

This article was downloaded by:

On: 28 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## 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>

### $\alpha$ -Halothioketones

M. G. Voronkov; L. G. Shagun; I. A. Dorofeev; T. L. Usova; V. A. Shagun

**To cite this Article** Voronkov, M. G. , Shagun, L. G. , Dorofeev, I. A. , Usova, T. L. and Shagun, V. A.(1997) ' $\alpha$ -Halothioketones', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 341 — 342

**To link to this Article:** DOI: 10.1080/10426509708545539

**URL:** <http://dx.doi.org/10.1080/10426509708545539>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

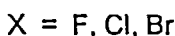
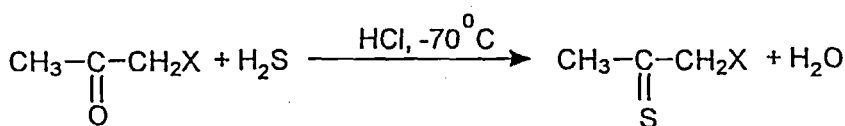
## $\alpha$ -HALOTHIOKETONES

M.G. Voronkov, L.G. Shagun, I.A. Dorofeev, T.L. Usova, and V.A. Shagun

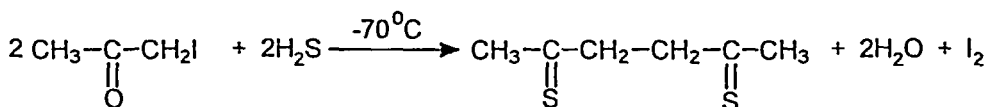
Irkutsk Institute of Organic Chemistry, Siberian Division of the  
 Academy of Sciences of Russia, Irkutsk, 664033, Russia

Thioketones and thioaldehydes having a halogen atom in the  $\alpha$ -position with respect to the thiocarbonyl group have not been known before our research.

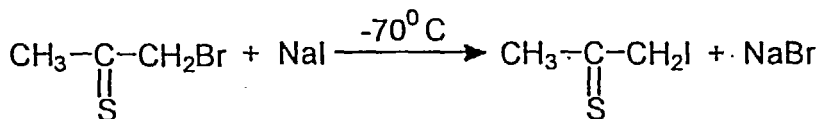
We have developed a method for the preparation of 1-halo-2-propanethiones, the first representatives of  $\alpha$ -halothioketones, by hydrothiolysis of haloacetones with a mixture of hydrogen sulfide and hydrogen chloride at  $-70^\circ\text{C}$  in the absence of solvent:



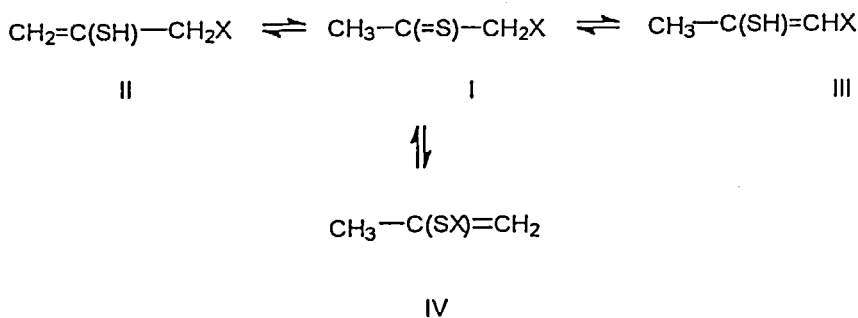
An attempt to prepare iodo-thioacetone under analogous conditions turned out to be unsuccessful. Instead of the above compound an unstable 2,5-hexanedithione has been isolated.



This reaction provides a new unexpected pathway to the formation of the C-C bond. We managed to synthesize iodo-propanethione by exchange reaction of bromo-thioacetone with sodium iodide in acetone at  $-70^\circ\text{C}$ .



The activation parameters and relative stability of halothioacetones were estimated by semiempiric AM1 and PM3 methods in accordance with potential intramolecular 1,3-sigmatropic rearrangements:

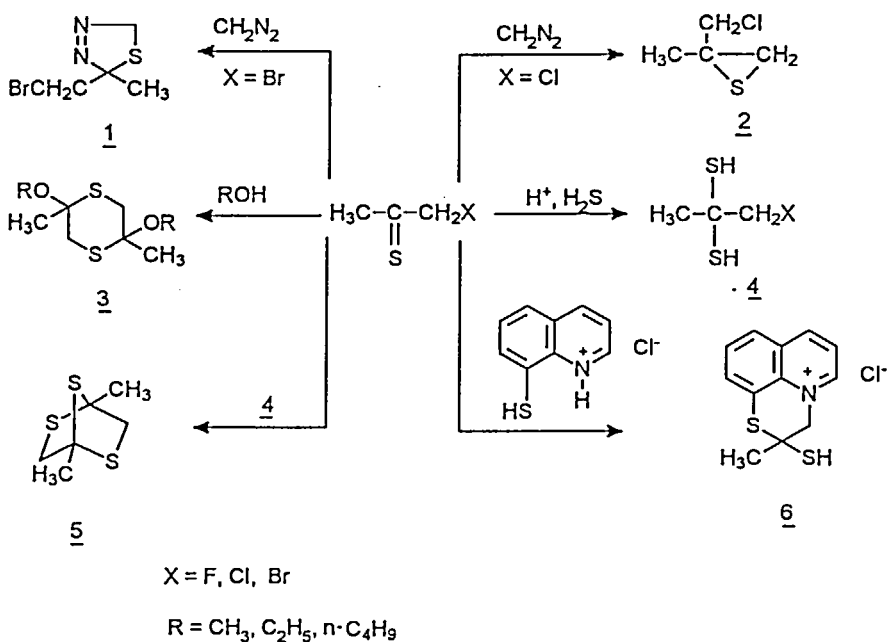


The calculated steady-state energies of gas-phase rearrangements allowed the relative stability sequence for certain sigmatropic forms to be drawn up:

IV > III > II > I (fluoro-, chloro- and bromo-thioacetones);

III > II > IV > I (iodo-thioacetone).

The halothioacetones present convenient synthons for the preparation of derivatives of thiadiazoline (1), thiirane (2), 1,4-dithiane (3), 1-halo-2,2-propanedithiols (4), trithianornbornane (5), tetrahydrothiazinoquinolinium salts (6).



Further investigation of the chemistry of  $\alpha$ -halothioketones is in progress.