093.
(16) Bunel, E.; Manzur, J.; Retuert, J. J. *Chem. Res. (S)* **1981**, 285.
(17) Fluck, E.; Binder, H. *Z. Anorg. Allg. Chem.* **1967**, *354*, 113.
(18) Meisel, M.; Grunze, H. *Z. Anorg. Allg. Chem.* **1968**, *360*, 277.
(19) Blachnik, R.; Matthiesen, J.; Müller, A.; Nowottnick, H.; Reuter, H. *Z. Krystallogr.* **1998**, *213*, 233.
(20) Vos, A.; Wiebenga, E. H. *Acta Crystallogr.* **1955**, *8*, 217.
(21) Barral, R.; Demarcq, M. C.; Mai, C. *J. Chem. Res. (S)* **1984**, 156.
(22) Bjorholm, T.; Jakobsen, H. J. *J. Am. Chem. Soc.* **1991**, *113*, 27.
(23) Andrew, E. R.; Vennart, W.; Bonnard, G.; Croiset, R. M.; Demarcq, M.; Mathieu, E. *Chem. Phys. Lett.* **1976**, *43*, 317.
(24) Thamm, R.; Heckmann, G.; Fluck, E. *Phosphorus Sulfur* **1982**, *12*, 319.
(25) Jensen, J. O.; Zeroka, D. *THEOCHEM* **1999**, *487*, 267.

