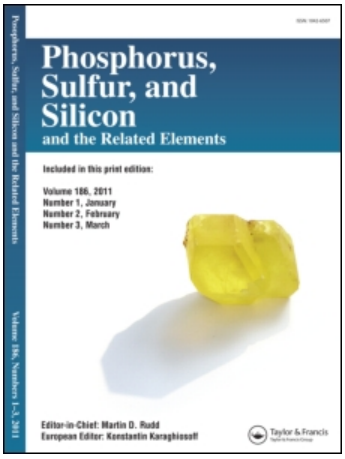

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ORGANOSELENIUM COMPOUNDS AS THE OXIDANTS AND OXIDATION CATALYSTS

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Useful oxidative conversions of halomethylarenes and aromatic alcohols into aldehydes, oxidation of aldehydes, ketones and their azomethine derivatives into carboxy esters, phenols, nitriles and carboxylic acids, epoxidation of low reactive vinylbenzenes, ketone regeneration from ketazines, and selective oxidation of sulfides have been elaborated. Selenium compounds such as selenium(IV) dioxide, selenoxides, seleninic and peroxyseleninic acids, diselenides, benzisoselenazolones and their analogs used as oxidants or as catalyst for hydrogen peroxide oxidation are presented and their synthesis is briefly discussed.

Key words: ebselen, hydrogen peroxide, selenium compounds, oxidation

Use of selenium reagents by organic chemists although longstanding received a new impetus during last thirty years. The oxidation reactions with selenium(IV) oxide, areneselenenic acids and anhydrides, selenoxides, selenuranes and diphenylselenium bis(trifluoroacetate) have been successively examined[1,2]. In our laboratory has been found that halomethylarenes and aromatic alcohols are efficiently oxidized to alde-

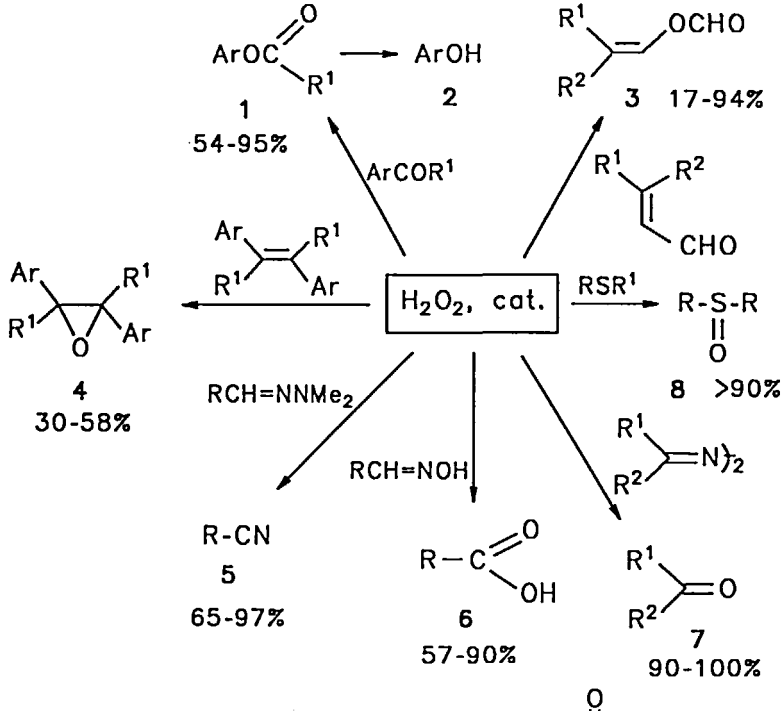
hydes with dimethylselenoxide. For oxidation of halomethylarenes potassium benzeneselenite has also been used[3].

It has also been known that selenium compounds are able to act as oxygen-transfer catalysts. Particularly they have been used as catalysts for hydrogen peroxide oxidation of various organic compounds. This process is attractive because hydrogen peroxide used as stoichiometric oxidant is cheap, ecologically neutral and useful for large scale synthesis[4].

