

Preparation of the First Organoselenium Peroxide, *t*-Butyl Benzeneperoxyseleminate

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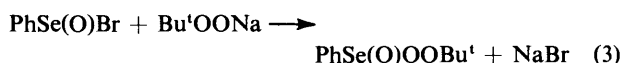
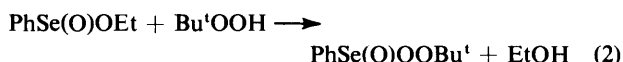
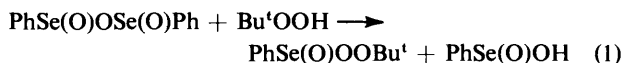
t-Butyl benzeneperoxyseleminate, PhSe(O)OOBu^t , has been prepared by the reaction of *t*-butyl hydroperoxide with PhSe(O)OSe(O)Ph or PhSe(O)OEt , and of sodium *t*-butyl peroxide with PhSe(O)Br . Formation of the less stable analogues *p*- $\text{MeC}_6\text{H}_4\text{Se(O)OOBu}^t$ and BuSe(O)OOBu^t from *t*-butyl hydroperoxide and the corresponding seleninyl anhydrides has been confirmed by ^{13}C n.m.r. spectroscopy.

Several organosulphur peroxides are known¹ but, as far as we are aware, no compound with a peroxide group linked to selenium has been satisfactorily characterised. Seleninyl peroxy-esters of the type RSe(O)OOBu^t have been postulated as intermediates in the catalytic decomposition of *t*-butyl hydroperoxide by a dialkyl diselenide and by alkane- and arene-seleninic anhydrides and acids in benzene at 75 °C.² More recently it has been suggested that areneperoxyseleminic acids, ArSe(O)OOH , may be involved in the epoxidation of alkenes by hydrogen peroxide in the presence of stoichiometric³ or catalytic⁴ amounts of areneseleminic acids. We now report the preparation, by three routes, of *t*-butyl benzeneperoxyseleminate, PhSe(O)OOBu^t , and the identification, by ^{13}C n.m.r. spectroscopy, of the less stable analogues *t*-butyl toluene-*p*-peroxyseleminate, 4- $\text{MeC}_6\text{H}_4\text{Se(O)OOBu}^t$, and *t*-butyl butane-1-peroxyseleminate, BuSe(O)OOBu^t .

Results and Discussion

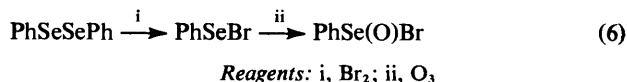
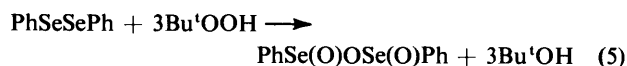
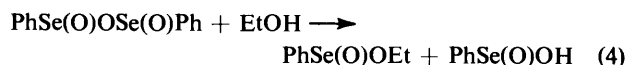
On the basis of the results of Woodbridge's work,² we anticipated that *t*-butyl peroxyseleminates, RSe(O)OOBu^t , would exhibit thermal instability at or below 75 °C. A ready susceptibility towards hydrolysis was also anticipated in view of the behaviour of the ester analogue ethyl benzeneseleminate.⁵ In devising preparative routes to the desired peroxides, we therefore concentrated on reactions expected to proceed to completion at or below room temperature and to afford readily removable by-products.

Of the four approaches we investigated, three [equations (1)–(3)] proved successful in affording *t*-butyl benzeneperoxyseleminate; no reaction occurred between benzeneseleminic acid, *t*-butyl hydroperoxide, and dicyclohexyl carbodi-imide.

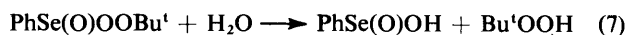


The samples of the organoselenium peroxide obtained by methods (1) and (3) contained traces of benzeneseleminic acid and sodium bromide, respectively. This arose because although these by-products were removed by filtration, each has a slight solubility in the solvent used. The product obtained by method (2), on the other hand, was both spectroscopically and analytically pure, the volatile by-product, ethanol, being removed under reduced pressure along with

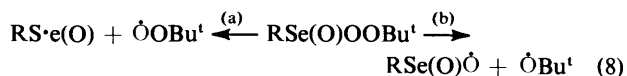
the solvent. The transesterification route [equation (2)] is thus the method of choice even though it involves the prior conversion of the anhydride, used in method (1), into the hydrolytically sensitive seleninyl ester [equation (4)] which must be isolated by vacuum sublimation.⁵ The anhydride was itself obtained from diphenyl diselenide by oxidation with *t*-butyl hydroperoxide⁵ [equation (5)], and the benzeneseleminyl bromide used in method (3) was also derived from the commercially available diselenide [equation (6)].