(26) Andrews, L.; Thompson, C.; Demarcq, M. C. *Inorg. Chem.* **1992**, *31*, 3173.
(27) Müller, A.; Cyvin, B. N.; Cyvin, S. J.; Pohl, S.; Krebs, B. *Spectrochim. Acta* **1976**, *32A*, 67.
(28) Picone, R. F.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* **1977**, *4*, 388.
(29) Tahri, Y.; Chermette, H. *J. Electron Spectrosc.* **1991**, *56*, 51.
(30) Brylewicz, Z.; Rudnicki, R. *Phosphorus Sulfur* **1994**, *88*, 163.
(31) Gigli, R.; Piacente, V.; Scardala, P. *J. Mater. Sci. Lett.* **1990**, *9*, 1148.
(32) Demarcq, M. C. *J. Mater. Sci. Lett.* **1992**, *11*, 758.
(33) Casida, J. E. *Acta Chem. Scand.* **1958**, *12*, 1691.
(34) Campaigne, E. *Chem. Rev.* **1946**, *39*, 1.
(35) Hurd, R. N.; Delamater, G. *Chem. Rev.* **1961**, *61*, 45.
(36) Weintraub, P. M. *Int. J. Sulfur Chem.* **1973**, *8*, 321.
(37) Nakayama, J.; Konishi, T.; Hoshino, M. *Heterocycles* **1988**, *27*, 1731.
(38) Brillon, D. *Sulfur Rep.* **1992**, *12*, 297.
(39) Metzner, P. *Synthesis* **1992**, 1185.
(40) McGregor, W. M.; Sherrington, D. C. *Chem. Soc. Rev.* **1993**, 199.
(41) Hartke, K.; Gerber, H.-D. *J. Prakt. Chem.* **1996**, *338*, 763.
(42) Polshettiwar, V. *Synlett* **2004**, 2245.
(43) Ishii, A.; Akazawa, T.; Ding, M.-X.; Honjo, T.; Maruta, T.; Nakamura, S.-Y.; Nagaya, H.; Ogura, M.; Teramoto, K.; Shiro, M.; Hashino, M.; Nakayama, J. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 509.
(44) Romanski, J.; Mloston, G. *Synthesis* **2002**, 1355.
(45) Willis, M. C.; Taylor, D.; Gillmore, A. T. *Tetrahedron* **2006**, *62*, 11513.
(46) Machiguchi, T.; Kano, Y.; Hasegawe, T. *Chem. Lett.* **1990**, 563.
(47) Machiguchi, T.; Otani, H.; Ishii, Y.; Hasegawa, T. *Tetrahedron Lett.* **1987**, *28*, 203.
(48) Scheeren, J. W.; Ooms, P. H. J.; Nivard, N. J. F. *Synthesis* **1973**, 149.
(49) Polshettiwar, V.; Kaushik, M. P. *Tetrahedron Lett.* **2004**, *45*, 6255.
(50) Noack, A.; Schröder, A.; Hartmann, H. *Phosphorus Sulfur* **2001**, *176*, 185.
(51) El-Barbary, A. A.; El-Ezz, A. Z. A.; Sharaf, A. M.; Nielsen, C. *Phosphorus Sulfur* **2007**, *182*, 1621.
(52) Vicario, J.; Walko, M.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2006**, *128*, 5127.
(53) Tokumitsu, T.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2348.
(54) Brothers, P. J.; Rickard, C. E. F.; Strange, C. M.; Ware, D. C. *Aust. J. Chem.* **1997**, *50*, 373.
(55) Denifl, P.; Bildstein, B. *J. Organomet. Chem.* **1993**, *453*, 53.
(56) Barnes, J. C.; Bell, W.; Glidewell, C.; Howie, R. A. *J. Organomet. Chem.* **1990**, *385*, 369.
(57) Ferguson, G. *J. Chem. Soc., Dalton Trans.* **1990**, 3697.
(58) Tatarets, A. L.; Fedyunyaeva, I. A.; Terpetschnig, E.; Patsenker, L. D. *Dyes Pigments* **2005**, *64*, 125.
(59) Frauenhoff, G. R.; Takusagawa, F.; Busch, D. H. *Inorg. Chem.* **1992**, *31*, 4002.
(60) Frauenhoff, G. R.; Busch, D. H. *J. Coord. Chem.* **1993**, *29*, 175.
(61) Elam, E.; Davis, H. E. *J. Org. Chem.* **1967**, *32*, 1562.
(62) Kim, S. H.; Han, S. K.; Kim, J. J.; Hwang, S. H.; Yoon, C. M.; Keum, S. R. *Dyes Pigments* **1998**, *39*, 77.
(63) Lamazouere, A.-M.; El-Batouti, N.; Sotiropoulos, J. *Z. Kristallogr.* **1995**, *210*, 597.
(64) Okuma, K.; Shibata, S.; Shioji, K.; Yokomori, Y. *Chem. Commun.* **2000**, 1535.
(65) Karakasa, T.; Motoki, S. *J. Org. Chem.* **1978**, *43*, 4147.
(66) Curphey, T. J. *J. Org. Chem.* **2002**, *67*, 6461.
(67) Karakasa, T.; Satsumabayashi, S.; Motoki, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 335.
(68) El-Kateb, A. A.; Hennawy, I. T.; Shabana, R.; Abdel-Malek, H. A. *Phosphorus Sulfur* **1991**, *63*, 13.
(69) Chetia, A.; Saikia, A.; Saikia, C. J.; Boruah, R. C. *Tetrahedron Lett.* **2003**, *44*, 2741.
(70) Lipkowitz, K. B.; Mundy, B. P. *Tetrahedron Lett.* **1977**, 3417.
(71) Boulos, L. S.; Hennawy, I. T.; Arsanious, M. H. N. *Heteroat. Chem.* **1994**, *5*, 27.
(72) Schmack, W.; Nakazawa, T.; Hafner, K. *Tetrahedron Lett.* **2000**, *41*, 8255.
(73) Beer, L.; Reed, R. W.; Robertson, C. M.; Oakley, R. T.; Tham, F. S.; Haddon, R. C. *Org. Lett.* **2008**, *10*, 3121.
(74) Saito, T.; Nagashima, M.; Karakasa, T.; Motoki, S. *J. Chem. Soc., Chem. Commun.* **1990**, 1665.
(75) Marei, M. G. *Phosphorus Sulfur* **1993**, *81*, 101.
(76) Marei, M. G.; Mishrikey, M. M. *Phosphorus Sulfur* **1992**, *73*, 229.
(77) Al-Ahmadi, A. A.; El-Zohry, M. F. *Phosphorus Sulfur* **1994**, *97*, 35.
(78) Kharchenko, V. G.; Krupina, T. I.; Klimenko, S. K.; Rassudova, A. A. *Khim. Geterotsikl.* **1972**, 1196.
(79) Padmavathi, V.; Balaiah, A.; Reddy, D. B. *J. Heterocycl. Chem.* **2002**, *39*, 649.
(80) Al-Thebeiti, M. S.; El-Zohry, M. F. *Heteroat. Chem.* **1995**, *6*, 567.
(81) Arcoleo, A.; Abbate, G.; Gottuso, M.; Fontana, G. *Heterocycles* **1988**, *27*, 2141.
(82) Stavaux, M.; Lozach, N. *Bull. Soc. Chim. Fr.* **1967**, 2082.
(83) Zhang, W.; Henry, Y. *Synlett* **2001**, 1129.
(84) Köll, P.; Rennecke, R.-W.; Heyns, K. *Chem. Ber.* **1976**, *109*, 2537.
(85) Okuma, K.; Shigetomi, T.; Shibata, S.; Shioji, K. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 187.
(86) Pogodin, S.; Agranat, I. *J. Am. Chem. Soc.* **2003**, *125*, 12829.
(87) Zimmermann, K.; Haenel, M. W. *Synlett* **1997**, 609.
(88) Arumugam, K.; Bollinger, J. E.; Fink, M.; Donahue, J. P. *Inorg. Chem.* **2007**, *46*, 3283.
(89) Dai, Z.-F.; Qun, L.; Peng, B.-X. *Dyes Pigments* **1997**, *35*, 23.
(90) Falaras, P.; Mitsopoulou, C.-A.; Argyropoulos, D.; Lyris, E.; Psaroudakis, N.; Vrachnou, E.; Katakis, D. *Inorg. Chem.* **1995**, *34*, 4536.
(91) Echarri, R.; Matheu, M. I.; Claver, C.; Castillion, S.; Alvarez-Larena, A.; Piniella, J. F. *Tetrahedron Lett.* **1997**, *38*, 6457.
(92) Hegab, M. I. *Acta Chim. Solv.* **2007**, *54*, 545.
(93) Dash, B.; Dora, E. K.; Panda, C. S. *Heterocycles* **1982**, *19*, 2093.
(94) Kitahara, Y.; Funamizu, M. *Bull. Chem. Soc. Jpn.* **1964**, 1897.
(95) Krebs, A. W. *Angew. Chem.* **1965**, *77*, 10.
(96) Laban, G.; Fabian, J.; Mayer, R. *Z. Chem.* **1968**, *8*, 414.
(97) Brown, E. I. G.; Leaver, D.; McKinnon, D. M. *J. Chem. Soc. (C)* **1970**, 1202.
(98) Paulussen, H.; Haitjema, H.; Vanasselt, R.; Mylle, P.; Adriaensens, P.; Gelan, J.; Vanderzande, D. *Polymer* **2000**, *41*, 3121.
(99) Yousif, N. M.; Fahmy, A. F. M.; Amine, M. S.; Gad, F. A.; Syed, H. H. *Phosphorus Sulfur* **1998**, *133*, 13.
(100) Sayed, H. H.; Ali, M. A. *Phosphorus Sulfur* **2008**, *183*, 156.
(101) Janosik, T.; Bergman, J.; Stensland, B.; Stalhandske, C. *J. Chem. Soc., Perkin Trans. 1* **2002**, 330.
(102) Curphey, T. J. *Tetrahedron Lett.* **2002**, *43*, 371.
(103) Filippi, J.-J.; Fernandez, X.; Lizzani-Cuvelier, L.; Loisseau, A.-M. *Tetrahedron Lett.* **2003**, *44*, 6647.
(104) Haas, A.; Praas, H.-W. *J. Fluorine Chem.* **1993**, *60*, 153.
(105) Elkafrawy, A. F. *Indian J. Chem.* **1992**, *31B*, 19.
(106) Pai, R. R.; Bendre, D. S.; Samant, S. D. *Indian J. Chem.* **2002**, *41B*, 191.
(107) Karmarkar, K. S.; Samant, S. D. *Indian J. Chem.* **1993**, *32B*, 1113.
(108) Deodhar, K. D.; Kekare, M. B.; Pednekar, S. R. *Synthesis* **1985**, 328.
(109) Schmarr, H.-G.; Einsenreich, W.; Engel, K.-H. *J. Agric. Food Chem.* **2001**, *49*, 5923.
(110) Landreau, C.; Deniaud, D.; Reliquet, F.; Reliquet, A.; Meslin, J. C. *Heterocycles* **2000**, *53*, 2667.
(111) Brook, D. J. R.; Noll, B. C.; Koch, T. H. *J. Chem. Soc., Perkin Trans. 1* **1998**, 289.
(112) Filippi, J.-J.; Fernandez, X.; Lizzani- Cuvelier, L.; Loiseau, A.-M. *Flavour Fragrance J.* **2006**, *21*, 175.
(113) Hashem, A. I.; El-Kousy, S. M.; El-Torgoman, A.; Salama, G. M. *Indian J. Chem.* **1985**, *24B*, 875.
(114) Usachev, B. I.; Shafeev, M. A.; Sosnovskikh, V. Y. *Russ. Chem. Bull.* **2006**, *55*, 523.
(115) El-Maghraby, A. A.; Bedair, A. H.; Aly, F. M.; Emam, H. A. *Indian J. Chem.* **1987**, *26B*, 979.
(116) Ibrahim, N. M. *Phosphorus Sulfur* **2006**, *181*, 1773.
(117) Gadre, J. N.; Audi, A. A.; Karambelkar, N. P. *Indian J. Chem.* **1996**, *35B*, 60.
(118) Agirbas, H.; Guner, S. *Phosphorus Sulfur* **2000**, *161*, 257.
(119) Mughal, E. U.; Hasan, A.; Rasheed, L. *Heterocycl. Commun.* **2005**, *11*, 445.
(120) Aitmambetov, A.; Ismailova, G. O.; Ibragimova, Z. Y. *Chem. Nat. Compd.* **2004**, *40*, 444.
(121) Yan, Y.-L.; Miller, M. T.; Cao, Y.; Cohen, S. M. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 1970.
(122) Usachev, B. I.; Shafeev, M. A.; Sosnovskikh, V. Y. *Russ. Chem. Bull.* **2004**, *53*, 2285.
(123) Sayed, M. A.; El-Kafrawy, A. F.; Soliman, A. Y.; El-Bassiouny, F. A. *Indian J. Chem.* **1991**, *30B*, 980.
(124) Aimar, M. L.; Rossi, R. H. *Tetrahedron Lett.* **1996**, *37*, 2137.
(125) Krugler, M. C.; Legouin, B.; Mouret, L.; Burgot, J.-L. *Phosphorus Sulfur* **2006**, *181*, 2307.
(126) Aimar, M. L.; De Rossi, R. H. *Synthesis* **2000**, 1749.
(127) Aimar, M. L.; Kreiker, J.; De Rossi, R. H. *Tetrahedron Lett.* **2002**, *43*, 1947.
(128) He, X.; Reeve, M.; Desai, U. R.; Kellogg, G. E.; Reynolds, K. A. *Antimicrob. Agents Chemother.* **2004**, *48*, 3093.
(129) Curphey, T. J. *Tetrahedron Lett.* **2000**, *41*, 9963.
(130) Bodrov, M. B.; Saloutin, V. I.; Pashkevich, K. I. *Bull. Acad. Sci. USSR, Chem.* **1986**, *35*, 799.
(131) Abasq, M. L.; Saidi, M.; Burgot, J.-L.; Darchen, A. *J. Organomet. Chem.* **2009**, *694*, 36.
(132) Trebaul, C.; Teste, J. *Bull. Soc. Chim. Fr.* **1970**, 2272.
(133) Trebaul, C. *Bull. Soc. Chim. Fr.* **1971**, 1102.
(134) Rioult, P.; Vialle, J. *Bull. Soc. Chim. Fr.* **1968**, 4483.