The reactions studied in our laboratory are presented in Scheme 1. We found that the aromatic aldehydes and aryl methyl ketones having electron-donating substituents in the aromatic ring or having polycondensed aromatic ring system were efficiently oxidized to phenol esters (**1**). Among different selenium compounds tested as the catalysts, the most effective were 2-nitrobenzeneseleninic acid, 2,4-dinitrobenzeneseleninic acid and related to them aryldiselenides. The formates or acetates formed were hydrolysed in one-pot procedure. As a result, a convenient and cheap method for synthesis of phenols (**2**) from aromatic aldehydes was elaborated[5]. Hydrogen peroxide oxidation of α,β-unsaturated aldehydes, catalysed by the same organoselenium compounds led to the vinyl formates (**3**) accompanied by the compounds being the result of their subsequent reaction[6].

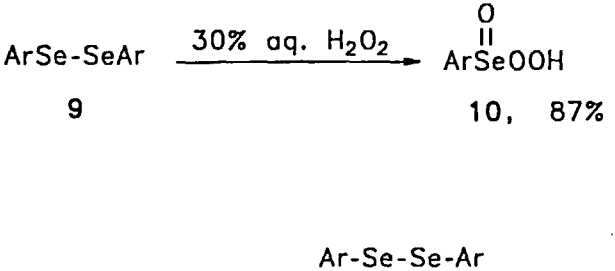
Selenium(IV) oxide, aryl diselenides and areneseleninic acids were also used as the catalysts for hydrogen peroxide oxidation of styrene and its analogs, and 2,4-dinitrophenyl diselenide was found as the most efficient catalyst. Although these resistant towards epoxidation olefines produced epoxides (**4**) in the yields not exceeded 58% unreacted substrate migh be recyclized and the reaction has a practical value[7]. Moreover, we found

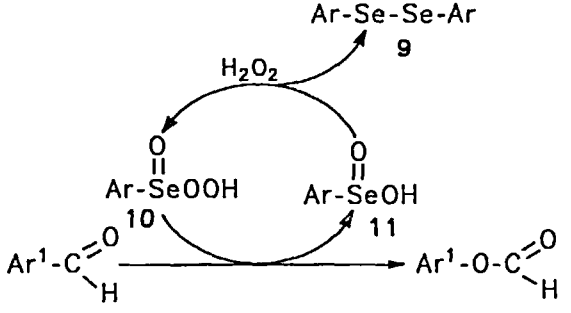
that selenium dioxide, or better 2-nitrobenzeneseleninic acid, were good catalysts for oxidative conversion of aromatic N,N-dimethylhydrazones into nitriles (**5**)[8]. With the same catalysts, aldoximes or their ethers oxidized in the presence of primary or secondary alcohol used as a solvent, yielded corresponding carboxy esters (**6**)[9]. Most recently, numerous organoselenium compounds were tested as catalysts of oxidation of aromatic aldazines and ketazines to parent carbonyl compounds (**7**)[10], and sulfides to sulfoxides (**8**)[10].



SCHEME 1

It has been a question, what is a role of the selenium catalyst. One could suppose that although stoichiometric oxidant was hydrogen peroxide, the active oxygen donor was peroxyseleninic acid formed in situ. Since peroxyseleninic acids were unknown compounds we synthesized two of them - benzeneperoxyseleninic acid (**10**, Ar=Ph) and 2,4-dinitrobenzeneperoxyseleninic acid (**10**, Ar=2,4-$(NO_2)_2C_6H_3$) by oxidation of corresponding diselenides (**9**) with hydrogen peroxide. When 2,4-dinitrobenzeneperoxyseleninic acid was used as stoichiometric oxidant for oxidation of aromatic aldehydes, aromatic ketones and for α,β-unsaturated aldehydes, the results were the same as while hydrogen peroxide, in the presence of 2,4-dinitrobenzeneseleninic acid as catalyst, was used as the oxidant[11].

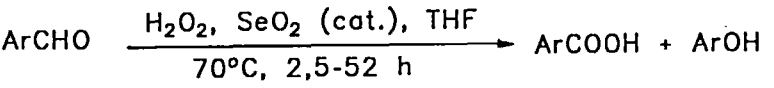




SCHEME 2

These results make the evidence that hydrogen peroxide oxidation of the organic substrate in the presence of areneseleninic acid (**11**) or aryldiselenide (**9**) proceeded via areneperoxyseleninic acid (**10**) being an active oxygen donor as it is shown in Scheme 2. Thus organoselenium catalyst plays a role of oxygen-transfer agent.

