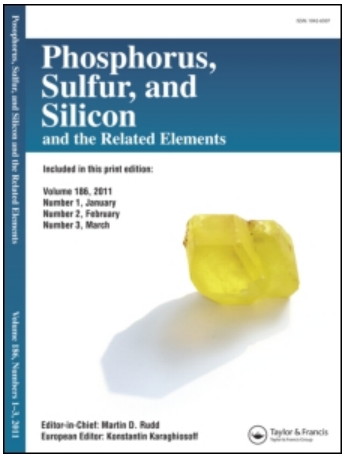

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NEW OXIDATION PROCEDURES BASED ON THE USE OF SELENIUM DERIVATIVES AS REAGENTS AND CATALYSTS*

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New procedures for the oxidation of selected groups of organic compounds based on the use of selenium derivatives as reagents and catalysts are described.

Keywords: oxidation, dichloroselenurane, diethyl selenite, selenides, selenoxides, sulfoxides, sulfones

INTRODUCTION

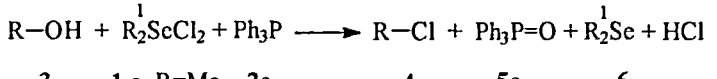
The very rapid development of synthetic methodology which has been observed in the last three decades is based mainly on the introduction of a great variety of heteroorganic derivatives as the reagents of choice.[1]

* Dedicated to Prof. Dr. Alfred Kolbe on the occasion of his 65th birthday

Due to the unique reactivity of these compounds it become possible to introduce and/or interconvert different functional groups even into the very complex chemical structures in chemo-, regio- and stereoselective manner under rather mild reaction conditions. Considering the synthetic utility of the particular functional groups interconversions it should be noted that the oxidative conversions are very often involved in contemporary organic synthesis.[2] During the past two decades it was shown unequivocally that the heteroorganic compounds containing the heteroatom-oxygen function besides the carbon-heteroatom linkages are the effective oxygen-transfer reagents which react with a variety of organic substrates under neutral conditions. Most of the synthetically useful oxidative procedures which have untill now been reported were based on the use of dimethyl sulfoxide[3] or selected group of selenoxides.[4] Continuing our interest in developing the heteroatom-mediated oxidative protocols,[5] we would like to describe below the new oxidation procedures based on the use of selenium derivatives as reagents and catalysts.

OXIDATIVE PROPERTIES OF THE SYSTEM: A DICHLOROSELNURANE / A HYDROXYLIC COMPONENT

Recently we have found[6] that the equimolar mixture of diphenyl(methyl)dichloroselenurane **1a** or **1b** and triphenylphosphine **2a** is able to convert very effectively a variety of alcohols **3** into the corresponding chlorides **4** in the reaction described by the general equation 1.

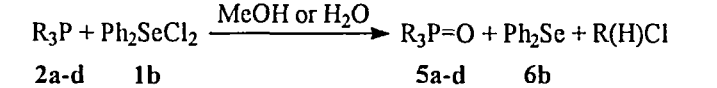


$$R{-}OH + {}^{1}R_2ScCl_2 + Ph_3P \longrightarrow R{-}Cl + Ph_3P{=}O + {}^{1}R_2Se + HCl$$

3 — 1 a, R=Me; b, R=Ph — 2a — 4 — 5a — 6 (1)

Considering this equation it can be easily noted that the conversion of alcohols **3** into the halides **4** is accompanied by the oxidation of triphenylphosphine **2a** to triphenylphosphine oxide **5a**. Taking into account this fact it is reasonable to expect that the dichloroselenuranes **1** in the presence of a hydroxylic component such as alcohol or water should be able to oxidise trivalent organophosphorus derivatives into the corresponding pentavalent, tetracoordinated analogues containing the phosphoryl group.