(135) Islam, A. M.; El-Sherief, A. M. S.; Ead, F. A. *Indian J. Chem.* **1978**, *16B*, 50.
(136) Zhou, N.; Lu, L.; Zhu, X.; Wang, X.; Zhu, J.; Zhou, D. *Polym. Bull.* **2006**, *57*, 491.
(137) Nomura, R.; Miyazaki, S.-I.; Nakano, T.; Matsuda, H. *Appl. Organomet. Chem.* **1991**, *5*, 513.
(138) Nomura, R.; Miyazaki, S.-I.; Nakano, T.; Matsuda, H. *Chem. Ber.* **1990**, *123*, 2081.
(139) Sudalai, A.; Kanagasabapathy, S.; Benicewicz, B. C. *Org. Lett.* **2000**, *2*, 3213.
(140) Dureault, A.; Taton, D.; Destarac, M.; Leising, F.; Gnanou, Y. *Macromolecules* **2004**, *37*, 5513.
(141) Blasoveshchenskii, V. S.; Vlasova, S. N. *J. Gen. Chem. USSR* **1971**, 1036.
(142) Blasoveshchenskii, V. S.; Kudryavtseva, S. N. USSR Pat. 1967, 207899; Chem. Abstr. 1968, *69*, 76627e.
(143) Davy, H.; Metzner, P. *Chem. Ind.—London* **1985**, 824.
(144) Brannock, K. C. *J. Am. Chem. Soc.* **1951**, *73*, 4953.
(145) Athawale, B. K.; Chattopadhyaya, J. B.; Rao, A. V. R. *Indian J. Chem.* **1975**, *13*, 812.
(146) Dabrowska, U.; Dabrowski, J. *Chem. Ber.* **1976**, *109*, 1779.
(147) Abdel-Ghany, H.; Khodairy, A. *Phosphorus Sulfur* **2000**, *166*, 45.
(148) Lin, S.-C.; Yang, F.-D.; Shiue, J.-S.; Yang, S.-M.; Fang, J.-M. *J. Org. Chem.* **1998**, *63*, 2909.
(149) Khan, A. Z.-Q.; Sandström, J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2085.
(150) Rees, C. W.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **1999**, *64*, 5010.
(151) Marcos, C. F.; Rakitin, O. A.; Rees, C. W.; Souvorva, L. I.; Torroba, T.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 453.
(152) Gompper, R.; Knieler, R.; Polborn, K. *Z. Naturforsch.* **1993**, *48b*, 1621.
(153) Zayed, S. E.; Hussin, I. A. *Phosphorus Sulfur* **1993**, *84*, 191.
(154) Brelivet, J.; Appriou, P.; Teste, J. C. R. *Acad. Sci. Paris* **1969**, *268*, 2231.
(155) Brelivet, J.; Appriou, P.; Teste, J. *Bull. Soc. Chim. Fr.* **1971**, 1344.
(156) Trebaul, C.; Teste, J. *Bull. Soc. Chim. Fr.* **1969**, 2456.
(157) Trebaul, C.; Teste, J. *Bull. Soc. Chim. Fr.* **1966**, 3042.
(158) Fowkes, F. S.; McClelland, E. W. *J. Chem. Soc.* **1941**, 187.
(159) Warrener, R. N.; Cain, E. N. *Chem. Ind.—London* **1966**, 289.
(160) Thuiller, A.; Vialle, J. *Bull. Soc. Chim. Fr.* **1959**, 1398.
(161) Schmidt, U.; Luttringhaus, A.; Trefzger, H. *Liebigs Ann. Chem.* **1960**, *631*, 129.
(162) Amoretti, L.; Mossini, F.; Plazzi, V. *Il Farmaco* **1968**, *23*, 583.
(163) Legrand, L.; Lozach, N. *Bull. Soc. Chim. Fr.* **1967**, 2067.
(164) Rao, C. S.; Murty, V. S. N.; Tattu, P. K. *Indian J. Chem.* **1981**, *20B*, 1083.
(165) Fernandes, M. A.; Reid, D. H. *Synlett* **2003**, 2231.
(166) Brillon, D. *Synth. Commun.* **1990**, *20*, 3085.
(167) Basavaraja, K. M.; Patil, V. M.; Agasimundin, Y. S. *Indian J. Heterocycl. Chem.* **2007**, *17*, 27.
(168) Uchikawa, O.; Fukatsu, K.; Aono, T. *J. Heterocycl. Chem.* **1994**, *31*, 877.
(169) Smiszek-Lindert, W.; Nowak, M.; Kusz, J. *Acta Crystallogr.* **2007**, *E63*, o3917.
(170) Sierra, M. L.; Beneton, V.; Boullay, A.-B.; Boyer, T.; Brewster, A. G.; Donche, F.; Forest, M.-C.; Fouchet, M.-H.; Gellibert, F. J.; Grillot, D. A.; Lambert, M. H.; Laroze, A.; Grumelec, C. L.; Linqet, J. M.; Montana, V. G.; Nguyen, V.-L.; Nicodeme, E.; Patel, V.; Penfornis, A.; Pineau, O.; Pohin, D.; Potvain, F.; Poulain, G.; Ruault, C. B.; Saunders, M.; Toum, J.; Xu, H. E.; Xu, R. X.; Pianetti, P. M. *J. Med. Chem.* **2007**, *50*, 685.
(171) Al-Awadi, N. A.; Ibrahim, Y. A.; Patel, M.; George, B. J.; Al-Etiabi, A. M. *Int. J. Chem. Kinet.* **2006**, *38*, 59.
(172) Pavlovic, G.; Tralic-Kulenovic, V.; Vinkovic, M.; Vikic-Topic, D.; Matanovic, I.; Popovic, Z. *Struct. Chem.* **2006**, *17*, 275.
(173) Katritzky, A. R.; Witek, R. M.; Rodriquez-Garcia, V.; Mohapatra, P. P.; Rogers, J. W.; Cusido, J.; Abdel-Fattah, A. A. A.; Steel, P. J. *J. Org. Chem.* **2005**, *70*, 7866.
(174) Shi, M.; Duan, W.-L.; Rong, G.-B. *Chirality* **2004**, *16*, 642.
(175) Polshettiwar, V.; Kaushik, M. P. *Tetrahedron Lett.* **2006**, *47*, 2315.
(176) Liebscher, J.; Patzel, M.; Kelboro, Y. F. *Synthesis* **1989**, 672.
(177) Kunes, J.; Balsanek, V.; Pour, M.; Waisser, K.; Kaustova, J. *Il Farmaco* **2002**, *57*, 777.
(178) Hartke, K.; Barrmeyer, S. *J. Prakt. Chem.* **1996**, *338*, 251.
(179) Poupaert, J. H.; Carato, P.; McCurdy, C. R. *Lett. Org. Chem.* **2005**, *2*, 330.
(180) Robert, J. M. H.; Robert-Piessard, S.; Courant, J.; Baut, G. L.; Robert, B.; Lang, F.; Petit, J. Y.; Grimaud, N.; Welin, L. *Eur. J. Med. Chem.* **1995**, *30*, 915.
(181) McClelland, E. W.; Salkeld, C. E. *J. Chem. Soc.* **1936**, 1143.
(182) Beilenson, B.; Hamer, F. M. *J. Chem. Soc.* **1936**, 1225.
(183) Köttgen, P.; Linden, A.; Heimgartner, H. *Acta Chim. Slov.* **2009**, *56*, 591.
(184) Bryce, M. R.; Gardiner, J. M. *Tetrahedron* **1988**, *44*, 599.
(185) Hennequin, L.; Blanc, S. P.-L. *Tetrahedron Lett.* **1999**, *40*, 3881.
(186) Kunick, C.; Link, A. *J. Heterocycl. Chem.* **1995**, *32*, 803.
(187) Mphahlele, M. J.; Kaye, P. T. *Magn. Reson. Chem.* **2000**, *38*, 207.
(188) Janciene, R.; Stumbreviciute, Z.; Podeniene, L.; Puodziunaite, B. *Chem. Heterocycl. Compd.* **2002**, *38*, 738.
(189) Ghani, E. A. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2032.
(190) Sayed, G. H.; Radwan, A.; Hamed, A. A.; Borqie, E.-S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 477.
(191) Halim, M. S. A.; Radwan, A.; Saad, M. A.; Sayed, G. H.; Khalil, M. *J. Chem. Soc., Pakistan* **1993**, *15*, 202.
(192) Kassab, R. R.; Sayed, G. H.; Radwan, A. M.; El-Azzez, N. A. *Rev. Roum. Chim.* **2001**, *46*, 649.
(193) Marei, M. G. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1172.
(194) Jarecka, D.; Besch, A.; Otto, H.-H. *Monatsh. Chem.* **2003**, *134*, 901.
(195) Nabar, U. V.; Mayadeo, M. S.; Deodhar, K. D. *Indian J. Chem.* **1988**, *27B*, 109.
(196) Amer, A. M.; El-Bermaui, M. A.; Ahmed, A. F. S.; Soliman, S. M. *Monatsh. Chem.* **1999**, *130*, 1409.
(197) Bobosik, V.; Krutosikova, A.; Jordis, U. *Monatsh. Chem.* **1995**, *126*, 747.
(198) Smolders, R. R.; Hanuise, J.; Coomans, R.; Proietto, V.; Voglet, N.; Waefelaer, A. *Synthesis* **1982**, 493.
(199) Siddiqui, A. A.; Kushnoor, A.; Wani, S. M. *Indian J. Heterocycl. Chem.* **2004**, *13*, 257.
(200) Rao, S. S.; Chowdary, K. S.; Prashant, A.; Krishnan, V. S. H. *Synth. Commun.* **2001**, *31*, 3469.
(201) Narayana, B.; Raj, K. K. V.; Ashalatha, B. V.; Kumari, N. S. *Eur. J. Med. Chem.* **2006**, *41*, 417.
(202) Duplantier, A. J.; Bachert, E. L.; Cheng, J. B.; Cohan, V. L.; Jenkinson, T. H.; Kraus, K. G.; McKechney, M. W.; Pillar, J. D.; Watson, J. W. *J. Med. Chem.* **2007**, *50*, 344.
(203) Bekhit, A. A.; Baraka, A. M. *Eur. J. Med. Chem.* **2005**, *40*, 1405.
(204) Datt, M. S.; de Koning, C. B.; Fernandes, M. A.; Michael, J. P. *Acta Crystallogr.* **2004**, *E60*, o2298.
(205) Pedras, M. S. C.; Suchy, M.; Ahiahonu, P. W. K. *Org. Biomol. Chem.* **2006**, *4*, 691.
(206) Klingsberg, E.; Papa, D. *J. Am. Chem. Soc.* **1951**, *73*, 4988.
(207) Cooke, G. W.; Gulland, J. M. *J. Chem. Soc.* **1939**, 873.
(208) Taylor, E. C.; Liu, B. *Tetrahedron Lett.* **1999**, *40*, 5291.
(209) Moustafa, O. S. *Phosphorus Sulfur* **1997**, *131*, 49.
(210) Moustafa, O. S.; Badr, M. Z. A. *Heterocycl. Commun.* **1997**, *3*, 465.
(211) Okafor, C. O.; Okoro, U. C. *Dyes Pigments* **1991**, *16*, 149.
(212) Bhaduri, A. P.; Khanna, N. M.; Dhar, M. L. *J. Sci. Ind. Res.* **1962**, *21B*, 378.
(213) Rao, C. S.; Dave, M. P. *J. Indian Inst. Sci., B: Phys.* **1977**, *59*, 94.
(214) Elwahy, A. H. M.; Masaret, G. S. *J. Heterocycl. Chem.* **2004**, *41*, 711.
(215) Sarac-Arneri, R.; Mintas, M.; Pustet, N.; Mannschreck, A. *Monatsh. Chem.* **1994**, *125*, 457.
(216) Zacharie, B.; Lagraoui, M.; Dimarco, M.; Penney, C. L.; Gagnon, L. *J. Med. Chem.* **1999**, *42*, 2046.
(217) Ibrahim, Y. A.; Kadry, A. M.; Ibrahim, M. R.; Lisgarten, J. N.; Potter, B. S.; Palmer, R. A. *Tetrahedron* **1999**, *55*, 13457.
(218) Claude, S.; Lehn, J.-M.; Vigneron, J.-P. *Tetrahedron Lett.* **1989**, *30*, 941.
(219) Harb, N. M. S. E. *J. Serb. Chem. Soc.* **1999**, *64*, 663.
(220) Iddon, B.; Redhouse, A. D.; Yat, P. N. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1083.
(221) Kamila, S.; Zhang, H.; Zhu, D.; Biehl, E. R. *Heterocycles* **2005**, *65*, 579.
(222) Heravi, M. M.; Rajabzadeh, G.; Rahimizadeh, M.; Bakavoli, M.; Ghassemzadeh, M. *Synth. Commun.* **2001**, *31*, 2231.
(223) Verkoyen, C.; Rademacher, P. *Chem. Ber.* **1985**, *118*, 653.
(224) Goel, O. P.; Krolls, U. *Synthesis* **1987**, 162.
(225) Atalla, A. A.; El-Dean, A. M. K.; Harb, A. E. A. *Collect. Czech. Chem. C* **1991**, *56*, 916.
(226) Fisera, L.; Jaroskova, L.; Matejkova, I.; Heimgartner, H. *Heterocycles* **1995**, *40*, 271.
(227) El- Rahman, N. M. A. *Heterocycl. Commun.* **2002**, *8*, 465.
(228) Goswami, S.; Maity, A. C.; Das, N. K. *J. Sulfur Chem.* **2007**, *28*, 233.
(229) Kaboudin, B.; Elhamifar, D. *Synthesis* **2006**, 224.
(230) Nomura, R.; Nakano, T.; Yamada, Y.; Matsuda, H. *J. Org. Chem.* **1991**, *56*, 4076.
(231) Nomura, R.; Hasegawa, Y.; Ishimoto, M.; Toyosaki, T.; Matsuda, H. *J. Org. Chem.* **1992**, *57*, 7339.
(232) Nilov, D. B.; Kadushkin, A. V.; Solov'eva, N. P.; Granik, V. G. *Mendelev Commun.* **1995**, 67.
(233) Nilov, D. B.; Granik, V. G. *Mendelev Commun.* **2003**, 78.
(234) Nagarajan, K.; Shenoy, S. J. *Helv. Chim. Acta* **1985**, *68*, 900.