The identity of *t*-butyl benzeneperoxyseleminate was established by a combination of elemental analysis, spectroscopic techniques, and chemical reaction. The ^1H n.m.r. spectrum showed the signals expected for *t*-butyl and phenyl protons, but no absorption corresponding to Bu^tOOH ; the absence of an OH group was confirmed by the i.r. spectrum. Most diagnostic was the ^{13}C n.m.r. spectrum, which showed *t*-butyl peaks at δ_c 83.62 and 26.35 p.p.m., compared with signals at δ_c 81.00 and 25.87 p.p.m. for *t*-butyl hydroperoxide. The compound gave a strongly positive peroxide test with acidified iron(II) thiocyanate,⁶ and was rapidly hydrolysed by atmospheric moisture to afford *t*-butyl hydroperoxide and benzeneseleminic acid [equation (7)].



The organoselenium peroxide decomposed when heated, either as the neat liquid or in refluxing benzene, and afforded an unidentified white solid together with diphenyl diselenide (t.l.c. and m.s.) among the products. This confirms the thermal instability of such peroxyseleminates postulated by Woodbridge,² who suggested that the peroxy-ester would undergo homolysis to give seleninyl radicals [equation (8a)] and/or seleninyloxy radicals [equation (8b)].



In an attempt to detect such selenium-containing radicals, we photolysed a solution of *t*-butyl benzeneperoxyseleminate

in cyclopropane in the cavity of an e.s.r. spectrometer. However, the only species observed was the *t*-butylperoxy radical, which probably arises by hydrogen abstraction from *t*-butyl hydroperoxide present as the result of adventitious hydrolysis.

In a preliminary attempt to prepare other organoselenium peroxides we examined the following three seleninyl anhydride-alkyl hydroperoxide mixtures: PhSe(O)OSe(O)Ph-cyclo-C₆H₁₁OOH, *p*-MeC₆H₄Se(O)OSe(O)C₆H₄Me-*p*-Bu^tOOH, and BuSe(O)OSe(O)Bu-Bu^tOOH. A reaction took place in each case, but the product derived from cyclohexyl hydroperoxide decomposed before any satisfactory characterisation could be achieved. Formation of the *t*-butyl peroxyesters of toluene-*p*-seleninic and butane-1-seleninic acids was confirmed by ¹³C n.m.r. spectroscopy, but whereas *t*-butyl benzeneperoxy-seleninate was stable at room temperature, these compounds slowly decomposed.

Experimental

60-MHz ¹H N.m.r. spectra were measured on a Perkin-Elmer R12 spectrometer for solutions in CDCl₃ with SiMe₄ as internal reference. ¹³C N.m.r. spectra were measured at 20 MHz on a Varian CFT 20 spectrometer for solutions in CDCl₃.

Preparation of Organoselenium Reagents.—Benzeneseleninic anhydride (m.p. 163–165 °C) was prepared from diphenyl diselenide and *t*-butyl hydroperoxide (3 mol equiv.) as described previously.⁵ **WARNING:** An attempt to use a route involving thermal dehydration of the benzeneseleninic acid obtained on oxidation of diphenyl diselenide with hydrogen peroxide⁷ afforded a solid which *exploded* at 53–55 °C; iodometric titration suggested that this solid may have been the complex PhSe(O)OH·H₂O₂. Ethyl benzeneseleninate was prepared from benzeneseleninic anhydride and ethanol and was purified by vacuum sublimation as described previously.⁵ Benzeneseleninyl bromide was prepared by ozonisation of benzeneselenenyl bromide⁸ (obtained from diphenyl diselenide and bromine in carbon tetrachloride) following a procedure similar to that previously used for the corresponding chloride.⁵

Toluene-*p*-seleninic anhydride, which was characterised by hydrolysis to the corresponding acid⁹ (m.p. 159–160 °C) (Found: C, 41.35; H, 4.1. Calc. for C₇H₈O₂Se: C, 41.40; H, 3.97%) was prepared in 90% yield from di-*p*-tolyl diselenide¹⁰ and *t*-butyl hydroperoxide using the same conditions as for benzeneseleninic anhydride.⁵ Di-*p*-tolyl diselenide (m.p. 46–47 °C) was in turn obtained in 86% yield by treating a refluxing solution of *p*-tolyl selenocyanate¹⁰ in methanol with ammonia as described previously¹¹ for diphenyl diselenide; purification was by chromatography on silica using dichloromethane–light petroleum (b.p. 40–60 °C) (1 : 1) as eluant.

Butane-1-seleninic anhydride⁵ was prepared by oxidation of butane-1-selenol¹² with *t*-butyl hydroperoxide (2 mol equiv.) in benzene. Butane-1-selenol was in turn prepared from butyl bromide by reaction of the corresponding Grignard reagent with selenium, followed by acid hydrolysis.¹³

Preparation of *t*-Butyl Benzeneperoxy-seleninate.—Apparatus, solvents, and nitrogen were rigorously dried, and care was taken to avoid adventitious hydrolysis during isolation and handling of the product.

(a) *From benzeneseleninic anhydride [method (1)].* *t*-Butyl hydroperoxide (0.45 g) was added to a suspension of benzeneseleninic anhydride (1.80 g) in benzene (40 cm³) under nitrogen and the mixture was stirred for 18 h. Filtration under nitrogen gave an insoluble residue of benzeneseleninic acid (0.88 g,

93%). Removal of the solvent from the filtrate under reduced pressure afforded *t*-butyl benzeneperoxy-seleninate (1.31 g) as a viscous oil. Although this product was analytically pure (Found: C, 45.4; H, 5.75. C₁₀H₁₄O₃Se requires C, 45.99; H, 5.40%), its ¹³C n.m.r. spectrum indicated the presence of a small amount of benzeneseleninic acid.

