CHEMISTRY LETTERS, pp. 809-810, 1986.

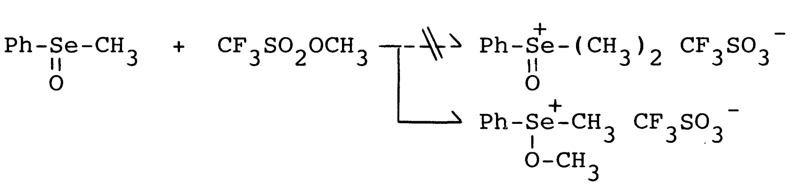
FIRST SYNTHESIS OF OXOSELENONIUM SALTS

Michio KOBAYASHI* and Takashi MIHOYA
Department of Chemistry, Faculty of Science, Tokyo Metropolitan
University, Fukazawa, Setagaya, Tokyo 158

Triaryloxoselenonium salts have been synthesized for the first time by oxidation of selenonium salts with peroxybenzoate anion.

Although in the chemistry of sulfur, oxosulfonium compounds such as trimethyloxosulfonium iodide[1)] or ethylmethylphenyloxosulfonium perchlorate[2)] are known for a long time, there has been no report on the synthesis of selenium analogue, oxoselenonium salt. We have succeeded to synthesize several triaryloxoselenonium salts, and detail will be described in this paper.

Attempts to prepare oxoselenonium salt by alkylation of selenoxide, similar to the method used in the preparation of trimethyloxosulfonium iodide from dimethyl sulfoxide and methyl iodide, were all unsuccessful. For instance, alkylation of diphenyl selenoxide or methyl phenyl selenoxide with methyl iodide-mercuric iodide,[3)] trimethyloxonium tetrafluoroborate, or methyl trifluoromethanesulfonate as alkylating reagents did not result in the formation of oxoselenonium salt but of unstable alkoxyselenonium salts in every case.



$$\underset{\mathrm{O}}{\overset{}{\mathrm{Ph{-}Se{-}CH_3}}} + \mathrm{CF_3SO_2OCH_3} \not\longrightarrow \mathrm{Ph{-}\overset{+}{Se}(=O){-}(CH_3)_2\ CF_3SO_3^-}$$

$$\longrightarrow \mathrm{Ph{-}\overset{+}{Se}(O{-}CH_3){-}CH_3\ CF_3SO_3^-}$$

Alternative attempt to synthesize oxoselenonium salts by oxidation of selenonium salt by peroxybenzoate under the alkaline conditions, which was verified as quite effective to prepare oxosulfonium salts from sulfonium salts,[4)] was unsuccessful in the cases of trialkylselenonium salts, dialkylarylselenonium salts, and alkyldiarylselenonium salts.

However, when triarylselenonium salts were subjected to similar oxidation, triaryloxoselenonium salts were produced, although in poor yields. For example, tri-p-tolyloxoselenonium salt was prepared in a following way. To a solution of 1.49 g (3.85 mmol) of tri-p-tolylselenonium chloride (**1**) in 90 ml of water were added 1.9 g (17.9 mmol) of sodium carbonate and 3.1 g (17.9 mmol) of m-chloroperbenzoic acid and the mixture was kept for 4 h at room temperature. After acidification by hydrochloric acid and removal of produced benzoic acid by extraction with ether, the reaction mixture was extracted with dichloromethane to give tri-p-tolyloxoselenonium chloride as oily substance, which was converted into crystalline tetraphenylborate (**2**) with sodium tetraphenylborate in acetone. Yield 44%. Mp 175-176 ℃(dec). ^{1}H-NMR(CH_2Cl_2) δ =2.50 (s, 9H), 6.82-7.37 (m, 20H), 7.49 (s, 12H).

IR(KBr); ν(Se=O) 910 cm^{-1}. Found: C, 78.89, H, 6.37%. Calcd for $C_{45}H_{41}SeOB$: C, 78.60; H, 5.97%.

$$(p\text{-}CH_3C_6H_4)_3Se^+\ Cl^- + PhCO_3^- \longrightarrow \underset{\mathbf{1}}{(p\text{-}CH_3C_6H_4)_3Se^+{=}O\ Cl^-}$$

$$\xrightarrow{NaBPh_4} \underset{\mathbf{2}}{(p\text{-}CH_3C_6H_4)_3Se^+{=}O\ BPh_4^-}$$

In a similar way, two other triaryloxoselenonium salts were prepared. Triphenyloxoselenonium teraphenylborate (**3**) was obtained from triphenylselenonium chloride in 10% yield. Mp 165-166 °C(dec). ^{1}H-NMR(CH_3CN) δ=6.80-7.43 (m, 20H), 7.91 (s, 15H). IR; ν(Se=O) 910 cm^{-1}. Found C, 78.56; H, 5.68%; Calcd for $C_{42}H_{35}SeOB$;C, 78.16; H, 5.43%. Tri-p-anisyloxoselenonium tetraphenylborate (**4**) was produced from corresponding selenonium salt in 33% yield. Mp 193.5-194.5 °C(dec). ^{1}H-NMR;δ=3.97 (s, 3H), 6.82-7.24 (m, 20H), 7.24-7.90 (q, 12H). IR ν(Se=O) 910 cm^{-1}. Found C, 73.10; H, 5.65%; Cald for $C_{45}H_{43}SeOB$;C, 73.49; H, 5.58%.

Oxidation of several other triarylselenonium salts such as phenyl-o-anisyl-naphthyl selenonium salt, tris(2-hydroxy-3-methyl)phenyl selenonium salt was attempted but failed to give oxoselenonium salt.

Reason why alkylselenonium salts could not be oxidized was unexplainable at present. When a mixture of 0.75 mmol of tri-p-tolylselenonium chloride and 0.75 mmol of dimethylphenyl selenonium perchlorate in 30 ml of water was oxidized with 5.8 mmol of m-chloroperbenzoic acid under alkaline conditions similar to the oxidation of tri-arylselenonium salt for 6 h, 84% of tri-p-tolylselenonium salt was oxidized to oxoselenonium salt while dimethylphenylselenonium salt was recovered unchanged. Also, oxidation of dimethylphenylselenonium perchlorate under many different conditions wasexamined by changing the pH, concentration of peracid, and ratio of peracid to selenonium salt, but results were unsatisfactory.

IR frequencies of several phenyl selenium compounds were shown below:

diphenyl selenoxide ν(Se=O) 820 cm^{-1}
diphenyl selenone ν(Se=O) 935 (asym), 875 (sym) cm^{-1}
triphenyloxoselenonium perchlorate ν(Se=O) 910 cm^{-1}

Se=O frequency of oxoselenonium ion is almost the same as mean value of two vibrations of selenone. This suggests that Se=O bond of oxoselenonium ion has consider rable higher double bond character than that of selenoxide.

References

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4) To be submitted.

(Received February 19, 1986)