(235) Bryce, M. R.; Matthews, R. S. *J. Organomet. Chem.* **1987**, *325*, 153.
(236) Acheson, R. M.; Lines, C. T. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1913.
(237) Sugasawa, T.; Toyota, T.; Sasakura, K.; Hidaka, T. *Chem. Pharm. Bull.* **1971**, *19*, 1971.
(238) Bergman, J.; Stalhandske, C. *Tetrahedron Lett.* **1994**, *35*, 5279.
(239) Blade-Font, A. *An. Quim.* **1982**, *78*, 266.
(240) Aly, Y. L.; El-Barbary, A. A.; El-Shehawy, A. A. *Phosphorus Sulfur* **2004**, *179*, 185.
(241) Voβ, J. *Liebigs Ann. Chem.* **1971**, *746*, 92.
(242) Gatemood, E. S.; Johnson, T. B. *J. Am. Chem. Soc.* **1926**, *48*, 2900.
(243) Sugasawa, S.; Satoda, S.; Yanagisawa, J. *Yakugaku Zasshi* **1938**, *58*, 29.
(244) Hino, T.; Yamada, K.; Akaboshi, S. *Chem. Ind.—London* **1967**, 275.
(245) Hino, T.; Tsuneoka, K.; Nakagawa, M.; Akaboshi, S. *Chem. Pharm. Bull.* **1969**, *17*, 550.
(246) Ficken, G. E.; Kendall, J. D. *J. Chem. Soc.* **1960**, 1529.
(247) Wieland, T.; Weiberg, O.; Fischer, E.; Hörlein, G. *Liebigs Ann.* **1954**, *587*, 146.
(248) Alahmadi, A. A. *Phosphorus Sulfur* **1997**, *122*, 121.
(249) Koltai, E.; Lempert, K. *Tetrahedron* **1973**, *29*, 2795.
(250) Mykhaylychenko, S. S.; Bouillon, J.-P.; Shermolovich, Y. G. *J. Fluorine Chem.* **2009**, *130*, 878.
(251) Golovko, T. V.; Solov'eva, N. P.; Granik, V. G. *Mendelev Commun.* **1995**, 191.
(252) Capuano, L.; Bolz, G.; Burger, R.; Burkhardt, V.; Huch, V. *Liebigs Ann. Chem.* **1990**, 239.
(253) Szostak, M.; Aube, J. *Chem. Commun.* **2009**, 7122.
(254) Waisser, K.; Gregor, J.; Kubicova, L.; Klimesova, V.; Kunes, J.; Machacek, M.; Kaustova, J. *Eur. J. Med. Chem.* **2000**, *35*, 733.
(255) Ong, C. W.; Chen, C. M.; Wang, L. F. *Tetrahedron Lett.* **1998**, *39*, 9191.
(256) Milewska, M. J.; Gdaniec, M.; Maluszyn'ska, H.; Polonski, T. *Tetrahedron: Asymmetry* **1998**, *9*, 3011.
(257) Marinov, M.; Minchev, S.; Stoyanov, N.; Ivanova, G.; Spassova, M.; Enchev, V. *Croat. Chem. Acta* **2005**, *78*, 9.
(258) Batty, C. A.; Manthey, M. K.; Kirk, J.; Manthey, M.; Christopherson, R. I. *J. Heterocycl. Chem.* **1997**, *34*, 1355.
(259) Sayed, G. H.; Radwan, A.; Elhalim, M. S. A.; Khalil, M. *J. Chem. Soc., Pakistan* **1994**, *16*, 265.
(260) El Massry, A. M. *Phosphorus Sulfur* **2003**, *178*, 1143.
(261) Legrand, L.; Lozach, N. *Bull. Soc. Chim. Fr. II—Chem.* **1975**, 1415.
(262) Marriott, G. J.; Robinson, R. *J. Chem. Soc.* **1939**, 134.
(263) Drew, H. D. K.; Kelly, D. B. *J. Chem. Soc.* **1941**, 625.
(264) Reissert, A.; Holle, H. *Ber.* **1911**, *44*, 3033.
(265) Carrington, H. C. *J. Chem. Soc.* **1944**, 124.
(266) Bigoli, F.; Deplano, P.; Devillanova, F. A.; Ferraro, J. R.; Lippolis, V.; Lukes, P. J.; Mercuri, M. L.; Pellinqhelli, M. A.; Trogu, E. F.; Williams, J. M. *Inorg. Chem.* **1997**, *36*, 1218.
(267) Papadopoulos, E. P.; Bedrosian, S. B. *J. Org. Chem.* **1968**, *33*, 4551.
(268) Wynberg, H.; Metselaar, J. *Synth. Commun.* **1984**, *14*, 1.
(269) Omar, M. T.; El-Aasar, N. K.; Saied, K. F. *Synthesis* **2001**, 413.
(270) Khan, T.; McDouall, J. J. W.; McInnes, E. J. L.; Skabara, P. J.; Frére, P.; Coles, S. J.; Hursthouse, M. B. *J. Mater. Chem.* **2003**, *13*, 2490.
(271) Skabara, P. J.; Serebryakov, I. M.; Roberts, D. M.; Perepichka, I. F.; Coles, S. J.; Hursthouse, M. B. *J. Org. Chem.* **1999**, *64*, 6418.
(272) Berridge, T.; Serebryakov, I. M.; Skabara, P. J.; Orti, E.; Viruela, R.; Pou-AméRigo, R.; Coles, S. J.; Hursthouse, M. B. *J. Mater. Chem.* **2004**, *14*, 2822.
(273) Musmanni, S.; Ferraris, J. P. *J. Chem. Soc., Chem. Commun.* **1993**, 172.
(274) Kiebooms, R. H.; Adriaensens, P. J. A.; Vanderzande, D. J. M.; Gelan, I. M. J. V. *J. Org. Chem.* **1997**, *62*, 1473.
(275) Görlitzer, K.; Bömeke, M. *Arch. Pharm. (Weinheim)* **1992**, *325*, 9.
(276) Bondarev, S. L.; Knyukshto, V. N.; Tikhomirov, S. A.; Kalosha, I. I.; Bobrov, D. N.; Masalov, N. V.; Nevar, N. M.; Tyvorskii, V. I.; Kel'in, A. V.; Kulinkovich, O. G.; Dzilinski, K. *J. Appl. Spectrosc.* **2002**, *69*, 230.
(277) Hadj-Abo, F.; Bienz, S.; Hesse, M. *Tetrahedron* **1994**, *50*, 8665.
(278) Ozturk, T.; Ertas, E.; Mert, O. *Chem. Rev.* **2007**, *107*, 5210.
(279) Scheibye, S.; Shabana, R.; Lawesson, S.-O.; Romming, C. *Tetrahedron* **1982**, *38*, 993.
(280) Kiji, J.; Okano, T.; Chiyoda, T.; Bertini, F.; Audisio, G. *J. Anal. Appl. Pyrol.* **1997**, *40—41*, 331.
(281) Lin, S.-C.; Yang, F.-D.; Shiue, J.-S.; Yang, S.-M.; Fang, J.-M. *J. Org. Chem.* **1998**, *63*, 2909.
(282) Sastry, C. V. R.; Marwah, A. K.; Marwah, P.; Rao, G. S.; Shridhar, D. R. *Synthesis* **1987**, 1024.
(283) Marwah, P.; Marwah, A. K.; Rao, G. S. *Synth. Commun.* **1989**, *19*, 2809.
