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

Seleno- and Tellurocarbenium Ions

Hansjörg Grützmacher; Grace Shiahuy Chen; Dietmar Ohlmann; Christina M. Marchand; Rainer Glaser

To cite this Article Grützmacher, Hansjörg , Chen, Grace Shiahuy , Ohlmann, Dietmar , Marchand, Christina M. and Glaser, Rainer(1998) 'Seleno- and Tellurocarbenium Ions', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1,287-290

To link to this Article: DOI: 10.1080/10426509808545952 URL: http://dx.doi.org/10.1080/10426509808545952

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. 287-290
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

SELENO- AND TELLUROCARBENIUM IONS

HANSJÖRG GRÜTZMACHER^a, GRACE SHIAHUY CHEN^a, DIETMAR OHLMANN^a, CHRISTINA M. MARCHAND, RAINER GLASER^b

^aETH-Zentrum, Universitätsstrasse 6, CH-8092 Zürich, email:gruetz@inorg.chem.ethz.ch; ^bUniversity of Missouri-Columbia, Department of Chemistry, 209 Chemistry Building, Columbia, Missouri 65211

Abstract: α -Chalcogeno substituted carbenium salts $[(RX)_3C]^+$ PF₆- $(X = S, Se, Te; R = 2,4,6-iPr_3C_6H_2)$ obtained from reaction of the copper complexes [(bipy)CuXR] with CBr₄ are stabilized to the same extent; but the electronic mechanism is very different.

<u>Keywords:</u> Carbenium Ions; Tellurium; Selenium; Stability; Ab initio calculations; Structures

INTRODUCTION

Stabilizing effects of chalcogeno centers are controversially discussed^[1]. The notion, that heteroatoms from the higher periods are poorer π -donors than their lighter congeners was repeatedly criticized^[2,3]. The influence of multiple substitution (n > 1) on the stability of ions [(HX)_nCH_{3-n}]⁺ (X = O, S, Se; n = 1-3) is little investigated^[4].

EXPERIMENTAL AND OUANTUM CHEMICAL RESULTS

We studied systematically chalcogeno carbenium ions $[(RX)_3C]^+$ as $CuBr_2^-(3a-c)$ or $PF_6^-(5a-c)$ salts and their corresponding methanes $(RX)_3CH$ (X = S, Se, Te) (8a-c) (Scheme 1)^[5].

SCHEME 1

Some selected physical data are given in Table I. The relative C-X bond shortening Δ in the ions, when compared to the methanes, slightly decreases S = Se > Te.

TABLE 1. Selected physical data for 3a-c and 8a-c						
•	CX _{exp} /CX _{cal}	Δ [%]	δ ¹³ C	δ ⁷⁷ Se/ ¹²⁵ Te	λ _{max} [nm]	
3a X=S	1.706 / 1.710	6.5	239.5		309	
3b X= Se	1.839 / 1.860	6.5	253.7	770	388	
3c X=Te	2.060 / 2.056	4.7	230.6	/ 1279	500	
8a X=S	1.817 / <i>1.821</i>		73.06		275	
8b X=Se	1.960 / <i>1.973</i>		39.77	280	300	
8c X=Te	2.156 / <i>2.169</i>		-64.24	/ 562	379	

Hydride transfer energies (HTE) and bond seperation energies (BSE) were calculated according to (1) and (2), respectively.

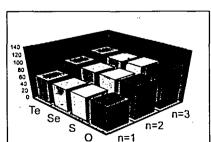
$$[(HX)_nCH_{3-n}]^+ + CH_4 \rightarrow (HX)_nCH_{4-n} + [CH_3]^+ (I)$$

 $[(HX)_nCH_{3-n}]^+ + n CH_4 \rightarrow n (HX)CH_3 + [CH_3]^+ (2)$

In Table II, total charges on carbon (NBA; MP2/LANL1DZ+P') are listed. Multiple substitution increasingly stabilizes all carbenium ions $[(HX)_nCH_{3-n}]^+$ to the same extent (see HTE's).

TABLE II NBA total charges on carbon in [(HX)_nCH_{3-n}]⁺

n	1	2	3
X = 0	0.476	0.823	1.212
X = S	-0.326	-0.493	-0.553
X = Se	-0.446	-0.700	-0.853
X = Te	-0.666	-1.065	-1.339



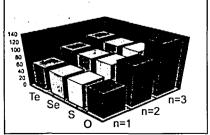


FIGURE 1 Presentation of the HTE's (left) and BSE's (right) of carbenium ions $[(HX)_n CH_{3-n}]^+$ (X = O, S, Se, Te; n = 1-3)

290 H. GRÜTZMACHER, G. S. CHEN, D. OHLMANN, CH. M. MARCHAND, R. GLASER

The electronic mechanism causing this phenomena is very different for X = O versus X = S, Se, Te. Instead of charge dispersal, an increased charge separation is seen in $[(HO)_nCH_{3-n}]^+$ leading to increasingly polar and increasingly stronger $C^{\delta+}$ - $O^{\delta-}$ bonds (manifested by the strong increase of BSE with increasing n). On the contrary, the heavier homologues are indeed stabilized by increasing $\sigma+\pi$ donation from the α -heteroatom to the carbenium center which leads to negatively charged carbon centers. Clearly, these heteroelements are the better π -donors. Note also that the most positively charged carbon nucleus in $[(HO)_3C]^+$ shows the lowest frequency shifted ^{13}C carbon resonance.

Acknowledgements

We thank the Swiss National Science Foundation and the NATO (CRG 940399) for financial support.

References

- [1.] Review: H. Grützmacher, Ch.M. Marchand, *Coord. Chem. Rev.*, 163, 287 (1997).
- [2.] G. Frenking, S. Fau, Ch. M. Marchand, H. Grützmacher, J. Am. Chem. Soc., 119, 6648 (1997).
- [3.] J. Kapp, C. Schade, A. M. El-Nahas, and P. v. R. Schleyer, Angew. Chem., 108 (1996) 2373.
- [4.] K. Ösapay, J. Delhalle, K. M. Nsunda, E. Rolli, R. Houriet, and L. Hevesi, J. Am. Chem. Soc., 111 (1989) 5028.
- [5.] H. Grützmacher, D. Ohlmann, C. M. Marchand, G. S. Chen, D. Farmer, R. Glaser, A. Currao, R. Nesper, and H. Pritzkow, Angew. Chem. Int. Ed. Engl., 35 (1996) 300.