Tetrahedron Letters No. 49-50, pp 4347 - 4350, 1974. Pergamon Press. Printed in Great Britain.

NUCLEOPHILIC SUBSTITUTION REACTIONS OF β-SUBSTITUTED SELENIDES.

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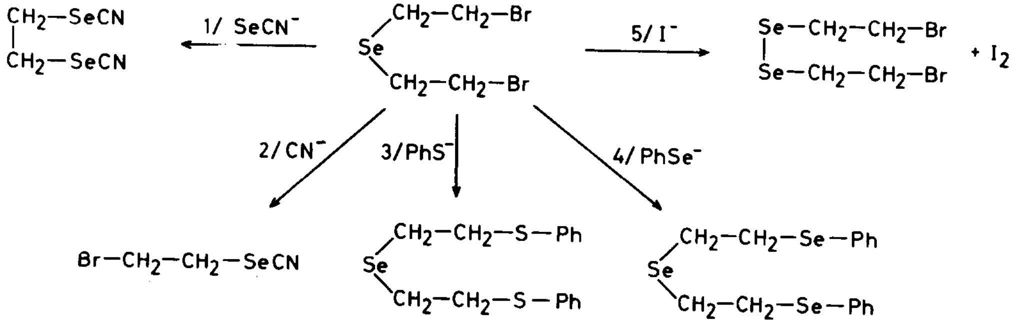
(Received in UK 9 October 1974; accepted for publication 30 October 1974)

As has been reported earlier[1] the reaction between bis(2-bromoethyl) selenide and the selenocyanate ion gives diselenocyanatoethane,ethylene and elemental selenium as products. The reaction has been performed in a number of solvents : for example,acetone,DMF,DMSO and ethylacetate,giving diselenocyanatoethane in varying yields. Bis(2-chloroethyl) selenide has also been used as substrate for this reaction,giving the same products as mentioned above.

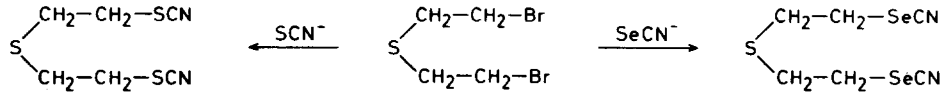
A number of nucleophiles have now been allowed to react with bis(2-bromoethyl) selenide, giving different products (Scheme 1).



(In reactions 1,2 and 5 formation of ethylene took place during the reaction)

Scheme 1.

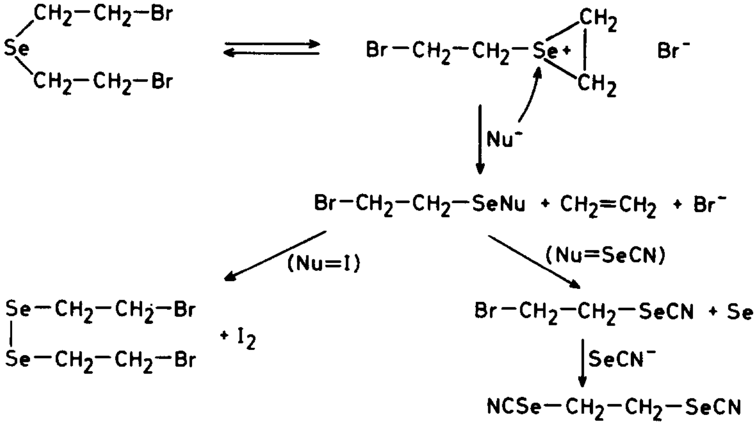
For the sake of comparison the reaction between bis(2-bromoethyl) sulfide and thiocyanate[2],as well as selenocyanate ion have been studied. In both cases the normal substitution products have been obtained (Scheme 2).



Scheme 2

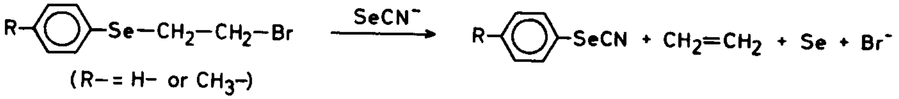
Reactions 3 and 4 in scheme 1 give normal substitution products. The problem is now to propose a mechanism for reactions 1,2 and 5.

In the preceding paper[1] a mechanism was proposed for the reaction between bis-(2-bromoethyl) selenide and selenocyanate ion. The first step in that mechanism consisted of the formation of a cyclic selenonium ion followed by attack by the nucleophile on the carbon α to the positive selenium atom to give 1-bromo-2-selenocyanatoethane and episelenide. This mechanism cannot however explain all the reactions in scheme 1. Reactions 1,2 and 5 can be satisfactorily explained if we presume that the nucleophilic attack takes place on the positive selenium atom of the selenonium ion (Scheme 3).



