

IV.—*Arylseleninic Acids.*

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Two tolueneseleninic acids have been recorded by Doughty and Elder (Eighth Inter. Congress Applied Chemistry, 1912, 6, 93) as resulting from the reduction by hydrochloric acid of the mixed tolueneselenonic acids obtained by the direct action of selenic acid on toluene. The *p*-substituted acid was described as containing $1\text{H}_2\text{O}$ and melting with decomposition at 160° , whereas the *o*-isomeride, with melting point $99\text{--}101^\circ$, was stated to contain $\frac{1}{2}\text{H}_2\text{O}$.

The *m*-seleninic acid and two xyleneseleninic acids not hitherto described and the foregoing *o*- and *p*-tolueneseleninic acids have now been obtained from definitely oriented aromatic derivatives.

A correction. The action of hydrogen peroxide on two arylselenoglycollic acids was stated by Morgan and Porritt (J., 1925, 127, 1758) to give rise to the corresponding arylselenoxyglycollic acids. Mr. F. C. Ray, of Battersea Polytechnic, kindly notified the author that this statement is erroneous, and further investigation has shown that the oxidising action of the hydrogen peroxide is sufficiently violent to remove the $\text{CH}_2\cdot\text{CO}_2\text{H}$ group and give the corresponding arylseleninic acids.

This oxidation process, which has been repeated and extended, affords a ready and general method for preparing arylseleninic acids containing substituents of known orientation. If the temperature is allowed to rise appreciably during the first stage of the reaction between hydrogen peroxide and the arylselenoglycollic acid, the formation of the arylseleninic acid is attended by the production of other oxidation products and diaryl diselenides also may be isolated. The tolueneseleninic acids as prepared by this general method are obtained in anhydrous forms.

EXPERIMENTAL.

o-Tolylselenoglycollic acid, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{Se}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, was prepared by the general method (Morgan and Porritt, *loc. cit.*, p. 1775) from magnesium *o*-tolyl bromide and selenium (Taboury, *Bull. Soc. chim.*, 1903, 29, 761), the condensation of the potassium salt of the mercaptan with sodium chloroacetate being effected in aqueous solution. The *selenoglycollic acid* separated as an oil from an acidified solution of its sodium salt and solidified slowly; after repeated crystallisation from boiling water, it was obtained in colourless, lustrous plates, m. p. 70—71° (Found: C, 47.2; H, 4.5. $\text{C}_9\text{H}_{10}\text{O}_2\text{Se}$ requires C, 47.2; H, 4.4%). It developed a reddish-brown colour in concentrated sulphuric acid.

m-Xylyl-4-selenoglycollic Acid, $(\text{CH}_3)_2\text{C}_6\text{H}_3\cdot\text{Se}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.—4-Iodo-*m*-xylene, prepared from *m*-4-xylylidine, was converted by the general reaction into the *selenoglycollic acid*, which separated as an oil and subsequently crystallised in colourless, lustrous plates, m. p. 90.5° (Found: C, 49.5; H, 5.0. $\text{C}_{10}\text{H}_{12}\text{O}_2\text{Se}$ requires C, 49.4; H, 4.9%). The acid developed a greenish-yellow colour in sulphuric acid.

o-Xylyl-4-selenoglycollic acid, prepared by the general method from 4-iodo-*o*-xylene obtained from *o*-4-xylylidine (m. p. 49°; Morgan and Hickinbottom, *J. Soc. Chem. Ind.*, 1926, 45, 222r), crystallised from hot water in colourless plates, m. p. 88°, and developed a violet coloration in sulphuric acid (Found: C, 49.5; H, 5.1%).

Toluene-o-seleninic acid, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SeO}_2\text{H}$, was prepared by adding an excess of 20% hydrogen peroxide to a suspension of *o*-tolylselenoglycollic acid in ice-cold water, the acid gradually dissolving. The product, which separated after several hours, crystallised from hot water in clusters of colourless needles, m. p. 126—127° (Found: C, 41.4; H, 4.0. $\text{C}_7\text{H}_8\text{O}_2\text{Se}$ requires C, 41.4; H, 3.9%). It dissolved sparingly in ether and more readily in alcohol or chloroform.

Toluene-p-seleninic acid, prepared from *p*-tolylselenoglycollic acid, crystallised from hot water in colourless, flattened needles, m. p. 171° (Found: C, 41.7; H, 4.3%). Like the preceding isomeride, it developed a violet coloration with warm concentrated sulphuric acid and liberated iodine from acidified solutions of potassium iodide.

Toluene-m-seleninic acid, prepared by the oxidation with hydrogen peroxide of oily *m*-tolylselenoglycollic acid obtained from 3-iodotoluene through the Taboury reaction, separated from hot water in colourless needles, m. p. 119—120° (Found: C, 41.5; H, 4.0%). It developed a deep blue coloration with warm sulphuric acid.

Bromobenzene-p-seleninic acid, $\text{C}_6\text{H}_4\text{Br} \cdot \text{SeO}_2\text{H}$, prepared from *p*-bromophenylselenoglycollic acid by oxidation with hydrogen peroxide in acetic acid solution, crystallised from hot water in colourless needles, decomp. 187° (Found: C, 27.4; H, 1.9. $\text{C}_6\text{H}_5\text{O}_2\text{BrSe}$ requires C, 26.9; H, 1.9%). The sulphuric acid coloration was reddish-purple.

m-Xylene-4-seleninic acid, $(\text{CH}_3)_2\text{C}_6\text{H}_3 \cdot \text{SeO}_2\text{H}$, prepared by the general method of oxidation from the corresponding selenoglycollic acid, crystallised from water in colourless needles, decomp. 146—147° (Found: C, 44.0; H, 4.5. $\text{C}_8\text{H}_{10}\text{O}_2\text{Se}$ requires C, 44.2; H, 4.6%).

o-Xylene-4-seleninic acid crystallised from hot water in colourless needles, decomp. 125° (Found: C, 44.4; H, 4.7%).

The two xyleneseleninic acids developed deep blue colorations with warm concentrated sulphuric acid.

Di-o-tolyl selenide, $\text{Se}(\text{C}_7\text{H}_7)_2$, was prepared by the action of selenium on magnesium *o*-tolyl bromide and isolated during the preparation of *o*-tolylselenoglycollic acid after extraction of the ethereal solution of the selenomagnesium bromide with aqueous caustic potash. By repeated crystallisation from absolute alcohol, it was obtained in flat, colourless, shining plates, m. p. 64° (Found: C, 64.5; H, 5.5. $\text{C}_{14}\text{H}_{14}\text{Se}$ requires C, 64.4; H, 5.4%).