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Organic Selenium Compounds

II. Preparation of Tetraalkylselenoureas

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In a study of the infrared spectra of thioamides and selenoamides we were interested in comparing the infrared spectra of tetraalkylthioureas and tetraalkylselenoureas. The latter had not hitherto been prepared. Since dialkylselenocarbamoyl chlorides are unknown the selenoureas could not be prepared in a similar manner as the corresponding thioureas. However, an obvious method to try was the reaction of a tetraalkylurea with phosphorus pentaselenide. Curiously enough, the preparation of thioureas from ureas and phosphorus pentasulfide do not seem to have been reported, so we first tried to prepare thioureas in this way to see whether there were some unexpected difficulties connected with this method. However, tetraethylthiourea was prepared in good yield from tetraethylurea and phosphorus pentasulfide. This may well be a convenient method of preparing tetraethylthiourea because the reaction of diethylthiocarbamoyl chloride with diethylamine has, in our hands, repeatedly yielded a tetraethylthiourea which was difficult to purify. That the method is not restricted to tetraalkylthioureas was shown by the preparation of benzylthiourea from benzylurea; however, for the preparation of mono-, di-, and trialkylthioureas other methods will usually be more convenient.

For the preparation of the thioureas the urea was treated with phosphorus pentasulfide in pyridine solution. This method could, however, not be used to prepare the selenoureas, because these are very sensitive to treatment with water and acid. Instead, the urea was refluxed with phosphorus pentaselenide in benzene solution. This reaction is very slow, and even after reflux for one week only a few percent of the urea had been transformed into the selenourea. However, in this way we succeeded in preparing tetramethylselenourea as a beautifully crystalline compound. It is possible that a higher yield may be obtained by another method; since, however, we were only interested in having a small sample of the pure compound, we found the method used wholly satisfactory.

Tetraethylurea yielded, in a similar manner, an oil which according to its infrared spectrum was fairly pure tetraethylselenourea. Attempts at high vacuum distillation caused complete decomposition with the formation of red selenium.

Experimental. Tetraethylthiourea. To a solution of tetraethylurea (25 g) in pyridine (50 ml), phosphorus pentasulfide (25 g) was added with stirring and the mixture was refluxed for 3 h. After cooling, the pyridine solution was decanted from the solid mass and extracted with ether. The ethereal solution was washed several times with water, then with dilute (*ca.* 0.1 N) hydrochloric acid and finally, again, with water. The solution was dried over $MgSO_4$, the ether removed by evaporation and the oily residue distilled *in vacuo*. Yield 11.5 g (45.5 %) of a colourless oil with b.p. 93–95°C at 0.8 mm Hg. (Found: C 57.20; H 10.84; N 15.17. Calc. for $C_9H_{20}N_2S$: C 57.45; H 10.64; N 14.90). Tetraethylselenourea could *not* be prepared in this manner.

Tetramethylselenourea. Finely ground phosphorus pentaselenide (11.5 g) was added to a solution of tetramethylurea (11.6 g) in carefully dried benzene (30 ml) and the mixture was heated with reflux in nitrogen atmosphere for 72 h. The mixture was filtered after cooling and benzene, excess tetramethylurea, and other volatile products were removed *in vacuo*, first at 10 mm Hg and finally at 0.1 mm Hg. On standing in a refrigerator, the residue formed oily yellowish crystals (yield 1.0 g, 5.6 %). On recrystallisation twice from hexane with addition of active carbon, colourless crystals with m.p. 78—79°C were obtained. (Found: C 33.80; H 6.86. Calc. for $C_5H_{12}N_2Se$: C 33.52; H 6.77). The compound is very sensitive to humidity and rapidly turns reddish in air; it should be kept in a sealed ampoule filled with nitrogen.

An analogous experiment with tetraethylurea yielded an oily residue which, after dissolving in hexane, filtering from some red selenium, and removal of the hexane, yielded 1.4 g of an almost colourless oil, which did not crystallise on cooling at −80°C. The infrared spectrum of the purified oil in CS_2 and CCl_4 indicated it to be tetraethylselenourea; however, attempts at distillation in a micro-apparatus under high vacuum caused complete decomposition with the formation of red selenium.

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