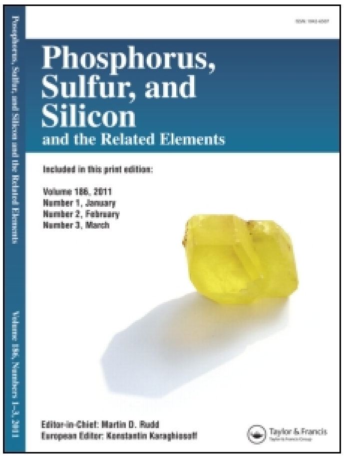
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Variety of Products from the Reaction Between Selone Donors and Halogen/Interhalogen Acceptors: The Case of *N*-Methylthiazolidine-2(3H)-Selone and *N*-Methylbenzo-Thiazole-2(3H)-Selone.

Francesco Demartin; Francesco A. Devillanova; Francesco Isaia; Vito Lippolis; Gaetano Verani

To cite this Article Demartin, Francesco , Devillanova, Francesco A. , Isaia, Francesco , Lippolis, Vito and Verani, Gaetano(1998) 'Variety of Products from the Reaction Between Selone Donors and Halogen/Interhalogen Acceptors: The Case of *N*-Methylthiazolidine-2(3H)-Selone and *N*-Methylbenzo-Thiazole-2(3H)-Selone.', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 283 — 286

To link to this Article: DOI: 10.1080/10426509808545951

URL: http://dx.doi.org/10.1080/10426509808545951

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.

Phosphorus Sulphur and Silicon
Vols. 136, 137 & 138 pp. 283–286
Reprints available directly from the publisher
Photocopying permitted by license only

© 1998 OPA (Overseas Publishers Association) N.V.
Published by license under the
Gordon and Breach Science Publishers imprint
Printed in Malaysia

Downloaded At: 16:23 28 January 2011

VARIETY OF PRODUCTS FROM THE REACTION BETWEEN SELONE DONORS AND HALOGEN/INTERHALOGEN ACCEPTORS: THE CASE OF *N*-METHYLTHIAZOLIDINE-2(3H)-SELONE AND *N*-METHYLBENZO-THIAZOLE-2(3H)-SELONE.

FRANCESCO DEMARTIN,[a] FRANCESCO A. DEVILLANOVA,[b,*] FRANCESCO ISAIA,[b] VITO LIPPOLIS[b] AND GAETANO VERANI[b]
[a]Istituto di Chimica Strutturistica Inorganica e Centro CNR, Università di Milano, Via G.Venezian 21, I-20133 Milano, Italy; [b]Dipartimento di Chimica e Tecnologie Inorganiche e Metallorganiche, Università di Cagliari, Via Ospedale 72, I-09124, Cagliari, Italy.

The great variety of products obtained from the reaction between selone donors and halogens (I_2, Br_2) or interahogens (IBr, ICl) is reported for the Title compounds as starting molecules. The characterization of these products by either X-ray crystal structure or Raman spectroscopy evidentiates the latter technique to be not always sufficient in identifying the nature of the products unambiguosly.

Keywords: donor/acceptor; halogens; interhalogens; selone donors

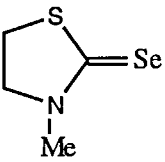
INTRODUCTION

For some time we have been interested in the donor/acceptor interaction between sulphur- or selenium-containing donors with acceptors

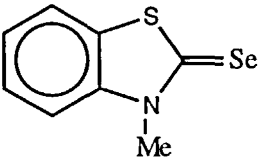
Downloaded At: 16:23 28 January 2011

of different strengths, such as I_2, Br_2, IBr, and ICl .[1-6] The characterization of the solid products obtained in this type of reaction both by X-ray structural determination and by Raman spectroscopy is particularly important in the field of conducting materials. In fact, halogens and interhalogens are generally used for the doping of several materials, and often the charge induced on the donor molecules is calculated on the basis of the nature of the halogen in the final product. In the case of non crystalline compounds, in the literature this is done by an extensive use of Raman spectroscopy.[7,8] However, since a great variety of different compounds can be obtained in these reactions, the correlation between the structural and vibrational features of innumerable different compounds can be very useful in ascertaining whether Raman spectroscopy always gives a clear indication of the products.

For this reason, we have undertaken a systematic characterization study by X-ray and vibrational spectroscopies of a large number of crystalline products, using mainly thionic and selonic compounds as starting materials. In the context of this research, we wish to present the solid products obtained by reacting the Title donors, i.e. *N*-methylthiazolidine-2-selone (**1**) and *N*-methylbenzothiazole-2-selone (**2**) with I_2, Br_2, IBr and ICl in CH_2Cl_2 solution, in 1:1 and 1:2 donor/acceptor molar ratios



(1)



(2)

in order to show the great variety of products obtainable in the reaction between selonic substrates and halogens or interhalogens.

