

δ 4.6 (3H), multiplets, H-5, H-6, H-6'; δ 5.00 (1H), $J < 1$ Hz, H-1; δ 5.25 (1H), multiplet, H-2; δ 6.12 (2H), multiplets, H-3 and H-4; δ 7.3–7.6 and 8.0–8.2 (10H) aromatic protons. These tentative NMR assignments are based on shift considerations (aromatic protons, H3- and H-4 olefinic protons, low-field signal for H-2 on benzyloxyated carbon) and upon the observation of the lanthanide induced shifts¹¹ caused by the successive addition of tris(dipivaloylmethanato) europium, which *inter alia* caused substantial down-field shift changes of the presumed H-2, H-6, and H-6' signals. The latter two signals became clearly differentiated. The down-field shift change of H-6 and H-6' clearly revealed H-5 as a multiplet at higher field; its coupling pattern showed coupling to three protons, excluding the possibility of the compound being a 4,5-hexenopyranoside. The small coupling constant of H-1 precludes the presence of a 2,3-hexenopyranoside, which for an α -D-glycoside would have $J_{1,2} = 2-3.5$ Hz¹² as displayed by III. The small coupling constant for H-2 and the above considerations indicate instead, the presence of a 3,4-hexenopyranoside, tentatively identified as methyl 2,6-di-O-benzoyl-3,4-dideoxy- α -D-threo-hex-3-enopyranoside V.

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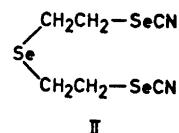
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The Reaction between Bis(2-bromoethyl)selenide and Potassium Selenocyanate

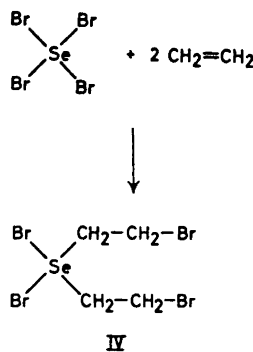
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Aliphatic selenocyanates are most conveniently synthesized by reacting the corresponding alkyl halide with potassium selenocyanate in acetone or ethanol.¹ The reaction between bis(2-bromoethyl) selenide (I) and potassium selenocyanate, however, did not give the expected bis(2-selenocyanatoethyl) selenide (II). The main product consisted of diselenocyanatoethane (III). Elemental selenium was also isolated from the reaction mixture.



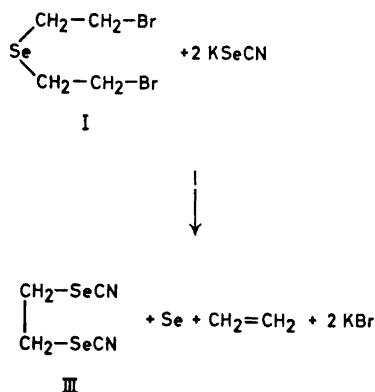
Bis(2-bromoethyl) selenide (I) has been subjected to some decomposition reactions and has been found to be a rather unstable compound. In several cases one of the decomposition products has been ethylene.² In order to investigate whether ethylene is produced also in this case, the gas evolved during the reaction was allowed to pass through a solution of selenium tetra-



Scheme 1.

bromide in benzene. After termination of the reaction it was possible to isolate yellow crystals of bis (2-bromoethyl) selenide dibromide (IV) from the benzene solution of selenium tetrabromide (Scheme 1).³

The stoichiometry of the reaction agreed well with that of Scheme 2. No quantitative estimation of the amount of ethylene evolved has been made.

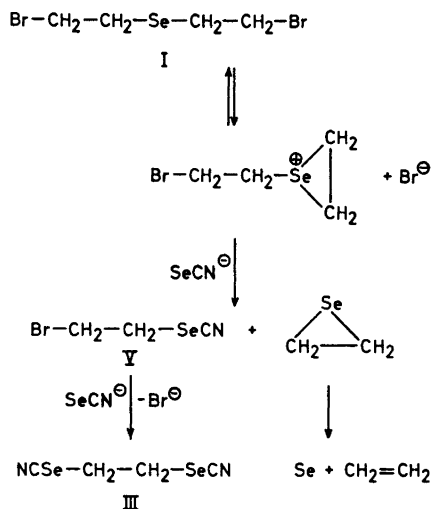


Scheme 2.

When repeating the reaction between bis(2-bromoethyl) selenide (I) and potassium selenocyanate using equimolar amounts of the starting materials, it was possible to isolate 1-bromo-2-selenocyanatoethane (V) from the reaction mixture.

With support from the above experiments and from investigations made on mustard gas (bis(2-chloroethyl) sulfide),^{4,5} the following reaction mechanism is proposed (Scheme 3).

The first step in this proposed reaction mechanism consists, quite analogously with the mustard gas case, of an intramolecular attack of the selenium atom on the 2-carbon atom producing a three-membered cyclic selenonium ion. This ion is attacked by a selenocyanate ion giving 1-bromo-2-selenocyanatoethane (V) and ethylene selenide. The intermediate V will undergo further reaction with selenocyanate ion giving diselenocyanatoethane (III). Ethylene selenide being unstable



Scheme 3.

decomposes to give selenium and ethylene.⁶

A more detailed investigation of this reaction is now being made and will be published later.

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