(b) *From ethyl benzeneseleninate [method (2)].* *t*-Butyl hydroperoxide (0.41 g) was added to a solution of ethyl benzeneseleninate (1.00 g) in benzene (20 cm³) under nitrogen and the mixture was stirred for 18 h. A small amount of white precipitate, which had been formed upon mixing, was filtered off. Removal of the solvent from the filtrate under reduced pressure afforded *t*-butyl benzeneperoxy-seleninate (0.94 g, 79%); δ_H 7.90 and 7.65 (total 5 H, m, Ph) and 1.30 (9 H, s, 3 × Me); δ_C 144.62 (s), 133.14 (d), 129.84 (d), 126.47 (d), 83.62 (s), and 26.35 p.p.m. (q) (Found: C, 45.5; H, 5.45. C₁₀H₁₄O₃Se requires C, 45.99, H, 5.40%).

(c) *From benzeneseleninyl bromide [method (3)].* A mixture of freshly prepared benzeneseleninyl bromide (1.00 g) and sodium *t*-butylperoxide (0.44 g) in diethyl ether–benzene (1 : 1) (20 cm³) was stirred for 20 h under nitrogen. Sodium bromide was filtered off and the solvent was removed from the filtrate under reduced pressure to give a cloudy, viscous oil (1.08 g). Although this product showed ¹³C n.m.r. resonances for *t*-butyl benzeneperoxy-seleninate alone, the yield (104%) and the opacity of the product, suggest the presence of some sodium bromide.

Formation of *t*-Butyl Toluene-*p*-peroxy-seleninate.—*t*-Butyl hydroperoxide (0.18 g) was added to a suspension of toluene-*p*-seleninic anhydride (0.77 g) in benzene (20 cm³) under nitrogen and the mixture was stirred for 18 h. Toluene-*p*-seleninic acid was filtered off and the solvent was removed from the filtrate to afford *t*-butyl toluene-*p*-peroxy-seleninate (0.54 g) as an oil which slowly decomposed with time; δ_H 7.65 (4 H, A₂B₂, ArH), 2.45 (3 H, s, ArMe), and 1.30 (9 H, s, 3 × Me); δ_C 143.94 (s), 141.74 (s), 130.12 (d), 126.42 (d), 83.50 (s), 26.35 (q) and 21.61 p.p.m. (q).

Formation of *t*-Butyl Butane-1-peroxy-seleninate.—A mixture of butane-1-seleninic anhydride (0.50 g) and *t*-butyl hydroperoxide (0.14 g) in benzene (10 cm³) was stirred under nitrogen for 18 h. The solution was concentrated under reduced pressure, deuteriochloroform was added, and the ¹³C n.m.r. spectrum was recorded. Signals at δ_C 83.49 and 26.32 p.p.m. were assigned to the *t*-butyl group of *t*-butyl butane-1-peroxy-seleninate, and the remaining signals at δ_C 55.22, 23.48, 22.68, and 13.66 p.p.m. were assigned to the butyl groups of *both* the peroxy-seleninate and butane-1-seleninic acid. Authentic butane-1-seleninic acid, obtained by hydrolysis of the anhydride, showed δ_C 55.38, 23.53, 22.62, and 13.67 p.p.m.

Acknowledgement

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References

- G. Sosnovsky and J. H. Brown, *Chem. Rev.*, 1966, 529.
- D. T. Woodbridge, *J. Chem. Soc. B*, 1966, 50.
- P. A. Grieco, Y. Yokoyama, S. Gilman, and M. Nishizawa, *J. Org. Chem.*, 1977, 42, 2034.
- H. J. Reich, F. Chow, and S. L. Peake, *Synthesis*, 1978, 299; M. Hori and K. B. Sharpless, *J. Org. Chem.*, 1978, 43, 1689.
- G. Ayrey, D. Barnard, and D. T. Woodbridge, *J. Chem. Soc.*, 1962, 2089.
- R. A. Johnson and E. G. Nidy, *J. Org. Chem.*, 1975, 40, 1680

- 7 J. D. McCullough and E. S. Gould, *J. Am. Chem. Soc.*, 1949, **71**, 674.
- 8 M. Fieser and L. F. Fieser, 'Reagents for Organic Synthesis,' Wiley-Interscience, New York, 1975, vol. 5, p. 518.
- 9 W. H. Porritt, *J. Chem. Soc.*, 1927, 27.
- 10 F. Challenger, A. T. Peters, and J. Halévy, *J. Chem. Soc.*, 1926, 1648.
- 11 O. Behaghel and H. Seibert, *Ber.*, 1932, **65**, 812.
- 12 L. Tschugaeff, *Ber.*, 1909, **42**, 49.
- 13 D. G. Foster, *Org. Synth.*, Coll. Vol. 3, 1955, 771.

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