A New Synthesis of 1,1,3,3-Tetramethyl-2-selenourea

By DANIEL L. KLAYMAN* and ROBERT J. SHINE

(*Division of Medicinal Chemistry, Walter Reed Army Institute of Research, Washington, D.C.* 20012)

THE synthesis of 1,1,3,3-tetramethyl-2-selenourea (I) was recently accomplished by Jensen, Felbert, and Kägi[1] by refluxing 1,1,3,3-tetramethylurea in anhydrous benzene with phosphorus pentaselenide for three days. Compound (I) was obtained as an air- and moisture-sensitive material in 5·6% yield.

We have developed a simple preparation of the selenourea (I) in good yield from 1,1,3,3-tetramethyl-2-thiourea (II). The latter was treated with methyl iodide in ethanol solution to give a quantitative yield of *S*-1,1,3,3-pentamethylisothiouronium iodide (III).[2] This *S*-methyl derivative was dissolved in 1 equiv. aqueous ethanolic sodium hydrogen carbonate, added immediately to an aqueous–ethanolic solution containing *ca.* 2 equiv. sodium hydroselenide,† and left at room temperature for *ca.* 17 hr. The solution was slowly acidified with 6N-sulphuric acid while nitrogen was passed through to dispel the hydrogen selenide and methyl mercaptan liberated. The small quantity

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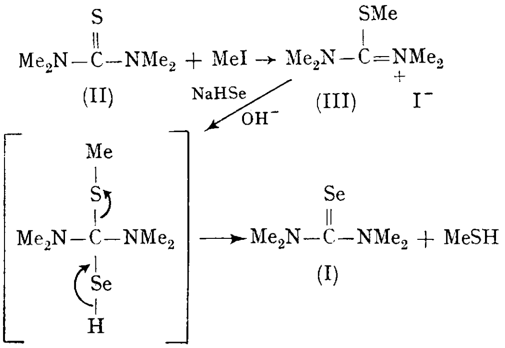
† Hydrogen selenide, prepared by the dropwise addition of 6N-sulphuric acid to 2 equiv. of powdered Al_2Se_3, was passed into an aqueous–ethanolic solution of 2 equiv. of sodium hydrogen carbonate at 0° to give a solution of sodium hydroselenide.

of elemental selenium present was removed by filtration; the colourless filtrate was concentrated to near dryness under reduced pressure at *ca.* 80° and cooled. White selenourea (I) (70%) was obtained which, after recrystallization from hexane, was surprisingly stable in air, m.p. 79—81° (lit.,[1] m.p. 78—79°). The selenourea was further identified by elemental analysis and its i.r. spectrum (KBr pellet) which showed bands at 1517, 1360, 1375, 1085, and 920 cm.$^{-1}$, in agreement with those reported by Jensen and Nielsen.[3] The n.m.r. spectrum‡ of the material exhibited a single peak at δ 3·16 (NMe).



This method has been applied to the preparation of other selenoureas by the displacement of methyl mercaptan from the *S*-methyl derivative of thiourea, as well as mono-, di-, and tri-substituted thioureas by the action of hydroselenide.

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‡ Determined on a Varian A-60 spectrometer as a 25% solution in CDCl$_3$ using Me$_4$Si as an internal standard.

[1] K. A. Jensen, G. Felbert, and B. Kägi, *Acta Chem. Scand.*, 1965, **20**, 281.
[2] H. Lecher and C. Heuck, *Annalen.*, 1924, **438**, 169.
[3] K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, 1966, **20**, 597.