Indeed, it was found that the treatment of trivalent phosphorus compounds **2a-d** with diphenyldichloroselenurane **1b** in the presence of water or methanol at room temperature gave the corresponding phosphoryl derivatives **5** and diphenyl selenide **6b** as the reduction product with the simultaneous formation of hydrogen chloride or methyl chloride respectively (equation 2).



$$R_3P + Ph_2SeCl_2 \xrightarrow{MeOH \text{ or } H_2O} R_3P{=}O + Ph_2Se + R(H)Cl$$

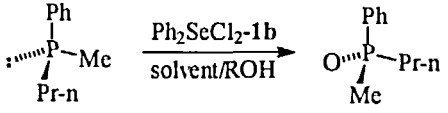
2a-d — **1b** — **5a-d** — **6b**

2, 5 **a**, R=Ph; **b**, R=Bu; **c**, R=Me_2N; **d**, R=EtO (2)

The reaction is quantitative and practically complete after a few minutes as evidenced by TLC. It should be pointed out that the oxidation of

triphenylphosphine **2a** by **1b** was much faster in comparison with the analogous oxidation by selenoxides.[5]

If the reaction of trivalent phosphorus compounds with diphenyldichloroselenurane in the presence of a hydroxylic component is stereospecific it would be a very useful method for the oxidation of chiral phosphines. With this in mind, we carried out the oxidation of optically active methylphenyl-n-propylphosphine **7** by **1b** under different reaction conditions (Scheme 1).



(+)-(S)-**7** (-)-(S)-**8**

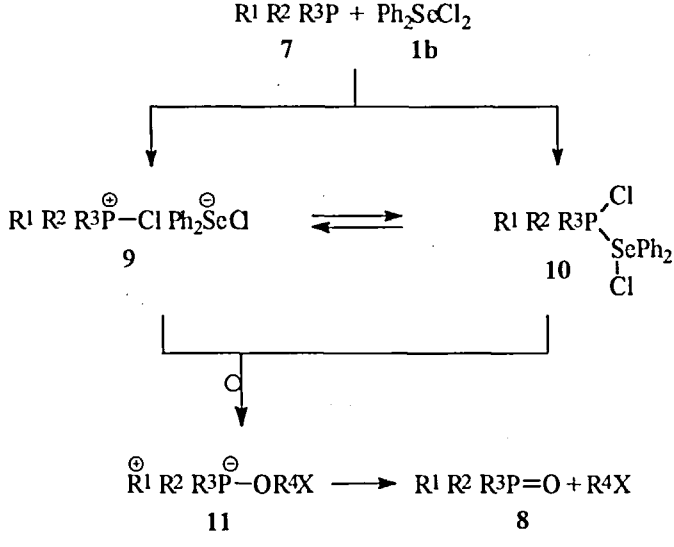
7					**8**	
$[\alpha]_{589}$	e.e.[%]	solvent	tem.[°C]	ROH	$[\alpha]_{589}$	e.e.[%]
+18.2	93.3	PhH	RT	t-Bu	0.00	0.00
+18.2	93.3	t-BuOH	RT	t-Bu	0.00	0.00
+18.2	93.3	CH_2Cl_2	RT	t-Bu	-1.00	
+18.2	93.3	MeOH	RT	Me	-7.08	42.00
+18.2	93.3	MeOH	-70	Me	-15.50	77.50
+18.2	93.3	MeOH/H_2O (8/2)	-70		-20.01	90.00
+18.2	93.3	MeOH/H_2O (8/2)	-20		-6.70	38.00

Scheme 1

The yields of the phosphine oxide **8** appear to be satisfactory from the preparative point of view (around 80%), however, stereoselectivity of the

conversion is not very high and strongly depends on the solvent used. Thus, when oxidation of 7 was carried out in benzene or methylene chloride with t-butyl alcohol the phosphine oxide **8** formed was almost racemic. When the oxidation was repeated in a water-methanol (2:8) mixture the phosphine oxide **8** formed with inversion of configuration at the phosphorus atom had ee 90%.

