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BENZENEPEROXYSELENINIC ACIDS - SYNTHESIS AND PROPERTIES

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Abstract: Benzeneperoxyseleninic acid (3) and its analogs, 2-nitro and 2,4-dinitrobenzeneperoxyseleninic acids (10, 11), were obtained by oxidation of corresponding arylseleninic acids or diaryldiselenides with hydrogen peroxide. Their chemical properties were studied and rearrangement of 3 to benzeneselenic acid 7 was found as an useful method for preparation of this compound. In was also shown that peroxyseleninic acid 10 can be used as an efficient oxidant in the Baeyer-Villiger transformation of the formyl group into formyloxy one.

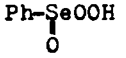
The chemistry of organoselenium compounds is actually extensively developing owing to their usefulness in organic synthesis[1-3]. Among various reactions, several ones involving oxidation or hydroxylation of organic compounds with hydrogen peroxide activated with selenium dioxide, organoseleninic acids or their precursors were elaborated. Thus, alkenes were hydroxylated to diols[4-7] or oxidized to epoxides[8-11], cyclic ketones were oxidized to lactones[12,13] and sulfides were converted into sulfoxides[11]. The methods based on oxidation of organic substrates with activated hydrogen peroxide seem to be substantially cheaper and more convenient than those using carboxylic peroxyacids.

In our laboratory was found that hydrogen peroxide activated with 2-nitro- or 2,4-dinitrobenzeneseleninic acid is a convenient reagent for transformation of aromatic aldehydes and ketones into phenols[14,15]. It seems possible that activation of hydrogen peroxide involves fast formation of peroxyseleninic acid 2 by the reversible reaction [4,8,10-13].

$$\underset{\underset{\displaystyle O}{\|}}{RSeOH} + H_2O_2 \rightleftharpoons \underset{\underset{\displaystyle O}{\|}}{RSeOOH} + H_2O$$

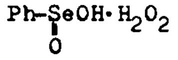
1 2

Nevertheless, peroxyseleninic acids remained unknown and the reaction of acid 1 mentioned above could not be confirmed, t-butyl ester of benzeneperoxyseleninic acid was reported only[16]. Thus, the aim of our work was to obtain benzeneperoxyseleninic acids and to study their properties as oxidants. We observed that benzeneseleninic acid treated with 30% aq. H_2O_2 at 0° or 20° C gave white solid sparingly soluble in water and organic solvents. It decomposed when dried in vacuo but could be dried without decomposition in thin layer in the air at darkness at room temperature. Heated in capillary, it decomposed explosively at 52-53° C. One could suppose that compound obtained was benzeneperoxyseleninic acid (3), although Bloodworth and Lapham[16] reported similar compound as additive complex 4.



$$Ph{-}\underset{\overset{\|}{O}}{Se}OOH$$

3

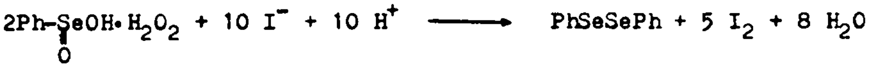


$$Ph{-}\underset{\overset{\|}{O}}{Se}OH\cdot H_2O_2$$

4

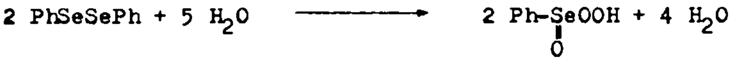
These two molecules differ in contents of active oxygen (19.5% for 3 and 17.8% for 4). It was determined iodometrically according to equations:

$$2Ph{-}\underset{\overset{\|}{O}}{Se}OOH + 10\ I^- + 10\ H^+ \longrightarrow PhSeSePh + 5\ I_2 + 6\ H_2O$$



$$2Ph{-}\underset{\overset{\|}{O}}{Se}OH\cdot H_2O_2 + 10\ I^- + 10\ H^+ \longrightarrow PhSeSePh + 5\ I_2 + 8\ H_2O$$

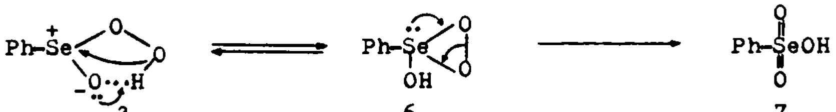
The analyses of various samples gave above 18.8% of active oxygen, thus the structure 3 seems to be confirmed. Full elemental analysis could not be done since fast decomposition of the compound. The formation of peroxy acid 3 instead of additive complex 4 corresponds with known fact of fast displacement of the OH group with ^{18}OH at Se(IV)[17,18], and higher nucleophilicity of OOH^- than OH^-. Our further experiments showed that benzeneperoxyseleninic acid (3) could be obtained in 85% yield in more convenient way, through oxidation of diphenyldiselenide (5) with excess of 30% aq. H_2O_2 at 0-5°C



$$2\ PhSeSePh + 5\ H_2O \longrightarrow 2\ Ph{-}\underset{\overset{\|}{O}}{Se}OOH + 4\ H_2O$$

