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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

THE SOLVOLYSIS AND NUCLEOPHILIC SUBSTITUTION IN SERIES OF CYCLIC HALOGENALKYLISOTHIOUREAS

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To cite this Article Fedoseev, V. M. , Churilin, V. S. and Tkachenko, S. E.(1979) 'THE SOLVOLYSIS AND NUCLEOPHILIC SUBSTITUTION IN SERIES OF CYCLIC HALOGENALKYLISOTHIOUREAS', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 6: 1, 87 — 88

To link to this Article: DOI: 10.1080/03086647908080317

URL: <http://dx.doi.org/10.1080/03086647908080317>

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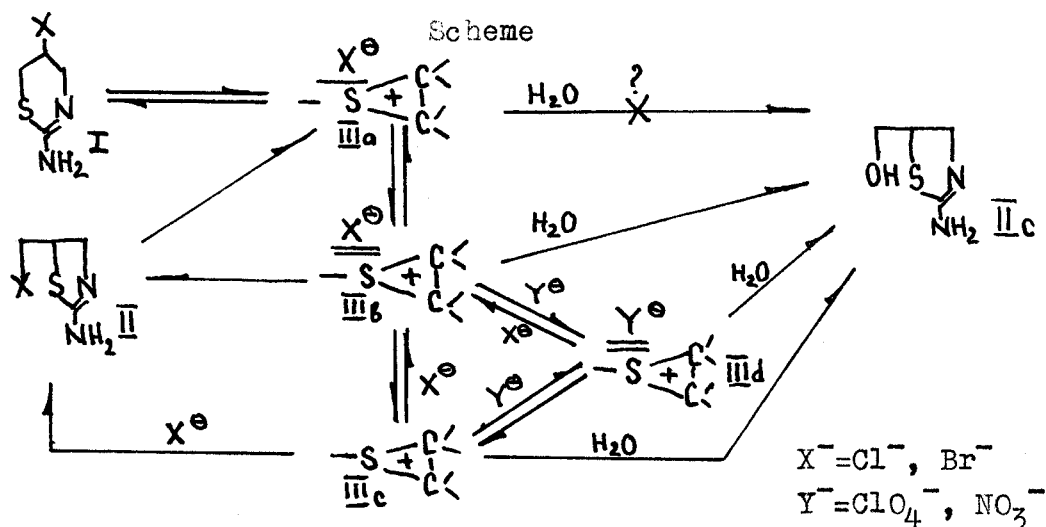
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THE SOLVOLYSIS AND NUCLEOPHILIC SUBSTITUTION IN SERIES OF CYCLIC HALOGENALKYLISOTHIUREAS

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Previously we reported ¹, that solvolytic rearrangement of salts and bases of 2-amino-5-X-5,6-dihydro-4H-1,3-thiazines /I a,b/, where a X=Cl, b X=Br/ proceeds with a contraction of cycle and results in salts and bases of 2-amino-5-X-methyl-2-thiazolines /II a-c/, where a X=Cl, b X=Br, c X=OH/. The reversibility of this reaction is shown now. It was found by means of radiochromatography that hydrolysis of ³⁵S-labelled IIb bromide gives rise to rearranged Ib besides hydrolytic product IIc. It was shown, also, that the solvolysis of salts IIa,b in 50% aqueous ethanol, when excess of Na³⁶Cl is present, gives both ordinary substitution products and certain amount of rearranged Ia. In the course of ³⁵S-labelled IIb bromide solvolysis in the same conditions the return of bromide ions takes place. It was found that the addition of salts affects the composition of Ib bromide hydrolysis products. This testifies that the composition of reaction products depends on the episulphonium III form present in the medium / scheme /. It is possible, that the formation of covalent system I is most probably due to internal return from IIIa, but covalent form II results from the other steps of the dissociation. This is confirmed by absence 2-amino-5-hydroxy-5,6-dihydro-4H-1,3-thiazine in reaction mixture. The addition of NaClO₄ and NaNO₃ suppresses bromine ions return owing to ion exchange resulting in new external pair IIId, what leads to the increase of the relative amount of IIc. On the other hand the addition of KBr and NaCl decrease the amount of IIc, due to the increase of the degree of ions return and the probability of halogen ions attack to episulphonium III.



The effective rate of rearrangement does not depend on the rate of exchange reaction. The main factor restricting velocity of process is the pH of medium. The addition of KBr and NaCl does not affect essentially the reaction rate, but the presence of NH_4Br , HCl slow it down. It had been shown², that the kinetic of base Ia solvolysis is in accordance with the mechanism of a reaction including the participation of neighbouring sulfur atom. On the other hand IIa,b salts are capable to enter into S_N -reaction without promotion of sulfur atom while the IIa,b bases react with considerable anchimeric assistance / nucleophils: Cl^- , H_2O , thiourea/. Thus, the sulfur atom participation in S_N -reaction and solvolysis of haloalkylisothioureas is possible when amidyne group of the substrate molecule is deprotonated.

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