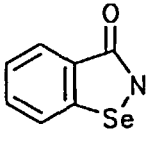
Nine years ago J.-K.Choi and coworkers reported a method for hydrogen peroxide oxidation of the aromatic and aliphatic aldehydes to carboxylic acids[12]. The catalyst was benzeneseleninic acid. Recently we reinvestigated this reaction using various selenium compounds (listed in the Scheme 3).



Ar = H, 4-$CH_3C_6H_4$, 4-ClC_6H_4, 2,6-$Cl_2C_6H_3$, 2,4-$Cl_2C_6H_3$, 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 3-$CH_3OC_6H_4$, α-naphthyl 86-97% 0-4%

Ar = 2-$CH_3OC_6H_4$, 4-$CH_3OC_6H_4$ 44-46% 41-49%

Catalysts tested: 2-$PhNHCOC_6H_4Se)_2$, 2-$PhNHSO_2C_6H_4Se)_2$ PhSe(O)OH, $PhSe)_2$, SeO_2



R=Ph (ebselen), COPh, SO_2Ph, 2-pyridyl, 4-$NO_2C_6H_4$, 4-$CH_3OC_6H_4$, 4-ClC_6H_4, 4-$CH(CH_3)COOH$, 4-$CH(CH_3)COOCH_3$

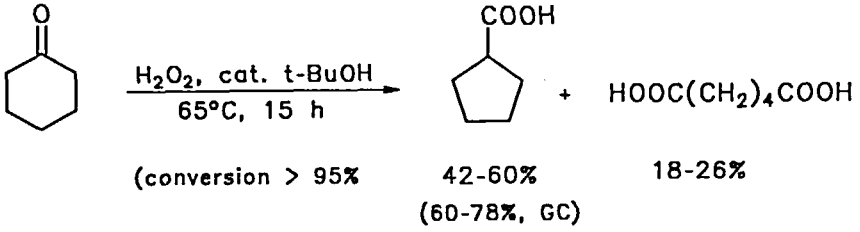
SCHEME 3

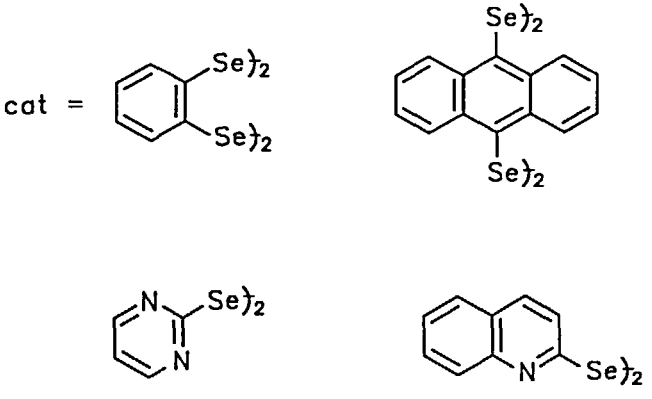
It has been found that the most eficient catalyst was easily available and cheap selenium(IV) oxide[13]. Aromatic aldehydes, such as benzaldehyde, p-tolylaldehyde and these having electron-withdrawing substituents produced arenecarboxylic acids in the preparative yields above 86%. Even when electron-efficient o-methoxy- or p-methoxybenzaldehyde was oxidized, substantial amounts of acids were obtained contrary to results reported earlier by Syper and Guzman where phenols were formed exclusively[5,14].

It has been known that cycloalkanones oxidized with hydrogen peroxide in the presence of selenium(IV) oxide underwent Favorski - type rearrangement leading to cycloalkanecarboxylic acids having one carbon atom less in the cycloalkane ring[15]. Although yields of the acids were low and did not exceeded 37%, the method was used for the synthesis of some natural products[16].

