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A FACILE FORMATION OF CYCLIC SELENURANES AND A CYCLIC SELENURANE OXIDE IN THE REACTION OF 2-METHYLSELENO- AND 2-PHENYLSELENOBENZOIC ACIDS AND THEIR DERIVATIVES WITH t-BUTYL HYDROPEROXIDE

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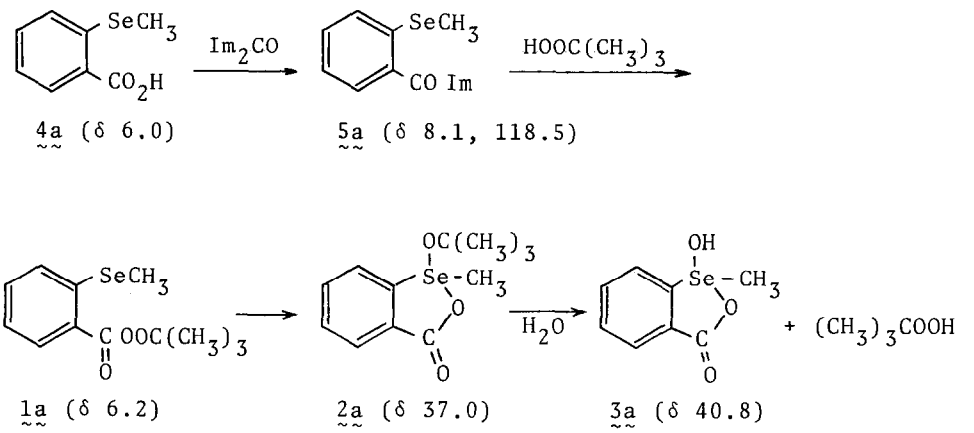
Abstract: The reaction of 2-methylselenobenzoic acid with 1,1'-carbonyldiimidazole followed by addition of t-butyl hydroperoxide gave cyclic selenuranes 2a and 3a, suggesting the intramolecular insertion of the neighboring selenium atom into the O-O bond of t-butyl 2-methylselenoperoxybenzoate. In the reaction of 2-phenylselenobenzoyl chloride with t-butyl hydroperoxide, cyclic selenurane 2b and the oxide 7 were obtained.

In view of the striking effect of a neighboring sulfur atom in the homolytic O-O bond cleavage of t-butyl 2-thioperoxybenzoates,[1] it seemed of interest to investigate a similar anchimeric assistance of the neighboring selenium atom in the decomposition of t-butyl 2-methylselenoperoxybenzoate (1a). We have now found the intramolecular insertion of the neighboring selenium atom into the O-O bond of 1a and the formation of a novel selenurane oxide (7) in the reaction of 2-phenylselenobenzoic acid (4b) and its chloride with t-butyl hydroperoxide.

2-Methylselenobenzoic acid (4a) was allowed to react with 1,1'-carbonyldiimidazole in THF, followed by addition of excess t-butyl hydroperoxide at low temperature.[2] The product obtained after usual workup was not the expected 1a but selenurane 2a carrying a t-butoxy group. During attempted purification, most of 2a was converted into 2-carboxyphenyl methyl selenoxide (3a). A sample of 3a was prepared independently for comparison and was shown to have the ring-closed selenurane structure.[3]

The above reaction was monitored by ^{13}C NMR spectroscopy. A solution of 100 mg of 4a in 1.5 ml of THF was placed in a 10 mm ϕ NMR tube fitted with a D_2O capillary for external lock. The methyl carbon of 4a had the chemical shift of δ 6.0 under these conditions. When 1,1'-carbonyldiimidazole was added

Scheme 1[7]



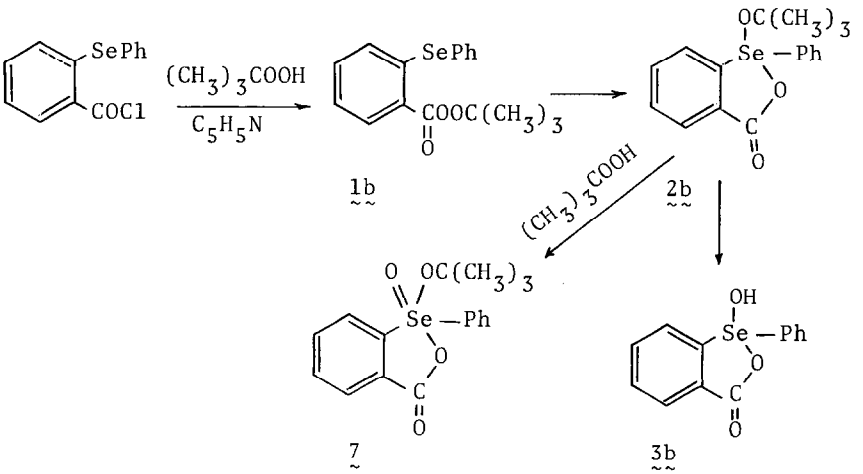
evolution of carbon dioxide took place in a few minutes. A new ^{13}C NMR signal appeared at δ 8.1 in place of the original signal at δ 6.0. The spectral change should correspond to the formation of imidazolide 5a of 4a. In the aromatic region, a signal at δ 118.5 was characteristic of 5a. When 3 molar excess of t-butyl hydroperoxide was added to the solution, a new signal at δ 6.2 replaced the peak at δ 8.1 in about one hour. A few hours later, an additional signal at δ 37.0 due to 2a grew up at the expense of the signal at δ 6.2. Addition of a drop of D_2O quenched the signal at δ 37.0 and the signals due to 3a (δ 40.8) and t-butyl alcohol developed (Scheme 1).

