

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>

Alkoxy Isothiocyanates - a New Class of Isothiocyanates a Flash Vacuum Pyrolysis Study

Carl Th. Pedersen; Allan T. Bech; Robert Flammang; Curt Wentrup

To cite this Article Pedersen, Carl Th. , Bech, Allan T. , Flammang, Robert and Wentrup, Curt(1999) 'Alkoxy Isothiocyanates - a New Class of Isothiocyanates a Flash Vacuum Pyrolysis Study', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 153: 1, 329 — 330

To link to this Article: DOI: 10.1080/10426509908546455

URL: <http://dx.doi.org/10.1080/10426509908546455>

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.

Alkoxy Isothiocyanates – a New Class of Isothiocyanates a Flash Vacuum Pyrolysis Study

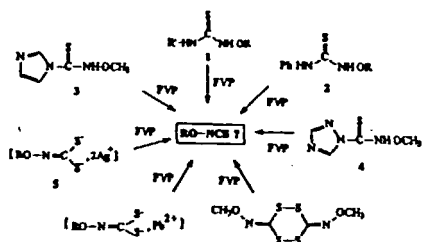
CARL TH. PEDERSEN^a, ALLAN T. BECH^a, ROBERT FLAMMANG^b
 and CURT WENTRUP^c

^aDepartment of Chemistry, Odense University, DK-5230 Odense M. Denmark,

^bOrganic Chemistry Laboratory, University of Mons-Hainaut, B-7000 Moss,
 Belgium and ^cDepartment of Chemistry, University of Queensland,
 Brisbane, Queensland 4072, Australia

The formation of methoxyisothiocyanate from a series of precursors such as silver salts of *N*-methoxydithiocarbamic acids, *N*-alkoxythioureas, *N*-methoxythiocarbamoyl imidazoles and -triazoles, alkoxyiminotrithiolanes and alkoxyiminotetrathianes. The formation of MeONCS was studied by FVP techniques where the pyrolysis products were isolated in an argon matrix at 10 K and studied by IR or the pyrolysis products were studied by MS

In addition to "normal" alkyl and aryl isothiocyanates several types of isothiocyanates with more unusual substituents such as alkoxycarbonyl, sulfonyl and dialkylamino groups are known. In a publication from 1920 [1] it is reported that the silver salt of *N*-methoxy dithiocarbamic acid upon heating gives off pungent smelling fumes. As it is well known that the thermal decomposition of metal salts of *N*-alkyl or *N*-aryl dithiocarbamic acids is a synthetic useful method for the preparation of isothiocyanates it is reasonable to assume that the pungent fumes could be methoxy isothiocyanate. We have therefore studied a series of possible precursors shown in the scheme for the synthesis of alkoxy isothiocyanates by a combination of FVP/MS and FVP/IR (matrix isolation) techniques.



Heterocyclic amides of the same type as 3 and 4 have been shown by Staab to be good thioacylation reagents [2]. Thioureas such as 1 and 2 have been shown to fragment thermally on both sides of the thiocarbonyl group [3]. The products of analytical FVP of such precursors were isolated in an Argon matrix at 10K. In most cases they show IR absorptions round 1900 cm^{-1} , *N,N*-dimethylamino isothiocyanate has ν_{NCS} at 2010 cm^{-1} . *Ab initio* calculations on methoxy isothiocyanate gives ν_{NCS} : $1860\text{--}1910\text{ cm}^{-1}$.

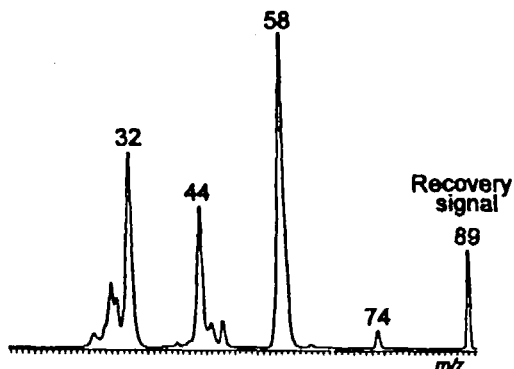


Fig. 1 Neutralization-reionization mass spectrum, NRMS of $\text{CH}_3\text{O-N=C=S}$ (m/z 89) ions, xenon and oxygen as collision gass.

Although it was not possible to obtain direct evidence for the formation of methoxy isothiocyanate from preparative FVP it is probably formed during the pyrolysis. By using tandem mass spectrometry we have been able to obtain evidence for the formation of methoxyisothiocyanate.

When the precursors for the methoxy isothiocyanate were pyrolysed in the ion source of the mass spectrometer abundant ions m/z 89 were observed corresponding to methoxy isothiocyanate. By recording the spectra at low ionization energies we have been able to obtain evidence that m/z 89 is not a fragment ion from the precursor but a molecular ion corresponding to thermal fragmentation of the precursor.

References

- [1] W. Traube, H. Olendorf and H. Zander, Ber. Deutsch. Chem. Gesell. 54 (1920), 1477.
- [2] H.A. Staab, G. Walther, Liebigs Ann. Chem. 657 (1962) 104.
- [3] H. Binder, Monatsh. Chem. 98 (1967) 431; R.H. Shapiro, J.W. Serum and A.M. Duffield, J. Org. Chem., 33 (1968) 243.