Recently we oxidized cycloalkanones with hydrogen peroxide in the presence of more than thirty various selenium compounds. Among them diselenides presented in Scheme 4 were the most active catalysts. For example, cyclohexanone oxidized in the presence of bis(2-quinolyl) diselenide or polymeric anthracenyl diselenide was converted almost quantitatively into carboxylic acids and the competitive Baeyer-Villiger lactone formation was not observed. The major product of the reaction was cyclopentanecarboxylic acid formed in 78% yield (based on GC analysis). It was accompanied by the minor amounts of adipic acid.

The preparative yield of cyclopentanecarboxylic acid was 60%. The elaborated method seems to be of practical value since price of cyclopentanecarboxylic acid is above four time higher than that of cyclohexanone.

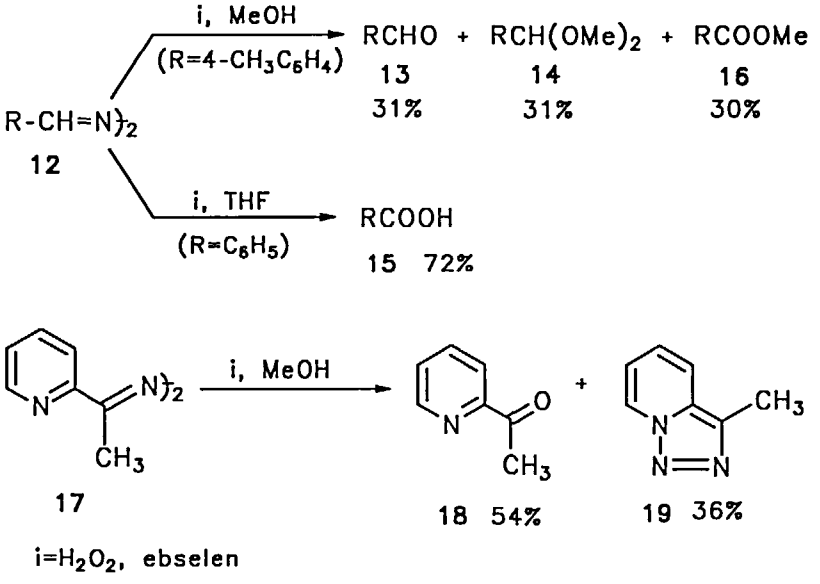




SCHEME 4

Some of the oxidation reactions were catalysed by 2-phenylbenziso-selenazolone named ebselen and bis[(2-carbamoylphenyl)phenyl] dise-lenide. These compounds have been known as antiinflammatory agents interacting with cellular oxygen species in the way similar to action of enzyme glutation peroxidase[18]. Although earlier had been reported that they do not catalyse oxidation of thiols to disulfides[19] we found them as good catalysts for the oxidation of the sulfides to sulfoxides, N,N-di-methylhydrazones to nitriles and ketazines to ketones[10].

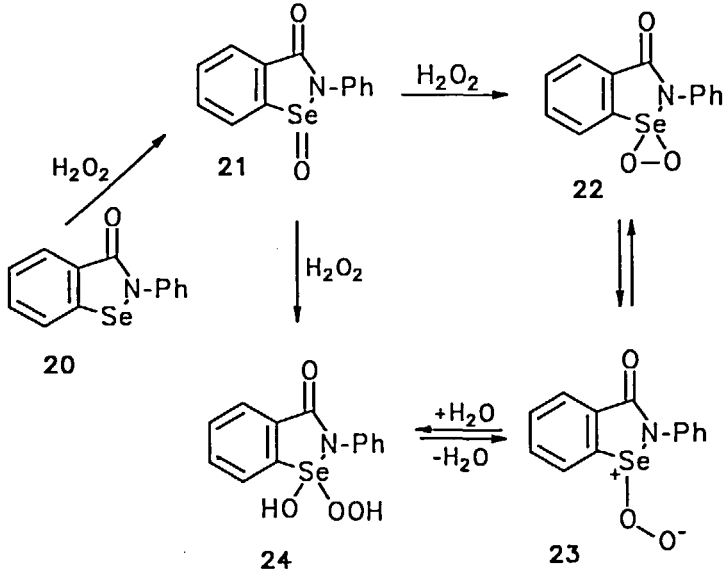
In the reaction presented in Scheme 5, aldazines (**12**) produced parent aldehydes (**13**), their acetals (**14**), and carboxylic acids (**16**) or their esters (**15**) depending on the solvent - tetrahydrofuran or methanol. Unexpected result was found when azine derived from 2-acetylpyridine (**17**) was oxidized. The regenerated ketone (**18**) was accompanied by substantial amount of triazole (**19**) being the product of its oxidative cyclization[20].