Inversion of configuration at the phosphorus observed in the oxidation of optically active phosphine 7 by diphenyldichloro-selenurane **1b** in the presence of water or alcohols may be easily explained by the mechanistic sequence presented in Scheme 2.



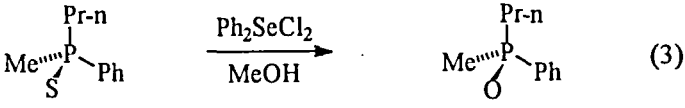
Scheme 2

It is reasonable to assume that the first step in the oxidative conversion of the phosphine **7** into the corresponding phosphine oxide **8** with the selenurane **1b** and alcohol (or water) constitutes the nucleophilic attack of the trivalent phosphorus atom of the substrate on the selenium or chloride atom of the selenurane **1b**, which results in the formation of the phosphonium salt **9** or phosphorane **10** as the first reactive intermediate. The salt **9** or phosphorane **10** may than react with an alcohol molecule (or water) to give the alkoxyphosphonium salt **11** with inversion of configuration at the stereogenic phosphorus atom. Decomposition of the phosphonium salt intermediate **11** gives the expected phosphine oxide **8** in which the absolute configuration at the phosphorus atom is inverted in comparison with the starting optically active phosphine **7**.

Very mild reaction conditions and high yields of the phosphoryl derivatives observed in the oxidation of trivalent organophosphorus derivatives with the dichloroselenurane/a hydroxylic component system prompted us to check the possibility of using this reagent for the oxidative conversion of pentavalent thio- and seleno-organophosphorus compounds into the corresponding phosphoryl derivatives.

As model reactions we selected the oxidation of optically active methylphenyl-n-propylphosphine sulfide **12** and methylphenyl-n-propylphosphine selenide **13** into the corresponding oxide **8** using diphenyldichloroselenurane/methanol as an oxidant. An analysis of the stereochemical course of these two reactions summarized in equations 3 and 4 clearly indicates that in both cases methylphenyl-n-propylphosphine oxide **8** is formed with predominant retention of configuration.

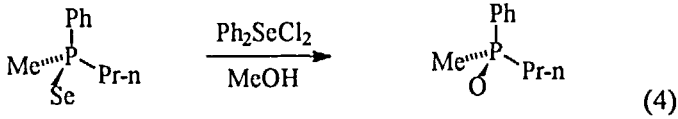
Unfortunately, the observed stereoselectivity is extremly low for the sulfide **12** (3.4%) and a little better for the selenide **13** (20.2%).



(3)

(-)-(S)-**12** (-)-(S)-**8**

$[\alpha]_{589}$ = - 18.73 (e.e.=84.2%) $[\alpha]_{589}$ = - 0.57 (e.e.=2.85%)

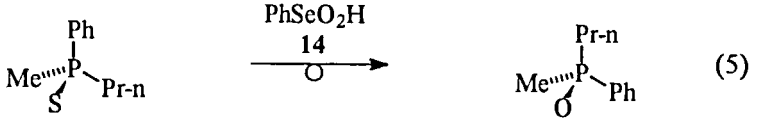


(4)

(+)-(R)-**13** (+)-(R)-**8**

$[\alpha]_{589}$ = +18.2 (e.e.=84%) $[\alpha]_{589}$ = +3.8 (e.e.=17%)

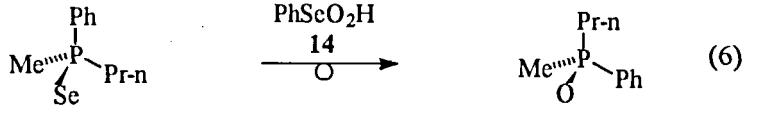
In this context it should be noted that the oxidation of the sulfide **12** and the selenide **13** into the corresponding oxide **8** is very highly stereoselective when phenylseleninic acid **14** is used as an oxidant (equation 5 and 6). It is of interest to note that the phosphine oxide **8** is formed in both reactions with almost full inversion of configuration at the stereogenic phosphorus atom.