Judging from the known pattern of the reaction of an organic imidazolide with t-butyl hydroperoxide[2] and from the typical ^{13}C NMR chemical shift value for nuclear substituted selenoanisoles,[4] the intermediate having the methyl carbon at δ 6.2 may be concluded to be 1a. Then the observed efficient conversion of 1a to 2a would be the O-O bond cleavage assisted by the neighboring selenium atom. The rate enhancement factor for the 2-methylseleno group is estimated to be about ten times as large as that of the 2-methylthio group in the decomposition of t-butyl peroxybenzoates. It might be argued that t-butyl hydroperoxide could have attacked the selenium atom of 5a directly. The contribution of this reaction seems to be small, as the reaction of the hydroperoxide with 4a is slower than that with 5a by a factor of 20 in THF.[5]

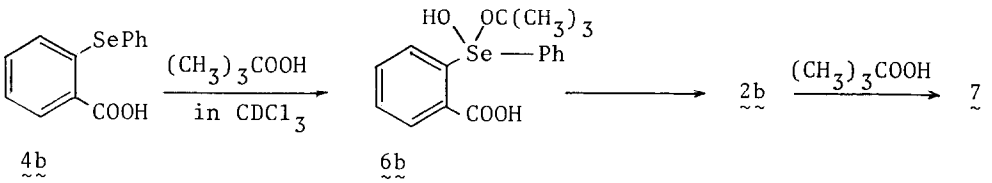
A mixture of two compounds 2b and 7 were obtained from the reaction of 2-phenylselenobenzoyl chloride with t-butyl hydroperoxide in ether in the presence of pyridine at low temperature. Chromatography on silica gel followed by crystallization from ether gave 7 as needles; mp 154-155 °C; Anal. Calcd for $C_{17}H_{18}O_4Se$: C, 55.89; H, 4.96. Found: C, 55.59; H, 4.97 %; ^1H NMR($CDCl_3$) δ 1.31 (9H, s), 7.34-7.50, 7.65-7.95 and 8.17-8.33 (9H, m); ^{13}C NMR($CDCl_3$) δ 26.4, 82.8, 127.8, 128.7, 129.9, 130.5, 131.9, 133.0, 133.5, 134.4, 135.8, 139.4 and

169.1; ^{77}Se NMR($CDCl_3$) δ(from CH_3SeCH_3) 785; IR(nujol) 1665 cm^{-1}. The data are consistent with the cyclic selenurane oxide structure 7. Since purification of 2b as monitored by its characteristic ^{1}H NMR signal at δ 1.25 was difficult owing to the sensitivity to moisture, it was identified as 2-carboxyphenyl phenyl selenoxide (3b) after hydrolysis (Scheme 2).[3] Cyclic selenurane oxide 7 was also obtained quantitatively from the reaction of 2-phenylselenobenzoic acid with two equivalents of t-butyl hydroperoxide in chloroform (Scheme 3). No ^{1}H and ^{13}C NMR signal due either to 6b or 2b was found during the reaction. Instead the signals due to 7 and t-butyl alcohol appeared from the beginning. The formation of 6b is thus suggested to be slow while cyclization to 2b and further oxidation to 7 may be relatively fast. The latter process is to be compared with oxidation of sulfuranes.[6]

Scheme 2



Scheme 3



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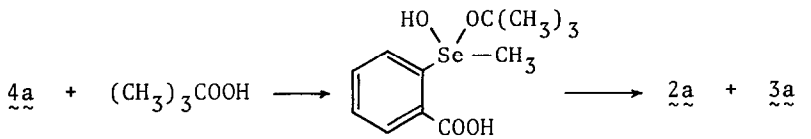
2) R. Hecht and C. Rüchardt, Chem. Ber., 96, 1281 (1963).

3) W. Nakanishi, S. Matsumoto, Y. Ikeda, T. Sugawara, Y. Kawada, and H. Iwamura, Chemistry Lett., in press. See also: B. Dahle'n, Acta Cryst., B 29, 595 (1973).

4) Chemical shifts due to the methyl carbon of nuclear substituted seleno-anisoles fall in the range δ 5.9-8.7. See: G. A. Kalabin, D. F. Kushnarev, and V. M. Bzesovsky, Org. Magn. Reson., 12, 598 (1979); ref. 3.

5) The reaction of 4a with t-butyl hydroperoxide in chloroform is completed in one hour giving predominantly 2a. In the presence of imidazole, the reaction produces 2a and 3a in a ratio of 1:9. Adduct 6a is considered to be a common intermediate from which 2a may be obtained by dehydration and 3a by base-catalyzed elimination of t-butyl alcohol.



6a

6) J. C. Martin and E. F. Perozzi, J. Am. Chem. Soc., 96, 3155 (1974); E. F. Perozzi and J. C. Martin, ibid., 94, 5519 (1972); E. F. Perozzi, J. C. Martin, and I. C. Paul, ibid., 96, 6735 (1974).

7) NMR monitoring of the reactions was performed at ambient probe temperatures of 29 °C.

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