SCHEME 5

Although the use of ebselen as oxygen transfer catalysts lead to excellent results, mechanism of its action remains unknown. Formation of peroxyseleninic acid as an active intermediate seems to be doubtful since ebselen (**20**) oxidized with hydrogen peroxide produced its oxide (**21**) and no cleavage of selenium-nitrogen bond has been observed. It seems to

be possible that the active oxygen donor is in situ formed selenodioxirane (**22**) or its dipolar form (**23**) or adduct (**24**) having hydroperoxide group on the selenium atom, presented in Scheme 6.

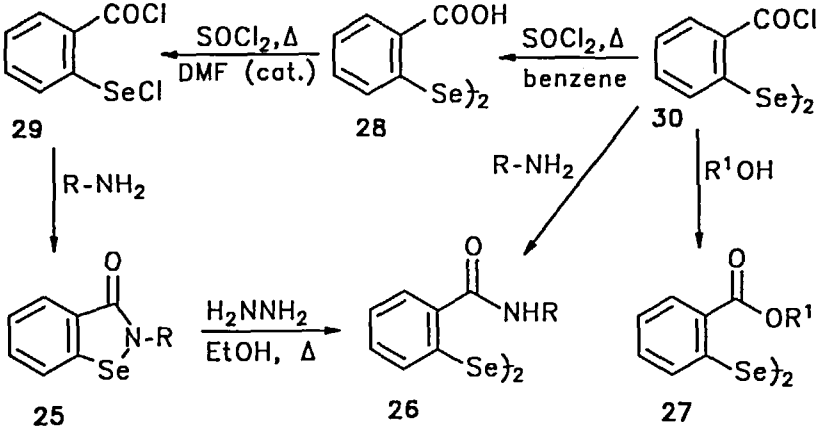


SCHEME 6

The important problem which had to be resolved was synthesis of these organoselenium compounds which were used or designed as new oxidants or oxygen transfer catalyst. Dimethyl selenoxide and benzeneseleninic acid potassium salt, were synthesized in the way reported in ref[21]. Aryl diselenides were obtained on three ways. First of them is based on the reaction of lithium diselenide (generated in situ from elemental selenium and lithium) with activated haloarenes such as for example 2-nitrophenyl chloride[22]. Second way involves reaction of arenediazonium

salts with sodium diselenide[23]. Some of the diselenides were also obtained by the recently reported method based on the reaction of aryllithium compounds with elemental selenium[24].

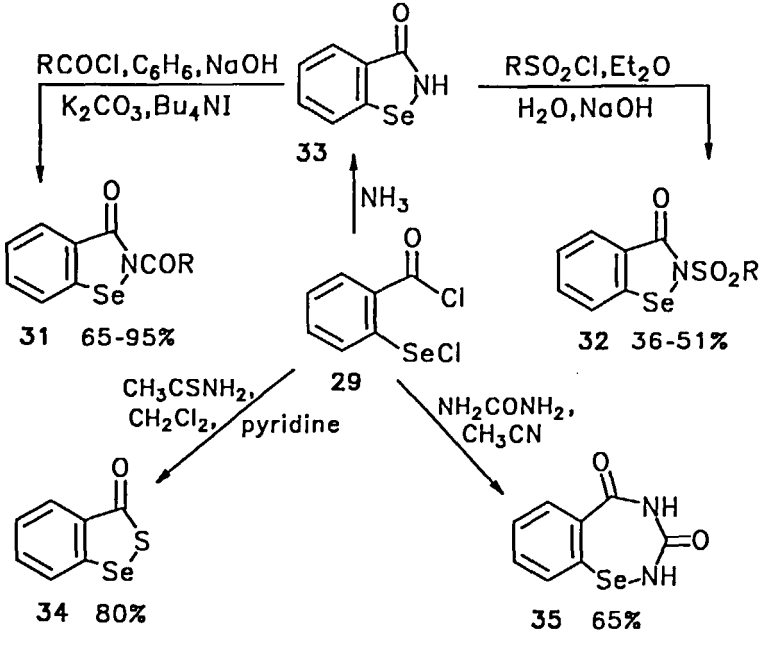
Benzisoselenazolones, such as ebselen and its analogs (**25**) and related to them diselenides having carbonyl group (**26**) or alkoxycarbonyl group (**27**) were synthesized from bis(2-carboxyphenyl) diselenide (**28**) via acid chloride **29** or **30** in the way presented in the Scheme 7. Most of them, having chiral substituents, were obtained as pure enantiomers[25]. We tested them as the catalysts for hydrogen peroxide oxidation of unsymmetrical sulfides into sulfoxides. Although appreciable catalytical activity and high chemoselectivity of the reaction have been achieved no steric effects of the oxidation were observed.