5 3

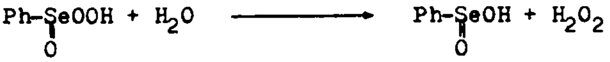
Benzeneperoxyseleninic acid (3), unlike other peroxy acids, underwent intramolecular rearrangement into benzeneselenic acid (7) in organic solvents (acetonitrile, chloroform, methylene chloride). This reaction proceeds also when 3 is allowed to stand on the air for 3-4 days. It seems possible that the reaction mechanism involves formation of tautomer 6 which rearranges intramolecularly into 7. The tendency of Se(IV) to form four single bonds was reported for the other examples[19-22].



3 6 7

We found that this rearrangement, carried out in acetonitrile gave pure 7 in 65% yield and is convenient method for synthesis of this compound, better than that reported in the literature[23-25].

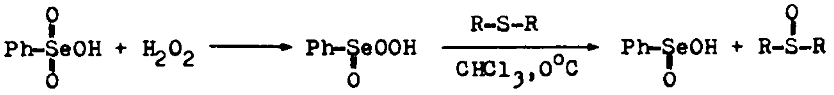
Acid 3 treated with water decomposed to benzeneseleninic acid 8 and hydrogen peroxide in the reaction reversed to formation of 3 from 8.



$$Ph{-}\underset{\overset{\|}{O}}{Se}OOH + H_2O \longrightarrow Ph{-}\underset{\overset{\|}{O}}{Se}OH + H_2O_2$$

3 8

Our further experiments revealed surprisingly that benzeneselenic acid (7) treated with hydrogen peroxide gave benzeneperoxyseleninic acid (3) instead of expected benzeneperoxyselenic acid.



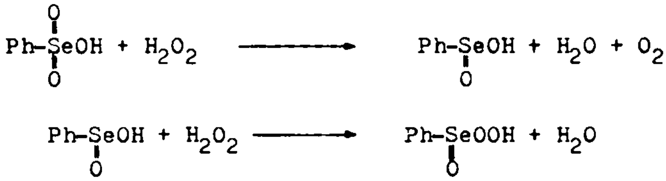
$$Ph{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Se}}OH + H_2O_2 \longrightarrow Ph{-}\underset{\overset{\|}{O}}{Se}OOH \xrightarrow[CHCl_3,0^{\circ}C]{R{-}S{-}R} Ph{-}\underset{\overset{\|}{O}}{Se}OH + R{-}\overset{\overset{O}{\|}}{S}{-}R$$

7 3 8 9

R = Et or Ph

The product 3 obtained by this way was compared with the original sample obtained from benzeneseleninic acid. Both of them decomposed at the same temperature and content of active oxygen was above 19.0%. Moreover, both samples were readily reduced with ethyl and phenyl sulfide to benzeneseleninic acid (8) in 78-91% yield. Independent experiments revealed that neither 7 nor 8 were reduced with these sulfides, thus confirming that selenium valency remained unchanged and that peroxy acid 3 formed from 7 contains tetravalent, not hexavalent selenium. Rearrangement of benzeneselenic acid (7) to benzeneperoxyseleninic acid (3) is a convenient way of its preparation in high purity (substantially higher than that obtained from 5) since the reaction mixture is homogeneous and product crystallizes along with the reaction progress.

Despite of facts mentioned above, the mechanism of the transformation of 7 into 3 remains difficult to explain. Possible sequence of reactions:

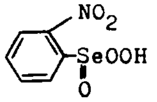


$$\mathrm{Ph\text{-}Se(O)_2OH + H_2O_2 \longrightarrow Ph\text{-}Se(O)OH + H_2O + O_2}$$

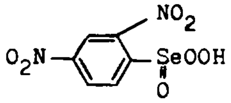
$$\mathrm{Ph\text{-}Se(O)OH + H_2O_2 \longrightarrow Ph\text{-}Se(O)OOH + H_2O}$$

could not be taken into account since emission of oxygen was not observed during the reaction.

