

## Derivatives of Selenium with Glycols

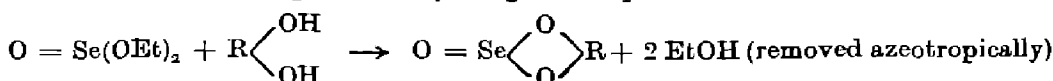
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In view of the interesting results obtained with the glycol derivatives of aluminium<sup>1</sup>, boron<sup>2</sup>, titanium<sup>3</sup>, germanium<sup>4</sup>, antimony<sup>5</sup>, tellurium<sup>6</sup>, and niobium<sup>7</sup>, it was considered worthwhile to extend these studies to selenium also, in absence of any reference in the literature on the preparation of the glycol derivatives of selenium.

The reactions of ethyl selenite with various glycols in equimolar ratio were carried out in benzene, the liberated ethanol was fractionated azeotropically and the progress of the reaction checked by estimating the amount of ethanol collected azeotropically. The reactions appeared to be quite facile and yielded alkylene selenites, except in the case of pinacol which provided a monoethyl monopinacol derivative. The latter compound also on heating under reduced pressure appeared to disproportionate, yielding pinacol selenite which could be sublimed. All the other alkylene selenites are also volatile under reduced pressure, except the pentamethylene derivative. These derivatives are all soluble in benzene, except the ethylene, tetramethylene, and pentamethylene selenites.

The refractive indices of the distilled derivatives were determined and also their molecular weights in benzene at 37°, using a Macrolab Vapour Pressure Osmometer. All the derivatives were found to be monomeric, except trimethylene and propylene, which showed an average molecular association of 1.1 and 1.4, respectively. In view of the tendency of the latter derivative, in particular, for dimerisation, its molecular complexity was determined after allowing it to age for different lengths of time. The freshly distilled sample showed a molecular complexity of about 1.4 which remained unaltered even after about 24 hr. On aging the sample for about a year, the molecular complexity was found to rise to about 2. Molecular weight of this derivative was measured ebullioscopically in benzene also, using a semimicro ebulliometer with thermister sensing, when it showed an average molecular association value of about 1.1 only.

The reactions can be represented by the general equation:



(where  $\text{R} \begin{array}{l} \text{OH} \\ \diagdown \\ \diagup \\ \text{OH} \end{array}$  stands for glycols, ethylene, 1,2-propylene, trimethylene, 1,3- and 2,3-butylene, tetramethylene, pentamethylene, hexylene, and pinacol).

1. Mehrotra and Mehrotra, *this Journal*, 1962, **39**, 635.
2. Mehrotra and Srivastava, *J. Chem. Soc.*, 1962, 1032.
3. Puri, Ph. D. Thesis, University of Gorakhpur, 1962.
4. Mehrotra and Chandra, *J. Chem. Soc.*, 1963, 2804.
5. Mehrotra and Bhatnagar, *this Journal*, 1965, **42**, 326.
6. Mehrotra and Mathur, *this issue*, p. 749.
7. Mehrotra and Kapoor, *J. Less-Common Metals* (in press).