(5)

(+)-(R)-12 (-)-(S)-8

$[\alpha]_{589}$ = +21.73 (e.e.=97.7%) $[\alpha]_{589}$ = - 17.98 (e.e.=92%



(6)

(+)-(R)-13 (-)-(S)-8

$[\alpha]_{589}$ = +18.2 (e.e.=84%) $[\alpha]_{589}$ = - 16.65 (e.e.=83%)

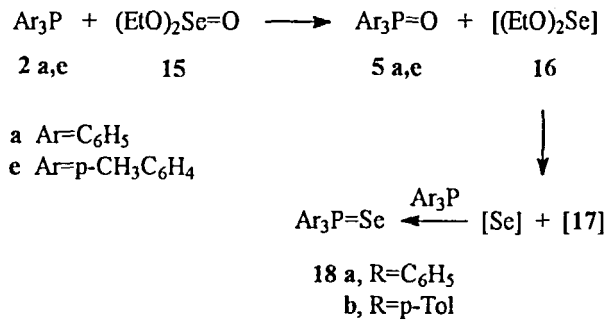
DIETHYL SELENITE AS A NEW OXIDANT

The search of the chemical literature indicates, that there is no single report on the application of the heteroorganic oxidants, containing the heteroatom-oxygen bond, in which the carbon-heteroatom linkages are replaced by the heteroatom-heteroatom bonds as efficient oxygen transfer reagents. Such change makes the oxygen atom of the heteroatom-oxygen function much less basic, thus lowering the oxidizing ability of the heteroorganic oxidant modified in this way. Here we would like to report the first example of the heteroorganic oxidant which after such modification still keeps oxidizing ability strong enough to make it a useful reagent in reactions of interest in organic and bioorganic chemistry. Namely, we have found, that diethyl selenite **15** which can be very easily prepared by the reaction of selenium dioxide with ethyl alcohol,[7] is able

to convert either thiophosphoryl compounds, selenophosphoryl derivatives or their trivalent phosphorus precursors into the corresponding phosphoryl compounds.

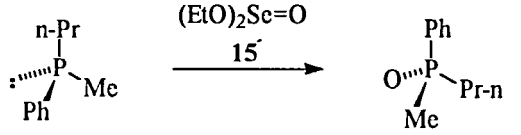
When triphenylphosphine **2a** was kept with equimolar amount of diethyl selenite **15** in a chloroform solution at room temperature the very slow formation of the corresponding triphenylphosphine oxide **5a** was observed (TLC and ^{31}P-NMR assay). When this reaction was repeated in refluxing benzene both substrates disappeared much faster and elemental selenium fell down from the solution. The ^{31}P-NMR and TLC analyses indicated that triphenylphosphine oxide **5a** and triphenylphosphine selenide **18** were simultaneously formed. They were isolated after column chromatography on silica gel in 80% and 20% yields respectively. When this experiment was carried out under the same conditions and after disapperance of the starting phosphine 50% molar excess of diethyl selenite was added to the reaction mixture triphenylphosphine oxide **5a** was isolated in 93% yield as a single reaction product. The analogous reaction course has been observed with tri-p-tolylphosphine **2e**.

The isolation, in the first experiment, of the oxide **5a** and selenide **18a** coupled with the simultaneous formation of elemental selenium indicates the partial decomposition of diethyl selenite **15** in the reaction mixture and that triphenylphosphine **2a** reacts firstly with the selenite **15** giving triphenylphosphine oxide **5a** and unstable diethyl selenoxylates **16**. Decomposition of the latter gives elemental selenium and an unknown organic structure **17**. Selenium formed in such a way converts triphenylphosphine **2a**, still present in the reaction medium, into the corresponding triphenylphosphine selenide **18**. Thus, the considered conversion can be described by Scheme 3.