In the way similar to synthesis of 3, 2-nitrobenzeneperoxyseleninic acid (10) and 2,4-dinitrobenzeneperoxyseleninic acid (11) were obtained from corresponding diselenides (11 also from 2,4-dinitrobenzeneseleninic acid) oxidized with 90% hydrogen peroxide.



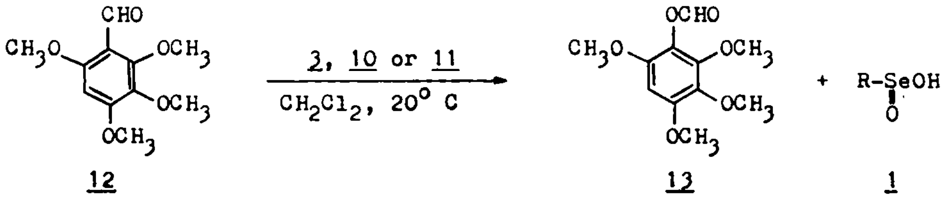
10



11

Both these peroxy acids were more stable than 3, could be dried in vacuo, and decomposed at higher temperatures. Heated with water or during long exposure to air, they gave corresponding benzeneseleninic acids but did not undergo transformation into benzeneselenic acids - analogs of 7.

Other investigations of benzeneperoxyseleninic acids 3, 10 and 11 involved testing of their usefulness as oxidants in the Baeyer-Villiger oxidation of aromatic aldehydes and ketones as well as α,β-unsaturated aldehydes. The results obtained for the oxidation of 2,3,4,6-tetramethoxybenzaldehyde to formate 13 with benzeneperoxyseleninic acids (Table 1) shown 2-nitrobenzeneperoxyseleninic acid 10 as the most useful reagent. The peroxy acid 3 was useless for this purpose since its rearrangement to benzeneselenic acid 7 competed with oxidation of 12.



$\mathrm{R = C_6H_5,\ 2\text{-}NO_2\text{-}C_6H_4,\ 2,4\text{-}(NO_2)_2C_6H_3}$

Table 1. Results of oxidative conversion of aldehyde 12 into formate 13 with benzeneperoxyseleninic acids

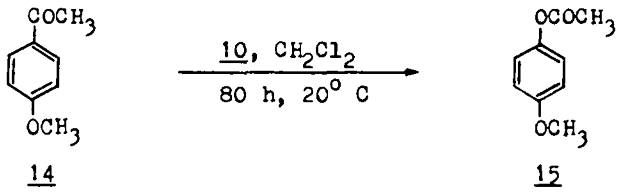
Oxidant	Reaction time, h	Yield of 13[a], %	Yield of 1, %
3	16	48[b]	58[c]
10	1.5	94	88
11	16	86	98

[a] Yield based on aldehyde 12

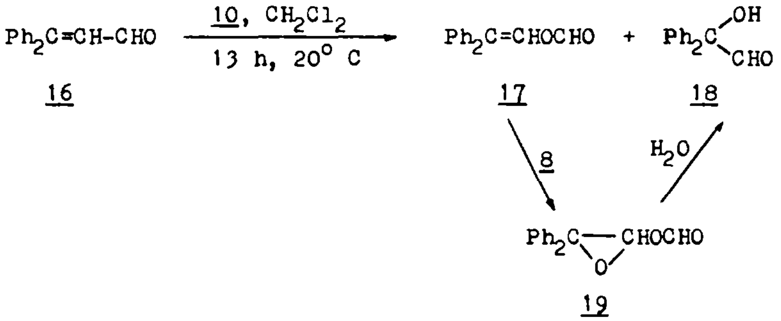
[b] Substrate 12 was recovered in 44% yield

[c] Yield of benzeneselenic acid 7 formed

A transformation of aromatic ketone 14 into acetate 15 with peroxy acid 10 was less effective. Product 15 was isolated from the reaction mixture in 44% yield only and substantial amount of substrate (47%) remained unreacted.



Moreover peroxy acid 10 oxidized smoothly α,β-unsaturated aldehydes. It was shown that 3,3-diphenylpropenal 16 underwent oxidative transformation to formate 17 (92%) accompanied by 2,2-diphenyl-2-hydroxyacetaldehyde 18 being a minor product (5%).



It seems probable that formation of 18 proceeds via epoxide 19 like to other epoxides reported in literature[26]. It is noteworthy that this reaction is significantly more efficient in comparison with oxidation of 16 with m-chloroperoxybenzoic acid. In the case when equimolar amounts of the reagents were used, we obtained 17 (28%), 18 (5%) and unreacted substrate 16 (62%). Even when the two-fold excess of m-chloroperoxybenzoic acid was used, only insignificantly improvement in the yield of the main product 17 (33%) was observed while 18 was isolated in 19% yield and unreacted 16 in 44% yield.