(284) Marwah, A. K.; Marwah, P.; Rao, G. S.; Trivedi, B. S. *Synth. Commun.* **1995**, *25*, 235.
(285) Morrison, B. J.; Musgrave, O. C. *Phosphorus Sulfur* **2002**, *177*, 2725.
(286) Burger, K.; Helmreich, B.; Jendrewski, O. *J. Fluorine Chem.* **1994**, *66*, 13.
(287) Lai, L.-L.; Reid, D. H.; Wang, S.-L.; Liao, F.-L. *Heteroat. Chem.* **1994**, *5*, 479.
(288) Ismailov, A. G.; Mamedov, E. I.; Ibragimov, V. G. *Zh. Org. Khim.* **1977**, *13*, 2612.
(289) Ponomareva, A. Y.; Beresnev, D. G.; Itsikson, N. A.; Chupakhin, O. N.; Rusinov, G. L. *Mendelev Commun.* **2006**, *1*, 16.
(290) Sakurai, A.; Goto, M. *Tetrahedron Lett.* **1968**, 2941.
(291) Goto, M.; Sakurai, A.; Ohta, K.; Yamakami, H. *Tetrahedron Lett.* **1967**, 4507.
(292) Taylor, E. J.; Sabb, A. L. *J. Org. Chem.* **1988**, *53*, 5839.
(293) Ibrahim, Y. A. *Chem. Ind.—London* **1978**, 585.
(294) Cullinane, N. M.; Davis, C. G.; Davies, G. I. *J. Chem. Soc.* **1936**, 1435.
(295) O'Brochta, J.; Lowy, A. *J. Am. Chem. Soc.* **1939**, *61*, 2765.
(296) Potts, K. T.; McKeough, D. *J. Am. Chem. Soc.* **1974**, *96*, 4276.
(297) Ertas, E.; Ozturk, T. *Tetrahedron Lett.* **2004**, *45*, 3405.
(298) Ozturk, T.; Ertas, E.; Mert, O. *Tetrahedron* **2005**, *61*, 11055.
(299) Fu, B.; Du, D.-M.; Xia, Q. *Synthesis* **2004**, 221.
(300) Aitken, R. A.; Armstrong, D. P.; Galt, R. H. B.; Mesher, S. T. E. *J. Chem. Soc., Perkin Trans. 1* **1997**, 935.
(301) Lu, S.-F.; Du, D.-M.; Zhang, S.-W.; Xu, J. *Tetrahedron: Asymmetry* **2004**, *15*, 3433.
(302) Miroshnichenko, Z. I.; Al'perovich, M. A. *J. Gen. Chem. USSR* **1962**, *32*, 602.
(303) Uchikawa, O.; Fukatsu, K.; Suno, M.; Aono, T.; Doi, T. *Chem. Pharm. Bull.* **1996**, *44*, 2070.
(304) Belyuga, A. G.; Brovarets, V. S.; Drach, B. S. *Russ. J. Gen. Chem.* **2004**, *74*, 1418.
(305) Moskalenko, Z. I.; Shumelyak, G. P. *Khim. Geterotsikl.* **1974**, 932.
(306) Sheldrake, P. W.; Matteucci, M.; McDonald, E. *Synlett* **2006**, 460.
(307) Slater, R. A. *Q. Rev. Sulfur Chem.* **1968**, *3*, 360.
(308) Lu, X.; Qi, Q.; Xiao, Y.; Li, N.; Fu, B. *Heterocycles* **2009**, *78*, 1031.
(309) Vingiello, F. A.; Rorer, M. P.; Ogliaruso, M. A. *Chem. Commun.* **1971**, 329.
(310) Charrier, J.-D.; Landreau, C.; Deniaud, D.; Reliquet, F.; Reliquet, A.; Meslin, J. C. *Tetrahedron* **2001**, *57*, 4195.
(311) Rafiqul, I. M.; Shimada, K.; Aoyagi, S.; Fujisawa, Y.; Takikawa, Y. *Heteroat. Chem.* **2004**, *15*, 208.
(312) Zur, Z.; Dykman, E. *Chem. Ind.—London* **1975**, 436.
(313) Singh, S. P.; Ranjana Indian, J. *Chemistry* **1993**, *32B*, 1130.
(314) El-Mariah, F.; Hosny, M.; Deeb, A. *Phosphorus Sulfur* **2006**, *181*, 809.
(315) Firoozi, F.; Javidnia, K.; Kamali, M.; Fooladi, A.; Foroumadi, A.; Shafiee, A. *J. Heterocycl. Chem.* **1995**, *32*, 123.
(316) Shafiee, A.; Naimi, E.; Mansobi, P.; Foroumadi, A.; Shekari, M. *J. Heterocycl. Chem.* **1995**, *32*, 1235.
(317) Tschierske, C.; Girdziunaite, D. *J. Prakt. Chem.* **1991**, *333*, 135.
(318) Polshettiwar, V.; Varma, R. S. *Tetrahedron Lett.* **2008**, *49*, 879.
(319) Korshin, E. E.; Sabirova, L. I.; Akhmadullin, A. G.; Levin, Y. A. *Russ. Chem. B* **1994**, *43*, 431.
(320) Machaj, M.; Pach, M.; Wolek, A.; Zabrzenska, A.; Ostrowska, K.; Kalinowska-Tluscik, J.; Oleksyn, B. *Monatsh. Chem.* **2007**, *138*, 1273.
(321) Moghadam, M.; Mohammadpoor-Baltork, I.; Mirkhani, V.; Tanqestaninejad, S.; Abdollahi Alibeik, M.; Yousefi, B. H.; Kargar, H. *Monatsh. Chem.* **2007**, *138*, 579.
(322) Bourdauducq, P.; Demarcq, M. C. *J. Chem. Soc., Dalton Trans.* **1987**, 1897.
(323) Hudson, H. R.; Pianka, M.; Powroznik, L.; Lynch, V. P. *J. Labelled Compd. Radiat.* **1980**, *17*, 341.
(324) Kalashnikov, V. P. *Zh. Obshch. Khim.* **1970**, *40*, 1954.
(325) Krolevets, A. A. *Zh. Obshch. Khim.* **1983**, *53*, 1679.
(326) Alfonsov, V. A.; Garifzyanova, G. G.; Dimukhametov, M. N.; Bredikhin, A. A. *Zh. Obshch. Khim.* **1998**, *68*, 517.
(327) Warshawsky, A.; Strikovsky, A. G.; Fernandez, F. M.; Jerabek, K. *Sep. Sci. Technol.* **2002**, *37*, 823.
(328) Zhang, X.-M.; Wang, D.-Q.; Chen, W.-Y. *Chin. J. Org. Chem.* **2007**, *27*, 623.
(329) Kumar, A.; Sharma, K. R.; Pandey, S. K. *Phosphorus Sulfur* **2007**, *182*, 1023.
(330) Kochansky, J. *J. Agric. Food Chem.* **2000**, *48*, 2826.
(331) Ohta, H.; Kita, M.; Kanno, H.; Kojima, M. *Inorg. Chim. Acta* **2000**, *311*, 75.
(332) Gumgum, B.; Biricik, N.; Baysal, A. *Phosphorus Sulfur* **2000**, *167*, 111.
(333) Jaeger, D. A.; Mendoza, A.; Apkarian, R. P. *Langmuir* **2006**, *22*, 1555.
(334) Yang, H.-C.; Lin, S.-M.; Liu, Y.-H.; Wang, Y.; Chen, M.-M.; Sheu, H.-s.; Tsou, D.-L.; Lin, C.-H.; Luh, T.-Y. *J. Organomet. Chem.* **2006**, *691*, 3196.