Scheme 3

On the other hand, the reaction of methylphenyl-n-propylphosphine **7** with diethyl selenite **15** in a chloroform solution at room temperature was much faster and gave after 22 h the corresponding oxide **8** exclusively (^{31}P-NMR assay). Reaction of tri-n-butylphosphine **2b** under the same conditions was even much faster and gave after 7 h the corresponding oxide **5b** exclusively (^{31}P-NMR assay). To determine the stereochemistry of the oxidation process (+)-(R)-methylphenyl-n-propylphosphine 7 was used as a model compound. Starting from the phosphine 7, $[\alpha]_{589}$=+14.5 (toluene); e.e.=74.4%; and using 50% molar excess of diethyl selenite **15** (-)-(S)-methylphenyl-n-propylphosphine oxide **8**[8] having $[\alpha]_{589}$=-3.6 (methanol); e.e.=18%; was obtained. This result indicated that the considered oxidation is taking place with predominant inversion of configuration and low stereoselectivity (equation 7).



(7)

(+)-(R)-7 (-)-(S)-8

[α]589 = +14.5 (toluene); c.c. 74.4%

[α]589 = - 3.6 (methanol); e.e. 18%

When triarylphosphine sulfides **19** were mixed with equimolar amount of diethyl selenite **15,** the relatively (in comparison with the oxidation of triarylphosphine) rapid formation of triarylphosphine oxide **5** was observed. The reaction was complete within 72 h. The produced triarylphosphine oxides **5** were isolated after crystallization in 85% yield. In contrast to that, triphenylphosphine selenide **18a** reacted with diethyl selenite **15** at room temperature very rapidly and gave triphenylphosphine oxide **5a** in almost quantitative yield (Scheme 4).

$Ar_3P{=}X + (EtO)_2SeO \longrightarrow Ar_3P{=}O + X + [(EtO)_2Se]$

18, 19 a,b **15** **5 a,b** **16**

18 X=Se

19 X=S

a Ar=C_6H_5

b Ar=p-$CH_3C_6H_4$

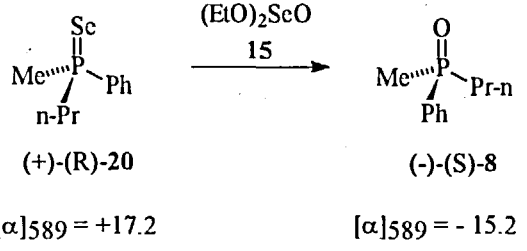
yield [%]

X=S; 85%

X=Se; 100%

Scheme 4

To determine the stereochemistry of the oxidation of selenophosphoryl derivatives (+)-(R)-methylphenyl-n-propyl selenide **20** was used as a substrate. The oxidation of the selenide (R)-**20**[9] with $[\alpha]_{589}$=+17.2 (methanol); e.e.=85% with equimolar amount of diethyl selenite **1** afforded the corresponding oxide (S)-**8**[8] with $[\alpha]_{589}$=-15.2 (methanol); e.e.=76%. These results clearly indicate that the oxidation process occurs with a net inversion of configuration and stereoselectivity approaching 90% (equation 8).



(+)-(R)-**20** (-)-(S)-**8** (8)

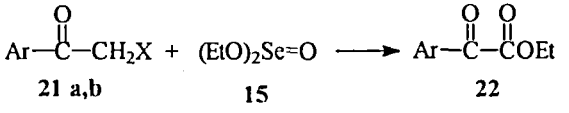
$[\alpha]_{589}$ = +17.2 $[\alpha]_{589}$ = - 15.2

It is hoped that this reagent by virtue of its convenient preparation and application can be deemed to be a valuable addition to those previously reported for the oxidation of selected organophosphorus compounds.

The ability of diethyl selenite **15** to oxidise the selected group of organophosphorus compounds prompted us to check if this compound can be used as an oxidant instead of dimethyl sulfoxide or some selenoxides for the oxidative conversion of the reactive halogenocarbons into the corresponding aldehydes (so called Kornblum oxidation).[10] The model reactions carried out using benzyl chloride and bromide as substrates have shown, however, that the expected conversion can not be

realized even after 24 h heating of both components in a sealed tube at temp. between 120-140°C.