EXPERIMENTAL SECTION

All m.ps and b.ps are uncorrected. ^{1}H-NMR spectra were recorded on a Tesla 100 MHz apparatus. The IR spectra were obtained on a Perkin-Elmer 621 spectrophotometer. Selenium was determined according to the literature[27]. Active oxygen was determined as follows: Into 150 ml conical flask containing accurately weighed amount of peroxy acid (60 - 100 mg), dry ice (ca. 10 g), glacial acetic acid (25 ml), 6N-hydrochloric acid (2.5 ml) and sodium iodide (2 g) were added and the mixture was heated on the water bath until all sodium iodide dissolved. Dry ice (ca. 5 g) was added to the solution and it was titrated with 0.05 N sodium thiosulfate solution under magnetical stirring until a pale straw colour occurred, then starch indicator solution (2 ml) was added and the titration was continued until the colour of the starch-iodine complex was discharged.

Synthesis of benzeneperoxyseleninic acid (3) from benzeneseleninic acid 8. To a vigorously stirred 30% aq. H_2O_2 (10 ml) on the ice-salt bath, acid 8 (2.0g 10.6 mmol) was added portionwise during 3 min. Then reaction was continued for 2 h. The product 3 was filtered off, washed with cold water and dried on the air in the darkness at room temperature for 24 h, then at 5° C for 20 h affording white powder (1.0 g, 49%), m.p. 52° C (with explosion). Active oxygen - calcd. 19.50% found 19.00%. Caution! The compound may be explosive.

Synthesis of benzeneperoxyseleninic acid (3) from diphenyldiselenide (5). To a vigorously stirred 30% aq. H_2O_2 (15 ml) on the ice-salt bath, diselenide 5 (3.0 g, 6.4 mmol) was added portionwise during 15 min. Then reaction was continued at 0° C for 2 h. Product 3 was filtered off, washed with cold water, cold dichloromethane and dried in thin layer in the darkness at room temperature for 24 h, then at 5° C for 15 h to afford white powder (3.45 g, 87%), m.p. 52° C (with explosion), active oxygen found 18.80%.

Synthesis of 2-nitrobenzeneperoxyseleninic acid (10). To bis(2-nitrophenyl)diselenide (3.0 g, 7.5 mmol), 90% H_2O_2 (10 ml) in one portion was added at 0° C during vigorous stirring and the reaction was continued at room temperature for 27 h. After the reaction finished, the mixture was cooled to 5° C, product 10 was filtered off, washed with cold water and dried in vacuo (15-20 mm) over KOH to furnish 3.53 g of pale yellow powder, m.p.72° C (with puffing). The analysis gave 15.75% of active oxygen (calcd. 15.95%), Se 31.20% (calcd. 31.56%).

Synthesis of 2,4-dinitrobenzeneperoxyseleninic acid (11). To 2,4-dinitrobenzeneseleninic acid (3.0 g, 10.1 mmol), 90% H_2O_2 (10 ml) was added during vigorous stirring at room temperature. The reaction was continued for 76 h and product 11 was isolated in the similar way as 10. It was pale yellow powder (3.1 g, 98%) m.p. 92°C (with puffing). Analysis gave 13.35% of active oxygen (calcd. 13.55%), Se 26.25% (calcd. 26.75%). The same compound 11 was obtained in a 95% yield (2.85 g) from bis(2,4-dinitrophenyl)diselenide (2.5 g, 5.0 mmol) in a similar way as 10.

Rearrangement of benzeneperoxyseleninic acid (3). The vigorously stirred suspension of peroxy acid 3 (1.2 g, 5.8 mmol) in acetonitrile (10 ml) was slowly heated to 80° C during 1 h. Then, the reaction mixture was cooled, benzeneselenic acid 7 formed was filtered off, washed with cold acetonitrile and dried in vacuo. Recrystallized from acetonitrile, it afforded 0.8 g (66%) of pure 7 as white needles, m.p. 144° C, lit.[23] m.p. 142° C.