Downloaded At: 16:23 28 January 2011

Except for the reactions with ICl, in which only the simple adducts are isolated in both ratios for **1** and for **2**,[9] in all the other cases the reactions generally give different products. In fact, while with diiodine **1** gives the 1:1 adduct in both ratios,[2] in the 1:1 molar ratio[1] the benzoderivative **2** gives a complex of I^+ and surprisingly, in the 1:2 molar ratio,[2] a simple adduct $\mathbf{2}\cdot 2I_2$ with the second diiodine molecule interacting with the first. The reactions with dibromine have reserved some surprises. In fact, while the reaction of **2** always gives the expected hypervalent selenium compound, **1** gives this type of compound only in the 1:1 molar ratio.[10] Unexpectedly, for the 1:2 molar ratio, a ionic compound is formed by breaking of the C=Se bond and oxidation of the selenium atom to hexabromoselenate ion.[10]

Also the reactions of the two substrates with IBr have reserved some unexpected results.[2] As with ICl, in the 1:1 molar ratio, simple adducts have been isolated for both donors; however, in the 1:2 molar ratio, in the case of **1**, increasing amount of IBr determines an increasing substitution of the terminal bromine with iodine (crystals corresponding to the formula $\mathbf{1}\cdot I_{1.25}Br_{0.75}$ have been obtained from 1:2 molar ratio);[2] for **2**, the second IBr molecule interacts so strongly with the first, that the product can be considered an ionic compound formed by a cation having a Se-I terminal bond interacting with an IBr_2^-. This formulation is suggested not only by the crystal data, but also by the analogy of the FT-Raman peaks of this compound with those reported for other IBr_2^- ions.[2]

Considering only the reaction between several selonic donors with diiodine,[1,2,4-6,9-10] we have identified the following types of compounds: simple C.T. complexes, C.T. complexes weakly interacting with other diiodine molecules to form networks of diiodine molecules, reduction of diiodine with formation of a great variety of polyiodides, hypervalent compounds, dications and iodonium salts. In our studies, we have shown the importance of the X-ray crystal structure determination for the identification of all these compounds.

The contemporary characterization of all the obtained compounds by X-ray diffraction and by Raman spectroscopy has evidentiated that the latter technique is not always able to identify unambiguosly the nature of the final products. In fact, in the case of 1,3-dimethyl-4-imidazolin-2-ylium diiodo selenanide,[4] which is a hypervalent selenium compound, a Raman peak at 106 cm^{-1} is observed; this frequency is very close to that reported as characteristic of triiodides.[8] On the other hand, in the case of 5,5-dimethyl-2-methylthio-4-oxoimidazolidinium triiodide,[11] which contains a very asymmetric triiodide, a peak at 167 cm^{-1} is observed, similar to those found for higher polyiodides. Hence, Raman spectroscopy should be used with extreme caution in the identification of the products coming from donor/acceptor interaction.

Downloaded At: 16:23 28 January 2011

References

[1.] F. Demartin, P Deplano, F. A. Devillanova, F. Isaia, V. Lippolis and G. Verani, *Inorg.Chem.*, **32**, 3694 (1993);
[2.] F. Cristiani, F. Demartin, P Deplano, F. A. Devillanova, F. Isaia, V. Lippolis and G. Verani, *Inorg.Chem.* , **33**, 6315 (1994).
[3.] P. Deplano, F. A. Devillanova, J.R. Ferraro, V. Lippolis, M.L. Mercuri, and E.F. Trogu, *Applied Spectroscopy*, **48**,1236 (1994)
[4.] F. Bigoli, M. A. Pellinghelli, P. Deplano, F. A. Devillanova, V. Lippolis, M. L. Mercuri and E. F. Trogu, *Gazz. Chim. It.,* **124**, 445 (1994)
[5.] F. Bigoli, F. Demartin, P. Deplano, F. A. Devillanova, F. Isaia, V. Lippolis, M. L. Mercuri, M. A. Pellinghelli and E. F. Trogu, *Inorg. Chem.*, **35**, 3194 (1996)
[6.] F. Demartin, F. A. Devillanova, F. Isaia, V. Lippolis and G. Verani, *Inorg. Chim. Acta,* **255**, 203 (1997)
[7.] J. R. Ferraro and J. M. Williams, "The Use of Vibrational spectroscopy in the Characterization of Synthetic Organic Electrical Conductors and Superconductors" in *Practical Fourier Transform Infrared Spectroscopy*, J. R. Ferraro and K. Krishanan, Eds. (Academic Press, New York, 1990), Chap.2, p.66
[8.] R. C. Teitebaum, S. L. Ruby and T. J. Marks, *J. Am. Chem. Soc.*, **102**, 3322 (1980)
[9.] F. A. Devillanova, F. Isaia, V. Lippolis, S. Piludu, G. Verani and F. Demartin, in preparation.
[10.] F. Demartin, F. A. Devillanova, P. Deplano, F. Isaia, V. Lippolis, M. L. Mercuri, S. Piludu and G. Verani, *Polyhedron*, in press (1997)
[11.] F. Cristiani, F. A. Devillanova, F. Isaia, G. Verani, L. Battaglia and A. Bonamartini Corradi, *J. Chem. Research (S)*, 32 (1989)