

small to permit a definite decision by comparison with the experimentally obtained ratios.

The colour reaction of TNM with many unsaturated compounds is currently used for detecting the presence of double bonds. The value of the test is somewhat restricted as no colour is obtained with some unsaturated compounds such as α,β -unsaturated acids. Coloured products are also formed with non-olefinic substances such as benzene and alkyl sulphides. It is evident that the light-induced radical reaction here described is sometimes more specific for the presence of olefinic double bonds than are the absorption spectra in the visible and ultraviolet of the complexes formed with TNM.

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Di-(hydroxyalkyl) Diselenides

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Di-(hydroxyalkyl) sulfides and disulfides have been known and studied over a long period. Thus di-(hydroxyethyl) disulfide was prepared as early as 1862 by F Guthrie¹, while the corresponding sulfide was prepared in 1886 by V Meyer². Considerable attention has since been paid to these compounds and some of their higher homologues have been obtained. By comparison the corresponding selenium compounds have been given much less attention. Only di-(hydroxyethyl) selenide has been prepared by Smedslund^{3,4} and while some

ether derivatives of di-(hydroxyethyl) diselenide have been prepared⁵ the diol itself has never been isolated.

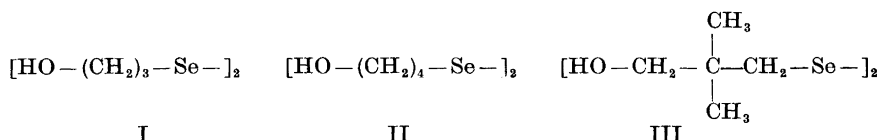
As part of an investigation of di-(hydroxyalkyl) diselenides which is being undertaken in this Institute, the compounds I, II, and III have been prepared by reacting halohydrines with sodium diselenide solution. The reaction is almost immediate and only a slight evolution of heat has been observed.

The lowest reaction rate was found in the preparation of III; this is clearly a consequence of steric hindrance in the hydroxyneopentyl group. Thus the two compounds with a straight carbon chain were obtained after shaking the components for a few minutes, while the hydroxyneopentyl derivative was obtained only after heating the reaction mixture on a water bath for some hours.

The compounds were obtained as red-yellow oils which are almost insoluble in water but which dissolve easily in chloroform and in a proportionately large amount of ether. They have characteristic, more or less unpleasant odours. They tend to decompose when attempts are made to purify them by fractionation. As the substances are very high-boiling, the temperature necessary to distil the substances has obviously reached the temperature known to decompose diselenides. Decomposition can be avoided and thus the yield raised by distilling in high-vacuum.

The products obtained have been identified by selenium analyses and by infra-red spectroscopy. A comparison of the spectra of the starting materials and the products shows that in all three cases the bands in the 3 and 9.5 μ ranges of $-\text{OH}$ are unchanged by the reaction. The absorption peaks arising from the carbon chains are not altered to such a degree that rearrangement may be suspected. In the region investigated, the Se-Se bond shows no absorption and in the long-wave region where this bond is expected giving an absorption band, nobody has so far been able to identify it.

A more detailed report on further compounds of this type is planned.



Experimental. Di-(3-hydroxypropyl) diselenide (I). A sodium diselenide solution was prepared by shaking 15.8 g (0.2 mole) of selenium, 8 g (0.2 mole) of sodium hydroxide, 15.4 g (0.1 mole) of sodium formaldehyde sulfoxylate, and 200 ml of water in a stoppered bottle for half an hour, and then adding 27.8 g (0.2 mole) of 3-bromopropanol-1. The bromohydrine reacted instantaneously and after shaking for a few minutes the water phase was colourless and a red-yellow oil had separated. The mixture was extracted with ether and the ether extract dried over sodium sulfate. After evaporating the ether, the residue was fractionated. During the distillation some decomposition was observed. The fraction boiling at 168–182°/0.2 mm was collected and found to weigh 15.2 g (52.5 %). When redistilled the product boiled at 160–170°/0.2 mm. n_D^{20} 1.5970. The product shows infra-red absorption peaks at 3.05, 3.49, 7.05, 8.05, 8.44, 8.80 μ . Found: Se 56.99. Calc. for $C_6H_{14}O_2Se_2$: Se 57.20).

Di-(4-hydroxybutyl) diselenide (II). A sodium diselenide solution was prepared by shaking 15.7 g (0.2 mole) of selenium, 8 g (0.2 mole) of sodium hydroxide, 15.4 g (0.1 mole) of sodium formaldehyde sulfoxylate, and 200 ml of water in a stoppered bottle for half an hour; 21.6 g (0.2 mole) of 4-chlorobutanol-1⁶ was then added and the mixture was shaken for half an hour. A slight rise of temperature was observed during the reaction. The water phase was then colourless and a red-yellow oil had separated. The reaction mixture was extracted with ether and the ether extract was dried over sodium sulfate. After evaporating the ether, the residue was fractionated. During the distillation some decomposition was observed. The main fraction boiled at 182–187°/0.1 mm and weighed 15.2 g (51 %). n_D^{20} 1.5500. The red-yellow, viscid oil had an extremely unpleasant odour. The product shows infra-red absorption peaks at 3.05, 3.46, 6.92, 7.75, 8.11, 8.45, 9.40, 9.67, 13.35, 13.85 μ . (Found: Se 52.27. Calc. for $C_8H_{18}O_2Se_2$: Se 51.92).

Di-(3-hydroxy-2,2-dimethylpropyl) diselenide (III). A sodium diselenide solution was prepared by shaking 7.9 g (0.1 mole) of selenium, 4 g (0.1 mole) of sodium hydroxide, 7.7 g (0.05 mole) of sodium formaldehyde sulfoxylate, and 100 ml of water in a stoppered bottle

for half an hour. The solution was placed in a flask with a mechanical stirrer and a reflux condenser and 16.7 g (0.1 mole) of 3-bromo-2,2-dimethylpropanol-1⁷ was added. The mixture was heated with stirring on a boiling water bath for 4 h. The water phase was then colourless and a red-yellow oil had separated. The reaction mixture was extracted with ether and the ether extract dried over sodium sulfate. After the ether was evaporated the residue was fractionated. The main fraction, which crystallized in the condenser, boiled at 170–180°/0.2–0.3 mm and weighed 9.8 g (59 %). The product, that was red-yellow, on recrystallization from cyclohexane yielded bright yellow crystals in featherlike aggregates, melting at 46–47.5°. The product shows infra-red absorption peaks at 2.95, 3.42, 6.81, 7.24, 7.34, 8.12, 8.70, 9.60, 9.90, 10.20, 11.19, 12.34 μ . (Found: Se 47.29. Calc. for $C_{10}H_{22}O_2Se_2$: Se 47.54).

The selenium analyses were carried out according to Fredga⁸.

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