Preparation and characterization of mercurated diphenylselenium(IV) derivatives

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The interaction of diorganoselenium(IV) derivatives with certain electrophiles such as Hg(OOCCH₃)₂ and Hg(OOCOCH₃)₂ in non-aqueous solvents yield organometallic compounds containing two different metal-carbon bonds (Se-C and Hg-C). The newly synthesized compounds have been characterized on the basis of elemental analysis, IR and NMR spectral data. The electrophiles mainly enter at the para position to the selenium atom in the phenyl ring.

The mercuration of aliphatic derivatives, chelating ligands and Schiff bases have been reported. The mercuration of aromatic arseno compounds, (CH₃C₆H₄AsO)₆, with mercuric acetate and of phosphines with Hg(OOCOCF₃)₂ was also investigated. Recently, mercuration of organotellurium(IV) derivatives have been reported and it was observed that mercuration mainly occurs in the phenyl ring at the para position to the tellurium atom. In cases where the para position of the ring is occupied, the interaction takes places at the ortho position.

In continuation of our studies on the organoselenium(IV) and organotellurium(IV) compounds, we now report the synthesis and characterization of some new organometallic compounds containing two different M-C bonds (RCOO-Hg-C₆H₄H₂SeX₂ (where X = Cl, OCOCH₃, R = CH₃ and CF₃).

Results and discussion

The reaction of HgO and CH₃COOH or CF₃COOH (20 ml) and HgO (2.16 g, 10 mmol) were mixed, when an exothermic reaction occurred and HgO dissolved completely. It was cooled to room temperature and a solution of Ph₂Se(OOCCH₃)₂ (1.75 g, 5 mmol) in 10 ml of CH₂Cl₂ was added. The excess solvent from the reaction mixture was distilled at reduced pressure. The viscous mass so obtained yielded a white solid on addition of CH₂Cl₂/solvent ether mixture. It was washed and dried in vacuo.

Experimental

All manipulations were carried out under dry nitrogen atmosphere. The infra red spectra were recorded on Perkin-Elmer 833 in CsI in the range 4000-200 cm⁻¹ and ¹H NMR spectra were recorded in Jeol FX90Q FT NMR spectrometer operating at 29.55 MHz. Ph₂SeCl₂ was prepared by chlorination of Ph₂Se₄. Ph₂Se(OOCCH₃)₂ was prepared by the interaction of Ph₂SeCl₂ with silver acetate in 1:2 molar ratio in benzene. CH₃COOH (BDH) and CF₃COOH (Koch-light) were distilled before use. Yellow HgO (BDH) was used as such. The representative reactions are given below:

Reaction of Ph₂SeCl₂ with HgO and CH₃COOH

A suspension of HgO (2.16 g, 10 mmol) in dichloromethane (25 ml) and glacial acetic acid (20 ml) was refluxed with stirring until HgO was dissolved.

A solution of Ph₂SeCl₂ (1.57 g, 10 mmol) in the same solvent (10 ml) was then added to it and the reaction mixture stirred for 4 h. The solvent was removed under reduced pressure. To the viscous mass so obtained, dichloromethane (10 ml) was added when a white product separated out. It was washed with CH₂Cl₂/pet. ether (40-60°C) mixture several times and dried in vacuo.

Reaction of Ph₂Se(OOCCH₃)₂ with HgO/CF₃COOH

CF₃COOH (20 ml) and HgO (2.16 g, 10 mmol) were mixed, when an exothermic reaction occurred and HgO dissolved completely. It was cooled to room temperature and a solution of Ph₂Se(OOCCH₃)₂ (1.75 g, 5 mmol) in 10 ml of CH₂Cl₂ was added. The excess solvent from the reaction mixture was distilled at reduced pressure. The viscous mass so obtained yielded a white solid on addition of CH₂Cl₂/solvent ether mixture. It was washed and dried in vacuo.

Where X = C, COOCF₃ and R' = CH₃, CF₃.
The products are white solids, partially soluble in non-polar solvents but dissolve in polar organic solvents such as methanol, ethanol, methyl cyanide, dimethyl sulfoxide and dimethyl formamide. They are stable towards atmospheric oxygen and moisture. They tend to decompose above 200°C without melting and gave the following elemental analysis:

- **Found**: Se = 9.2, Hg = 48.2, C = 23.2, H = 1.5, Cl = 8.5%  
  **Calc.**: for (CH$_3$COO-Hg-C$_6$H$_4$)$_2$SeCl$_2$, Se = 9.4, Hg = 48.3, C = 23.3, H = 1.7, Cl = 8.6%

- **Found**: Se = 8.3, Hg = 42.7, C = 20.4, H = 1.01, Cl = 7.4%  
  **Calc.**: for (CF$_3$COO-Hg-C$_6$H$_4$)$_2$SeCl$_2$, Se = 8.5, Hg = 43.2, C = 20.6, H = 0.96, Cl = 7.4%.