(335) Castle, R. N.; Shoup, R. R.; Adachi, K.; Aldous, D. L. *J. Heterocycl. Chem.* **1964**, *1*, 98.
(336) Blagoveshchenskii, V. S.; Vlasova, S. N. *Zh. Obshch. Khim.* **1971**, *41*, 1032.
(337) Scott, C. B.; Menefee, A.; Alford, D. O. *J. Org. Chem.* **1957**, *22*, 789.
(338) Castle, R. N.; Kaji, K. *Tetrahedron Lett.* **1962**, 393.
(339) Castle, R. N.; Kaji, K.; Gerhardt, G. A.; Guither, W. D.; Weber, C.; Malm, M. P.; Shoup, R. R.; Rhoads, W. D. *J. Heterocycl. Chem* **1966**, *3*, 79.
(340) Toda, F.; Tokunaga, Y. *Chem. Lett.* **1987**, 1299.
(341) Démarcq, M. C. *J. Chem. Soc., Dalton Trans.* **1988**, 2221.
(342) Larsen, L.; Rowe, D. J.; Garner, C. D.; Joule, J. A. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2317.
(343) Kaboudin, B.; Norouzi, H. *Synthesis* **2004**, 2035.
(344) Nivsarkar, M.; Gupta, A. K.; Kaushik, M. P. *Tetrahedron Lett.* **2004**, *45*, 6863.
(345) Keglevich, G.; Toke, L.; Lovasz, C.; Ujszaszy, K.; Szalontai, G. *Heteroat. Chem.* **1994**, *5*, 395.
(346) Balueva, A. S.; Dokuchaev, A. S.; Prokhorova, S. R.; Filippova, A. P.; Nikonov, G. N. *Russ. Chem. B* **1993**, *42*, 1381.
(347) Omelanczuk, J.; Mikolajczyk, M. *Tetrahedron* **1971**, *27*, 5587.
(348) Sanchez, J. M.; Hidalgo, M.; Valiente, M.; Salvado, V. *J. Polym. Sci. A1* **2000**, *38*, 269.
(349) Vasyanina, M. A.; Khairullin, V. K. *Zh. Obshch. Khim.* **1972**, *42*, 2644.
(350) Nifant'ev, E. E.; Shilov, I. V.; Blagoveshchenskii, V. S.; Komlev, I. V. *Zh. Obshch. Khim.* **1975**, *45*, 295.
(351) Still, I. W. J.; Hasan, S. K.; Turnbull, K. *Can. J. Chem.* **1978**, *56*, 1423.
(352) Still, I. W. J.; Hasan, S. K.; Turnbull, K. *Synthesis* **1977**, 468.
(353) Baechler, R. D.; Daley, S. K. *Tetrahedron Lett.* **1978**, 101.
(354) Still, I. W. J.; Hasan, S. K.; Turnbull, K. *Phosphorus Sulfur* **1979**, *6*, 293.
(355) Still, I. W. J.; Turnbull, K. *Synthesis* **1978**, 540.
(356) Kuipers, J. A. M.; Lammerink, B. H. M.; Still, I. W. J.; Zwanenburg, B. *Synthesis* **1981**, 295.
(357) Kong, Y. C.; Kim, K. *J. Heterocycl. Chem.* **1999**, *36*, 515.
(358) Oae, S.; Togo, H. *Tetrahedron Lett.* **1982**, *23*, 4701.
(359) Lee, W. W.; Martinez, A. P.; Blackford, R. W.; Bartuska, V. J.; Reist, E. J.; Goodman, L. *J. Med. Chem.* **1971**, *14*, 819.
(360) Montgomery, J. A.; Thomas, H. J. *J. Org. Chem.* **1963**, *28*, 2304.
(361) Bergmann, F.; Kalmus, A. *J. Org. Chem.* **1961**, *26*, 1660.
(362) Bergmann, F.; Kalmus, A. *Bull. Res. Counc. Isr.* **1961**, *10A*, 133.
(363) Bergmann, F.; Kalmus, A. *J. Chem. Soc.* **1962**, 860.
(364) Elion, G. B.; Burgi, E.; Hitchings, G. H. *J. Am. Chem. Soc.* **1952**, *74*, 411.
(365) Elion, G. B.; Mueller, S.; Hitchings, G. H. *J. Am. Chem. Soc.* **1959**, *81*, 3042.
(366) Youssif, S.; Mohamed, S. F. *Monatsh. Chem.* **2008**, *139*, 161.
(367) Nagarajan, A.; Meltsner, B. R.; Delia, T. J. *J. Heterocycl. Chem.* **1997**, *34*, 1581.
(368) Abdel-Gawad, S. M.; Ghorab, M. M.; El-Sharief, A. M. S.; El-Telbany, F. A.; Abdel-Alla, M. *Heteroat. Chem.* **2003**, *14*, 530.
(369) Lapucha, A. R. *Synthesis* **1987**, 256.
(370) Hamamura, E. H.; Sato, K.; Moffat, J. G. *J. Med. Chem.* **1972**, *15*, 1061.
(371) Mizuno, Y.; Ikehara, M.; Watanabe, K. A. *Chem. Pharm. Bull.* **1962**, *10*, 647.
(372) Levin, G.; Kalmus, A.; Bergmann, F. *J. Org. Chem.* **1960**, *25*, 1752.
(373) Beaman, A. G. *J. Am. Chem. Soc.* **1954**, *76*, 5633.
(374) Bergmann, F.; Kalmus, A. *Bull. Res. Counc. Isr.* **1962**, *11A*, 1.
(375) Neiman, Z. *Chem. Commun.* **1968**, 200.
(376) Stratmann, J. *Chem.—Ztg.* **1991**, *115*, 59.
(377) Hurst, D. T.; Atcha, S.; Marshall, K. L. *Aust. J. Chem.* **1991**, *44*, 129.
(378) Sharma, A. K.; Mahajan, M. P. *Heterocycles* **1995**, *40*, 787.
(379) Lolli, M.; Medana, C.; Romagnano, S.; Castoldi, F.; Pozzoli, S.; Vago, F.; Fanelli, R.; Airoldi, L. *J. Labelled Compd. Radiopharm.* **1998**, *41*, 243.
(380) Wooldridge, R. H.; Slack, R. *J. Chem. Soc.* **1962**, 1863.
(381) Fox, J. J.; Praag, D. V.; Wempen, I.; Doerr, I. L.; Cheang, L.; Knoll, J. E.; Eidinoff, M. L.; Bendich, A.; Brown, G. B. *J. Am. Chem. Soc.* **1959**, *81*, 178.
(382) Fox, J. J.; Wempen, I.; Hampton, A.; Doerr, I. L. *J. Am. Chem. Soc.* **1958**, *80*, 1669.
(383) Ueda, T.; Iida, Y.; Ikeda, K.; Mizuno, Y. *Chem. Pharm. Bull.* **1968**, *16*, 1788.
(384) Faerber, P.; Scheit, K.-H. *Chem. Ber.* **1970**, *103*, 1307.
(385) Vanasselt, R.; Hoogmartens, I.; Vanderzande, D.; Gelan, J.; Froehling, P. E.; Aussems, M.; Aagaard, O.; Schellekens, R. *Synth. Met.* **1995**, *74*, 65.
(386) Vanasselt, R.; Vanderzande, D.; Gelan, J.; Froehling, P. E.; Aagaard, O. *J. Polym. Sci. A1* **1996**, *34*, 1553.