R= $CH(R^2)COOR^3$ where R^2= H, alkyl, aryl; R^3= H, CH_3, C_2H_5
R^1= (+) and (-) menthyl, (-) bornyl, quininyl

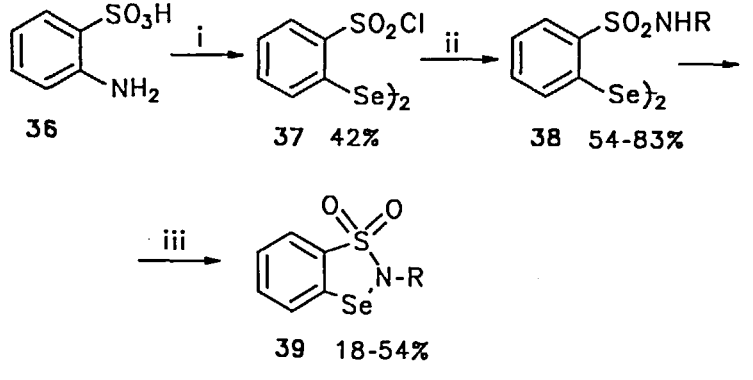
SCHEME 7

Other selenium compounds - cyclic N-selenocarbonyl- and N-seleno-sulfonylamides (**31** and **32**) were synthesized from 2-chloroseleno-benzoyl chloride (**29**) on the two alternative ways. First of them was based on its reaction with carbamides or sulfonamides. The second one, presented in Scheme 8, involved its reaction with ammonia and then acylation or sulfonylation of formed benzisoselenazolone (**33**). Treating of dichloride **29** with thioacetamide yielded 2,1-benzothiaselenaphenone (**34**) while its reaction with urea led to the compound **35** having new seven-membered ring with one selenium and two nitrogen atoms[26].



SCHEME 8

Most recently we synthesized diselenides (**38**) with sulfamoyl group in the ortho position of benzene ring. Their oxidative cyclization led to the new unique compounds benz-2,3-azaselenathiophene 1,1-dioxides (**39**) having selenium sulfur and nitrogen atoms in five-membered ring according to the reactions presented in Scheme 9[27]. The crucial steps involved transformation of aniline-2-sulfonic acid (**36**) into bis[(2-chlorosulphonyl)phenyl] diselenide (**37**) being the starting substrate for synthesis of diselenides (**38**) and cyclic sulfonamides (**39**)[28]. Study on the activity of the compounds **43** and **44** as the catalysts for hydrogen peroxide oxidation of various organic substrates are in progress.



i = 1.Na_2CO_3,H_2O; 2.$NaNO_2$,H_2SO_4, -10°C;
3.KSeCN,H_2O_2, 0°C; 4.PCl_5, 150°C
ii = RNH_2 (excess), C_2H_5OH, CH_3CN, 20°C
iii = $(PhC(O)O)_2$, benzene, reflux
R = CH_3, C_3H_7, $(CH_3)_3C$, C_6H_5, 4-$CH_3C_6H_4$

SCHEME 9

Acknowledgment

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