Scheme 3

The reactions between the analogous substrates (2-bromoethyl)-phenyl selenide and (2-bromoethyl)-p-tolyl selenide and selenocyanate ion have been studied. Ethylene was evolved in this case as well and selenium and the corresponding selenocyanates could be isolated (Scheme 4).

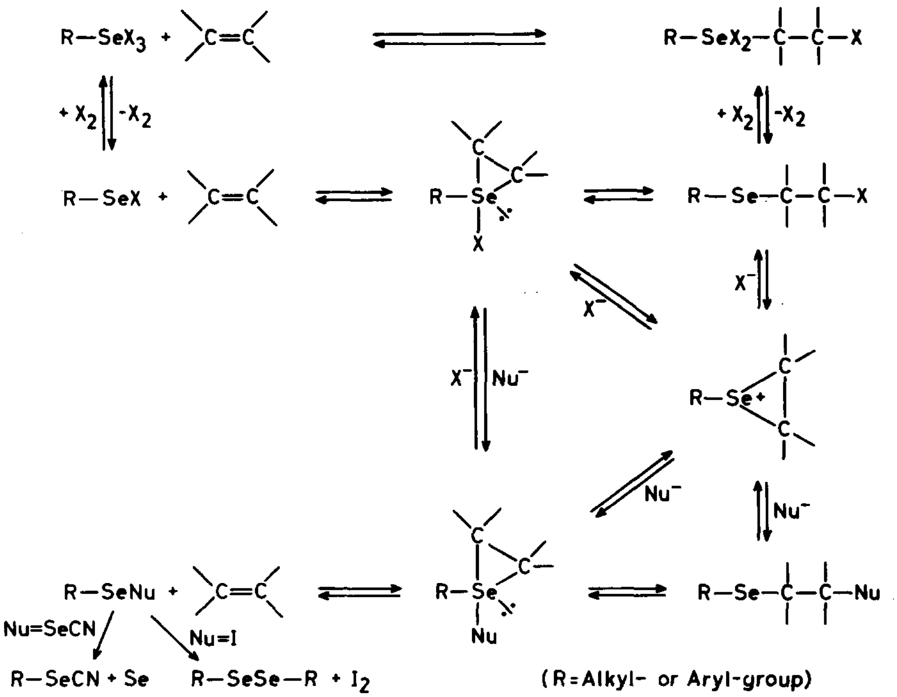


Scheme 4

When treating (2-bromoethyl)-phenyl selenide with iodide ion immediate formation of iodine and ethylene was observed,and diphenyldiselenide could be isolated from the reaction mixture. The results of the reactions using aromatic substrates could also be explained by attack of the nucleophile on the positive selenium atom of a cyclic selenonium ion.

The formation of cyclic selenonium ions as intermediates has up to now been proposed only sparingly. In the works of F. Lautenschlaeger[3], C.D. Hurd and O.Fancher[4] and H.J. Reich[5] episelenonium ions are, however, mentioned as intermediates. In contrast to this, episulfonium ions are frequently discussed as intermediates, for example in the work of P.D. Bartlett and C.G. Swain[6] on bis(2-chloroethyl) sulfide. A number of stable episulfonium salts have also been synthesized, which have been subjected to nucleophilic substitution reactions giving competing attack on positive sulfur as well as on carbon[7], in the same way as in this work. During these nucleophilic substitution reactions an intermediate has been detected, the structure of which has been proposed to be an episulfurane[8]. Quite recently an analogous episelenurane has been isolated when reacting p-tolueneselenenyl chloride with ethylene[9]. The episelenurane isomerizes on standing to give (2-chloroethyl)-p-tolyl selenide. The addition of a selenenyl halide over ethylene can be considered the reverse of the nucleophilic substitution reactions mentioned here, that give ethylene as a product. An episelenurane could also be proposed as an intermediate in this case, based on the principle of microreversability, although no such intermediate has been isolated. A general scheme encompassing all the reactions discussed here will now be presented (Scheme 5). A scheme concerning analogous reactions in sulfur chemistry has earlier been proposed by G.K. Helmkamp[10]. The addition of selenium trihalides over a double bond demonstrated in scheme 5 does not necessarily mean a direct addition. An equilibrium between selenium trihalide and selenenyl halide could first be established whereupon the selenenyl halide would act as the electrophile and the product formed would then be trapped by free halogen[11]. A number of reactions published in earlier papers[3,4,5,12,13] as well as the new nucleophilic reactions discribed here may well be explained in terms of scheme 5 if suitable relative rates and equilibrium constants are asumed. A more detailed account of this work will be published later.

Acknowledgement: I thank Prof. G.Bergson and Dr. L-B. Agenäs for valuable discussions and for their interest in this project.



Scheme 5

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