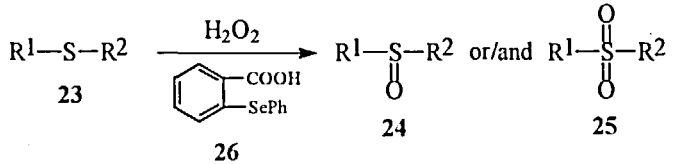
On the other hand, when a few phenacyl chlorides **21a** and bromides **21b** were used as substrates the appropriate ethyl esters of phenylglyoxalic acid **22** were isolated as single reaction products in yields approaching 70% (equation 9).



(9)

2-PHENYLSELENOBENZOIC ACID AS A CATALYST FOR THE OXIDATION OF SULFIDES WITH HYDROGEN PEROXIDE

A lot of interest has long been focused on the oxidation of sulfides to the corresponding sulfoxides[11] and sulfones.[12] Recently, intensive research has been carried out on catalytic oxidation processes based on the ecologically friendly and inexpensive hydrogen peroxide as an oxygen donor.[13] Here we would like to report that the oxidation of sulfides **23** to the corresponding sulfoxides **24** or sulfones **25** with hydrogen peroxide can be catalyzed effectively by 2-phenylseleno-benzoic acid **26** (equation 10).[14]



(10)

This oxidation procedure may be applied to dialkyl, alkyl aryl and diaryl sulfides **23**. The data summarized in Tables 1 and 2 indicate that the reaction course depends on the reaction time and after 4 h only sulfoxides **24** are formed quantitatively. When the reaction time was extended above 100 h the corresponding sulfones **25** were isolated as a single reaction product in yields higher than 80%.

Table 1. Oxidation of sulfides, R^1-S-R^2 **23** to sulfoxides, $R^1S(O)R^2$ **24** with hydrogen peroxide/o-phenylseleno-benzoic acid **26**.

R^1	R^2	Time [h]	H_2O_2(eq)[a]	Yield [%]	
				^{1}H-NMR	Purified
Me	Bu	4.0	4	100	85
Me	Ph	5.0	4	100	87
Et	Ph	2.5	4	100	100
Pr	Ph	5.0	4	100	93
Me	p-Tol	4.0	4	100	91
n-Bu	p-Tol	5.5	4	100	90
Me	CH_2Ph	4.0	4	100	90

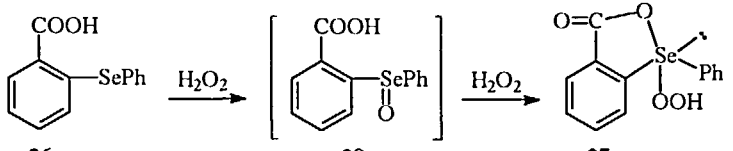
[a] all reactions were carried out using 0.1 equivalent of a catalyst in methanol

Table 2. Oxidation of sulfides, R^1SR^2 **23**, to sulfones, $R^1SO_2R^2$ **25** with hydrogen peroxide/o-phenylselenobenzoic acid **26**[a].

R^1	R^2	Time [h]	Yield [%]
Me	n-Pr	144	84
Me	n-Bu	144	86
Me	Ph	120	96
Et	Ph	144	94
n-Bu	Ph	144	83
$n\text{-}C_{12}H_{25}$	Ph	144	91
n-Bu	p-Tol	120	94
i-Pr	$p\text{-MeO-}C_6H_4$	100	92

[a] all reactions were carried out using 0.1 equivalent of a catalyst in methanol.

As far as the nature of the reagent concerns, it seems that the sulfurane structure **27** my be considered as the true oxidising agent. It can be formed *in situ* from hydrogen peroxide and 2-phenylseleninylbenzoic acid **28**, which in turn is generated by the oxidation of the selenide **26** with hydrogen peroxide.



26 **28** **27**

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