TABLE I

Reactants.	Selenites formed.	Yield		%Selenium. Found. Calc.	EtOH in azeotrope. Found. Calc.		Molecular weight. Found. Calc.	Ref. index.
		I.	II.					
E. S. (2.4 g.) + ethylene-G (0.79 g.)	O=Se(O <sub>2</sub> C <sub>2</sub> H <sub>4</sub> ). Colorless viscous liquid, distilling at 100°/6 mm.	2.06 g. (100%)	1.52 to 1.02 g. (66%)	50.94	50.94	1.63 g.	1.67 g.	1.5122
E. S. (3.98 g.) + propane-1,2- diol (1.64 g.)	O=Se(O <sub>2</sub> C <sub>3</sub> H <sub>6</sub> ). Colorless viscous liquid, distilling at 108°/6 mm.	3.25 g. (89%)	2.7 to 1.00 g. (70%)	47.15	46.72	1.87	1.94	166.0, 1.4902
E. S. (2.5 g.) + trimethyl- ene-G (1.1 g.)	O=Se(O <sub>2</sub> C <sub>3</sub> H <sub>6</sub> ). White crystalline solid, m.p. 63-66°, distilling at 72°/0.5 mm.	2.16 g. 89.7%	1.5 to 1.2 g. (80%)	46.83	46.72	1.04	1.10	189.0
E. S. (4.05 g.) + butane-2,3- diol (1.95 g.)	O=Se(O <sub>2</sub> C <sub>4</sub> H <sub>8</sub> ). Colorless viscous liquid, distilling at 88°/1 mm.	3.82 g. (96.5%)	3.2 to 2.6 g. (81.27%)	43.16	43.13	1.89	1.95	183.1 1.5060
E. S. (3.19 g.) + butane-1,3- diol (1.52 g.)	O=Se(O <sub>2</sub> C <sub>4</sub> H <sub>8</sub> ). Colorless viscous liquid, distilling at 82°/2.5 mm.	3.02 g. (97%)	2.0 to 1.75 g. (88%)	43.04	43.13	1.53	1.55	183.1, 1.4898
E. S. (3.78 g.) + tetramethy- lene-G (1.84 g.)	O=Se(O <sub>2</sub> C <sub>4</sub> H <sub>8</sub> ). Colorless viscous liquid, distilling at 60°/0.05 mm.	3.52 g. (94%)	3.0 to 2.5 g. (84%)	43.04	43.13	1.98	2.07	183.1, 1.5448
E. S. (4.17 g.) + pentamethyl- ene-G (2.35 g.)	O=Se(O <sub>2</sub> C <sub>5</sub> H <sub>10</sub> ). Colorless viscous liquid, decomposing on distillation.	4.43 g. (100%)	..	39.98	40.07	2.00	2.03	..
E. S. (3.18 g.) + hexylene-G (2.03 g.)	O=Se(O <sub>2</sub> C <sub>6</sub> H <sub>12</sub> ). Colorless viscous liquid, distilling at 91°/4.5 mm	3.60 g. (100%)	2.8 to 2.45 g. (88%)	37.47	37.41	1.53	1.55	214 2110 1.5235

\*Enthalpically determined M. W. 198.

N, B. In Columns 3 and 4, I and II refer respectively to undistilled and distilled product.

E. S. denotes ethyl selenite and G refers to glycol.

All-glass apparatus fitted with standard interchangeable joints was used throughout the work and special precautions were taken to exclude moisture. For fractionation, a column packed with Raschig rings and fitted to a total-condensation variable take-off stillhead was used.

The reagents were dried in the usual manner as described earlier<sup>8</sup>. Glycols were purified by distillation before use. Ethyl selenite was prepared by the azeotropic dehydration of selenous acid, in the presence of ethyl alcohol and benzene<sup>9</sup>. Refractive indices were determined by Abbe's refractometer.

Selenium was estimated in the elementary form, using  $\text{SO}_2$  in  $\text{HCl}$  as the precipitating agent. The ethanol in the azeotrope was estimated by an oxidimetric method<sup>9</sup>.

*Pinacol Selenite*.—To ethyl selenite (2.66 g.) in benzene was added pinacol (1.7g.) and the contents were refluxed under a column for 1 hr. The binary azeotrope of ethanol and benzene appearing at  $68^\circ$  was slowly fractionated. Refluxing was continued till the distilling liquid did not show any tendency of lowering the temperature below  $80^\circ$ . Excess of the solvent was distilled at a high reflux ratio and on distilling the volatile contents under reduced pressure, a white crystalline solid, monethyl monopinacol selenite, was obtained. On sublimation at  $110^\circ/2$  mm, pinacol selenite was obtained.

*Unsublimed product*: [Found: Se, 30.78.  $\text{Se}(\text{C}_8\text{H}_{10}\text{O}_4)$  requires Se, 30.74%]. Alcohol in azeotropic: (Found: 0.62 g. Calc. 0.65g.); yield 3.61 g. (100%)

*Sublimed product*: [Found: Se, 37.31.  $\text{Se}(\text{C}_6\text{H}_{12}\text{O}_3)$  requires Se, 37.41%]; yield from 3.0g., 1.85g. (61%); M.W. found, 211; calc. 211.

Similar reactions were carried out with other glycols (Table I).

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8. Mehrotra and Mathur, this *Journal*, 1964, **41**, 111.

9. Bradley *et al.*, *J. Chem. Soc.*, 1950, 3450.