(387) Vanasselt, R.; Vanderzande, D.; Gelan, J.; Froehling, P. E.; Aagaard, O. *Synth. Met.* **2000**, *110*, 25.
(388) Huskic, M.; Vanderzande, D.; Gelan, J. *Acta Chim. Slov.* **1998**, *45*, 389.
(389) Huskic, M.; Vanderzande, D.; Gelan, J. *Synth. Met.* **1999**, *99*, 143.
(390) Haagan, A. J.; Moratti, S. C.; Sage, I. C. *Synth. Met.* **2001**, *119*, 147.
(391) Polec, I.; Henckens, A.; Goris, L.; Nicolas, M.; Loi, M. A.; Adriaensens, P. J.; Lutsen, L.; Manca, J. V.; Vanderzande, D.; Sariciftci, N. S. *J. Polym. Sci. A1* **2003**, *41*, 1034.
(392) Paulussen, H.; Adriaensens, P.; Vanderzande, D.; Gelan, J. *Tetrahedron* **1996**, *52*, 11867.
(393) Prey, V.; Kondler, P. *Monatsh. Chem.* **1958**, *89*, 505.
(394) Agirbas, H.; Kahraman, K. *Phosphorus Sulfur* **1998**, *134/135*, 381.
(395) Baker, W.; Ollis, W. D.; Poole, V. D. *J. Chem. Soc.* **1950**, 3389.
(396) Sugimoto, K.; Ohta, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2921.
(397) Allen, C.; Boeyens, J. C. A.; Briggs, A. G.; Denner, L.; Markwell, A. J.; Reid, D. H.; Rose, B. J. *J. Chem. Soc., Chem. Commun.* **1987**, 967.
(398) Selzer, T.; Rappoport, Z. *J. Org. Chem.* **1996**, *61*, 7326.
(399) Kim, H. S.; Kim, E. A.; Jeong, G.; Park, Y. T.; Hong, Y. S.; Okamoto, Y.; Kurasawa, Y. *J. Heterocycl. Chem.* **1998**, *35*, 445.
(400) Buck, A. C.; Bartleson, J. D.; Lankelma, H. P. *J. Am. Chem. Soc.* **1948**, *70*, 744.
(401) Wise, G.; Lankelma, H. P. *J. Am. Chem. Soc.* **1952**, *74*, 529.
(402) Fluck, E.; Binder, H. *Z. Anorg. Allg. Chem.* **1968**, *359*, 102.
(403) Pinkas, J.; Verkade, J. G. *Heteroat. Chem.* **1998**, *9*, 115.
(404) Nomura, R.; Shimokawatoko, T.; Matsuda, H.; Baba, A. *J. Mater. Chem.* **1994**, *4*, 51.
(405) Murav'ev, I. V.; Fedorovich, I. S. *Zh. Obshch. Khim.* **1975**, *45*, 1746.
(406) Murav'ev, I. V.; Fedorovich, I. S. *Zh. Obshch. Khim.* **1976**, *46*, 1262.
(407) Nilov, D. B.; Kadushkin, A. V.; Solov'eva, N. P.; Sedov, A. L.; Granik, V. G. *Mendeleev Commun.* **1996**, 191.
(408) Kirby, G. W.; McGregor, W. M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 3175.
(409) Ozturk, T. *Tetrahedron Lett.* **1996**, *37*, 2821.
(410) Turksoy, F.; Wallis, J. D.; Tunca, U.; Ozturk, T. *Tetrahedron* **2003**, *59*, 8107.
(411) Ertas, E.; Ozturk, T. *Chem. Commun.* **2000**, 2093.
(412) Ozturk, T.; Turksoy, F.; Ertas, E. *Phosphorus Sulfur* **1999**, *153−154*, 417.
(413) Kaynak, F. B.; Ozbey, S.; Ozturk, T.; Ertas, E. *Acta Crystallogr.* **2001**, *C57*, 926.
(414) Kaynak, F. B.; Ozbey, S.; Ozturk, T.; Ertas, E. *Acta Crystallogr.* **2001**, *C57*, 319.
(415) Kaynak, F. B.; Ozbey, S.; Ozturk, T.; Ertas, E. *Acta Crystallogr.* **2001**, *C57*, 1125.
(416) Ertas, E.; Kaynak, F. B.; Ozbey, S.; Osken, I.; Ozturk, T. *Tetrahedron* **2008**, *64*, 10581.
(417) Celik, M. A.; Ozturk, T.; Yurtsever, M. Unpublished results.
(418) Bildirir, H.; Ertas, E.; Gundogan, A. S.; Osken, I.; Sahin, O.; Ozturk, T. Unpublished results.
(419) Davy, H. *J. Chem. Soc., Chem. Commun.* **1982**, 457.
(420) Yokoyama, M.; Hasegawa, Y.; Hatanaka, H.; Kawazoe, Y.; Imamoto, T. *Synthesis* **1984**, 827.
(421) Lajoie, G.; Lépine, F.; Maziak, L.; Belleau, B. *Tetrahedron Lett.* **1983**, *24*, 3815.
(422) Yousif, N. M.; Pedersen, U.; Yde, B.; Lawesson, S.-O. *Tetrahedron* **1984**, *40*, 2663.
(423) Fay, P.; Lankelma, H. P. *J. Am. Chem. Soc.* **1952**, *74*, 4933.
(424) Olah, G. A.; Berrier, A.; Ohannesian, L. *New J. Chem.* **1986**, *10*, 253.
(425) Foreman, M. R. S. J.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1996**, 3653.
(426) Foreman, M. R. S. J.; Novosad, J.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1997**, 1347.
(427) Foreman, M. R. S. J.; Slawin, A. M. Z.; Woollins, J. D. *Heteroat. Chem.* **1999**, *10*, 651.
(428) Kaleta, Z.; Makowski, B. T.; Soos, T.; Dembinski, R. *Org. Lett.* **2006**, *8*, 1625.
(429) Kaleta, Z.; Tarkanyi, G.; Gomory, A.; Kalman, F.; Nagy, T.; Soos, T. *Org. Lett.* **2006**, *8*, 1093.
(430) Poh, Z.; Flavel, B. S.; Shearer, C. J.; Shapter, J. G.; Ellis, A. V. *Mater. Lett.* **2009**, *63*, 757.
(431) Curran, S. A.; Cech, J.; Zhang, D.; Dewald, J. L.; Avadhanula, A.; Kandadai, M.; Roth, S. *J. Mater. Res.* **2006**, *21*, 1012.
(432) Yalpani, M. *Carbohydr. Polym.* **1992**, *19*, 35.
(433) Nizamov, I. S.; Almetkina, L. A.; Garifzyanova, G. G.; Batyeva, E. S.; Al'fonsov, V. A.; Pudovik, A. N. *Phosphorus Sulfur* **1993**, *83*, 191.
(434) Nizamov, I. S.; Al'metkina, L. A.; Garifzyanova, G. G.; Batyeva, E. S.; Al'fonsov, V. A. *Russ. Chem. B* **1993**, *42*, 1254.
(435) Nizamov, I. S.; Garifzyanova, G. G.; Batyeva, E. S. *Phosphorus Sulfur* **1994**, *88*, 39.
(436) Nizamov, I. S.; Garifzyanova, G. G.; Batyeva, E. S. *Russ. Chem. B* **1996**, *45*, 222.

