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THE OXIDATION OF ARYL DISELENIDES WITH AN EQUIMOLAR AMOUNT OF tert-BUTYL HYDROPEROXIDE: EVIDENCE AGAINST THE FORMATION OF SIGNIFICANT AMOUNTS OF A SELENENIC ANHYDRIDE[1]

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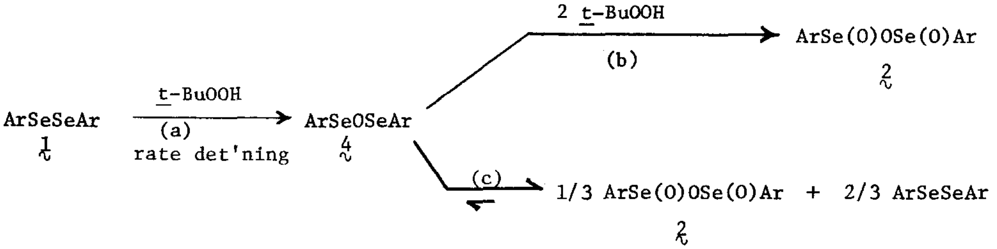
Abstract: Reaction of equimolar quantities of an aryl diselenide (**1**) and *tert*-butyl hydroperoxide does not lead, as has been suggested,[2] to a substantial amount of the corresponding selenenic anhydride (**4**), but rather to a mixture of seleninic anhydride (**2**) and unreacted diselenide, in a mole ratio of 1:2.

Shimizu, Takeda, and Kuwajima[2] have recently suggested, based on the ability of the product mixture to add to alkenes to give α-phenylseleno carbonyl compounds, that treatment of an aryl diselenide (ArSeSeAr, Ar = Ph) with an equimolar quantity of *tert*-butyl hydroperoxide leads to the formation of a high concentration of the selenenic anhydride, PhSeOSePh. We wish to report that observation of the ^{19}F nmr during the oxidation of *p*-fluorophenyl diselenide, **1** (ArSeSeAr, Ar = *p*-FC_6H_4), with an equimolar amount of *tert*-butyl hydroperoxide shows that, in actual fact, there is no significant amount of selenenic anhydride present at any time during the reaction. Instead one has a mixture of *p*-fluorobenzeneseleninic anhydride[4], **2** [ArSe(O)OSe(O)Ar, Ar = *p*-FC_6H_4], and unchanged diselenide **1**, with these being present at the end of the reaction in a molar ratio of 1:2.

When *tert*-butyl hydroperoxide[5] (0.88 mmol) is added to **1** (0.88 mmol) in 0.4 ml of carbon tetrachloride at 35°C and the ^{19}F nmr spectrum of the solution is monitored with time, one observes a gradual decrease over a period of several hours to two-thirds of its initial intensity in the signal (Φ = 108.02 ppm[6]) for the fluorines of **1** and the appearance, and gradual appropriate corresponding increase, of a signal (Φ = 100.50 ppm) due to the fluorines in **2**. The only other ^{19}F resonance of any magnitude that is observed is a relatively weak signal (Φ = 101.52 ppm) that can be shown to be due to a small amount of *p*-fluorobenzeneseleninic acid,[3] **3** ($ArSeO_2H$, Ar = *p*-FC_6H_4), a compound that probably arises from adventitious hydrolysis of a small portion of the seleninic anhydride. At no time during the oxidation is there any other ^{19}F resonance of appreciable intensity, such as would be required if a significant amount of the selenenic anhydride ArSeOSeAr, **4** (Ar = *p*-FC_6H_4) were present.[7]

Obviously, if, as seems likely, selenenic anhydride **4** is an intermediate in the oxidation of **1** to **2**, then the rate constant for its conversion to 2, either by oxidation by t-BuOOH (eq 1, step b), or by disproportionation (eq 1, step c), must be rapid compared to the rate constant at which **1** is oxidized to **4** (eq 1, step a). Furthermore, the equilibrium for the



(1)

disproportionation (eq 1, step c) must lie far over on the side of the seleninic anhydride, just as the equilibrium for the corresponding disproportionation of selenenic acids (eq 2) lies far to the right.[8]

$$3\ \mathrm{ArSeOH} \rightleftharpoons \mathrm{ArSeO_2H} + \mathrm{ArSeSeAr} + \mathrm{H_2O} \qquad (2)$$

The observation by Shimizu, Takeda and Kuwajima[2] that the product mixture from the oxidation of diphenyl diselenide with one mole of tert-butyl hydroperoxide can add to alkenes to yield α-phenylseleno carbonyl compounds thus does not mean that a large amount of PhSeOSePh is present, but rather that there is a small amount of this compound present in equilibrium with PhSeSePh and PhSe(O)OSe(O)Ph, and that as this adds to the alkene additional selenenic anhydride is generated from PhSeSePh and PhSe(O)OSe(O)Ph in order to restore equilibrium. The situation appears to be closely analogous to the successful addition of ArSeOH to alkenes achieved by both Reich *et al.*[8a] and Hori and Sharpless[8b] via the capture by an alkene of the small amount of selenenic acid present in equilibrium (eq 2) with a mixture of seleninic acid and diselenide.

References and Notes

(1) This research supported by the National Science Foundation, Grant CHE-79-18877.
(2) M. Shimizu, R. Takeda, and I. Kuwajima, *Tetrahedron Letters*, 419 (1979).
(3) J. D. McCullough and E. S. Gould, *J. Am. Chem. Soc.*, **71**, 674 (1949).
(4) A known sample of **2** was prepared by dehydration of p-fluorobenzeneseleninic acid[3] in vacuo over P_2O_5 at room temperature.
(5) Commercial tert-butyl hydroperoxide was purified to remove water. The material used for the oxidations was 95% t-BuOOH - 5% t-BuOH.
(6) All ^{19}F chemical shifts are expressed as ppm upfield from Freon 11.
(7) In the earliest stages of the oxidation a very weak signal is observed at ∿103.5 ppm. This does not increase further in intensity and by the end of the reaction has become so weak as to no longer be clearly detectable. Possibly this signal is due to **4** present at very low concentration. However, its integrated intensity is always less than 1% of the integrated intensity of the signal for **1**.
(8) (a) H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow and D. F. Wendelborn, *J. Org. Chem.*, **43**, 1697 (1978); (b) T. Hori and K. B. Sharpless, *J. Org. Chem.*, **43**, 1689 (1978).

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