- **Found**: Se = 8.9, Hg = 45.9, C = 27.4, H = 2.2%  
  **Calc.**: for (CH$_3$COO-Hg-C$_6$H$_4$)$_2$Se(OOCCH$_3$)$_2$, Se = 9.1, Hg = 46.2, C = 27.6, H = 2.3%.

- **Found**: Se = 8.0, Hg = 41.4, C = 24.6, H = 1.2%  
  **Calc.**: for (CF$_3$COO-Hg-C$_6$H$_4$)$_2$Se(OOCCH$_3$)$_2$, Se = 8.1, Hg = 41.3, C = 24.8, H = 1.4%.

The molar conductance of their (1 0$^{-3}$ M) solution at ambient temperature lies in the range 2.5-14.10 ohm$^{-1}$ cm² mol$^{-1}$ suggesting their non-electrolytic nature. The molecular weight in freezing nitrobenzene indicates their monomeric nature in solution.

The IR active absorption of diagnostic importance are discussed below:

The $v_{asy}$OCC and $v_{sym}$OCC modes of vibration in compounds containing $-\text{OCOCF}_3$ and $-\text{OOCCH}_3$ groups attached to mercury atom lie at 1680 ± 10 and 1620 ± 10 cm$^{-1}$ and 1420 ± 10 and 1240 ± 10 cm$^{-1}$ respectively. The frequency difference between the two modes of vibration $-\Delta$vOCC due to $-\text{OCOCF}_3$ and $-\text{OOCCH}_3$ are 260 ± 10 and 380 ± 10 cm$^{-1}$ respectively indicating the unidentate nature of the carboxylate group$^{12,13}$. The $v_{asy}$OCC and $v_{sym}$OCC modes of vibration of OOCCH$_3$ group attached to selenium atom lies at 1670 and 1270 cm$^{-1}$ respectively and $-\Delta$vOCC = 400 cm$^{-1}$ is close to that for Ph$_2$Se(OOCCH$_3$)$_2$ where a unidentate carboxylate group has been reported$^{14}$. A strong to medium band appearing at 510 ± 10 cm$^{-1}$ is assigned to Hg-O in accordance to the earlier report$^{15}$. A weak to medium absorption at 330 cm$^{-1}$ may be due to (Se-O) (ref. 16).

The $^1$HNMR spectra of a few representative compounds were recorded in CDCl$_3$. The $^1$HNMR spectra showed two distinct sets of aromatic multiplets arising from ortho protons at low field and meta and para protons at high field. In Ph$_2$SeCl$_2$, the multiplets occur at 8.27-7.08 ppm due to phenyl groups and are separated from each other at 28.5 Hz which appear at 7.74-6.86 ppm on mercuration in (CH$_3$COO-Hg-C$_6$H$_4$)$_2$SeCl$_2$. A singlet observed at $\delta$ 1.98 is due to CH$_3$ of $-\text{HgOCOCH}_3$. (The separation between ortho protons and meta and para protons multiplets is 7.16 Hz). The chemical shift in the position of phenyl protons of mercurated derivatives as compared to that of parent compounds indicates replacement of the ring hydrogen by RCOO-Hg. In the $^1$HNMR spectrum of Ph$_2$Se(OOCCH$_3$)$_2$, the phenyl groups occur at 7.87-7.08 ppm as multiplets. The CH$_3$ protons of Se-OCOCH$_3$ occur at 1.95 ppm as a singlet.

The substitution at the phenyl ring depends on the experimental conditions and the reactivity of the ring attached to selenium atom$^{1,4}$. The selenium atom attached to phenyl group exhibits electron withdrawing inductive (polar) effect (-I) and tends to yield substitution products mainly at ortho and para positions to the selenium atom. In the reactions described herein, $-\text{HgCOR}$ (R = CF$_3$ and CH$_3$) group prefers an electrophilic attack at the para position rather than that at the sterically hindered ortho position in a trigonal bipyramidal geometry around selenium atom. Due to the presence of ortho, para directing selenium atom adjacent to phenyl group, and the -I effect, the electron density of the ring mainly at the para position is lowered making it more convenient for electrophilic substitution$^1$.

On the basis of the above observations, the proposed geometry around central selenium atom is trigonal bipyramidal in which the two electronegative groups (X = Cl, OOCCH$_3$) are at axial positions while the two mercurated phenyl groups bonded to selenium atom and the lone pair of electrons occupy the three equatorial positions.

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**References**