(437) Nizamov, I. S.; Kuznetzov, V. A.; Batyeva, E. S.; Al'fonsov, V. A.; Pudovik, A. N. *Phosphorus Sulfur* **1993**, *79*, 179.

(438) Nizamov, I. S.; Popovich, A. E.; Batyeva, E. S.; Al'fonsov, V. A. *Heteroat. Chem.* **2000**, *11*, 276.

(439) Nizamov, I. S.; Popovich, A. E.; Batyeva, E. S.; Azancheev, N. M.; Al'fonsov, V. A. *Phosphorus Sulfur* **2000**, *158*, 167.

(440) Nizamov, I. S.; Bolshakova, O. V.; Almetkina, L. A.; Nizamov, I. D.; Sergeenko, G. G.; Frolova, L. V.; Krivolapov, D. B.; Batyeva, E. S.; Litvinov, I. A. *Heteroat. Chem.* **2006**, *17*, 670.

(441) Nizamov, I. S.; Kuznetzov, V. A.; Batyeva, E. S. *Phosphorus Sulfur* **1994**, *88*, 67.

(442) Nizamov, I. S.; Al'fonzov, V.; Batyeva, E. S. *Phosphorus Sulfur* **1996**, *109−110*, 453.

(443) Nizamov, I. S.; Matseevskii, A. V.; Batyeva, E. S.; Abalonin, B. E.; Vandyukova, I. I.; Shagidullin, R. R. *Heteroat. Chem.* **1997**, *8*, 329.

(444) Nizamov, I. S.; Sergeenko, G. G.; Batyeva, E. S.; Azancheev, N. M.; Al'fonsov, V. A. *Heteroat. Chem.* **2000**, *11*, 102.

(445) Nizamov, I. S.; Sergeenko, G. G.; Batyeva, E. S.; Azancheev, N. M.; Al'fonsov, V. A. *Phosphorus Sulfur* **2000**, *158*, 157.

(446) Nizamov, I. S.; Sergeenko, G. G.; Matseevskii, A. V.; Batyeva, E. S. *Phosphorus Sulfur* **1998**, *143*, 133.

(447) Nizamov, I. S.; Sergeenko, G. G.; Matseevskii, A. V.; Batyeva, E. S. *Phosphorus Sulfur* **1998**, *132*, 85.

(448) Ibrahim, N. M.; Yosef, H. A. A.; Yakout, E. M. A.; Mahran, M. R. H. *Phosphorus Sulfur* **2009**, *184*, 1124.

CR900243D