Reaction of benzeneperoxyseleninic acid 3 with water. The vigorously stirred suspension of peroxy acid 3 (1.5 g, 7.3 mmol) in water (10 ml) was maintained at room temperature for 1 h and slowly heated up to 40° C for additional 1 h. After the reaction finished, the reaction mixture was cooled to 5° C, benzeneseleninic acid 8 formed was filtered off, washed with cold water and dried in vacuo furnishing 1.13 g (82%) of pure 8 as white powder, m.p. 125° C, lit.[25] m.p. 124-125° C.

Reaction of benzeneperoxybenzeneseleninic acid with phenyl sulfide. To a ice-cooled stirred suspension of peroxy acid 3 (0.8 g, 3.9 mmol) in chloroform (3 ml), the solution of phenylsulfide (1.5 g, 8 mmol) in chloroform (3 ml) was added dropwise for 10 min and the reaction was continued for additional 1 h. The reaction mixture worked up in the same manner as described above to yielded 0.55 g (75%) of pure benzeneseleninic acid 8. The filtrate left over removing of crude 8 was concentrated in vacuo and column chromatography on silica gel with ethyl ether - light petroleum (1:1) as an eluent was employed to isolation of phenyl sulfoxide (0.74 g, 98% based on the amount of peroxy acid 3 used), m.p. 70° C, lit.[28] m.p. 70.5° C.

Oxidation of aldehyde 12. The mixture of aldehyde 12 (1.1 g, 4.85 mmol), methylene chloride (15 ml) and peroxy acid 10 (1.3 g, 5.20 mmol) was vigorously stirred at room temperature for 1.5 h. After the reaction finished, solid was filtered off, washed with methylene chloride and dried. 1.07 g (88%) of pure 2-nitrobenzeneseleninic acid, m.p. 184-186° C (decomp.) lit.[29] m.p. 184° C were obtained. The filtrate was washed twice with water, dried over sodium sulfate, concentrated in vacuo to a small volume and column chromatography on silica gel with ethyl ether - light petroleum (1:1) was employed to isolation of 1.0 g (94%) of 2,3,4,6-tetramethoxyphenol formate 13. Colourless flakes from hexane - isopropyl ether, m.p. 88° C; IR (KBr) $\nu_{C=O}$ 1742 cm^{-1}; ^1H-NMR ($CDCl_3$), δ (TMS), ppm 3.88, 3.90, 3.92 and 3.93 (ts, 12H, OCH_3); 6.33 (s, 1H, Ar-H); 8.22 (s, 1H, OCHO). Found: C, 54.31% ; H, 6.01%. Calcd. for $C_{11}H_{14}O_3$: C, 54,54% ; H, 5.82%. The reaction of aldehyde 12 with peroxy acids 3 and 11 were carried out in the same manner.

Oxidation of ketone 14. The mixture of ketone 14 (0.75 g, 5.0 mmol), chloroform (20 ml) and peroxy acid 10 (2.0 g, 8.0 mmol) was vigorously stirred at room temperature for 80 h. The reaction mixture was worked up in the same way as described for oxidation of 12. They were obtained: 2-nitrobenzeneseleninic acid (1.7 g, 90%), 4-methoxyphenol acetate 15 (0.37 g, 44%), m.p. 32° C lit.[30] m.p. 32° C, and unreacted substrate 14 (0.35 g, 47%).

Oxidation of aldehyde 16. The mixture of solution of 16 (1.0 g, 4.8 mmol) in methylene chloride (15 ml) and peroxy acid 10 (1.3 g, 5.20 mmol) was vigorously stirred at room temperature for 13 h. The reaction mixture was worked up in the same way as described for oxidation of 12. The eluent for chromatography was ethyl ether - light petroleum and 0.98 g (92%) of 2,2-diphenylvinyl formate 17 was obtained; b.p. 120° C/ 0.03 mm, IR $\nu_{C=O}$ 1728 cm^{-1}, ^1H-NMR (CCl_4), δ (HMDSO), ppm 6.70- 6.75 (m, 10H, Ar-H); 7.94 (s, 1H, C<u>H</u>OCHO); 8.06 (s, 1H, CHOC<u>H</u>O), found C, 80.83% ; H, 5.12% ; calcd. for $C_{15}H_{12}O_2$: C, 80.35% ; H, 5.36%.
The latter fractions afforded 0.05 g (5%) of 2,2-diphenyl-2-hydroxyacetaldehyde 18, m.p. 56° C (hexane), lit.[31] m.p. 52-53° C ; phenylhydrazone m.p. 130° C, lit.[32] m.p. 132° C, semicarbazone, m.p. 242° C, lit.[33] m.p. 243° C. The reaction of aldehyde 16 with m-chloroperoxybenzoic acid was carried out in the same manner as described above.

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