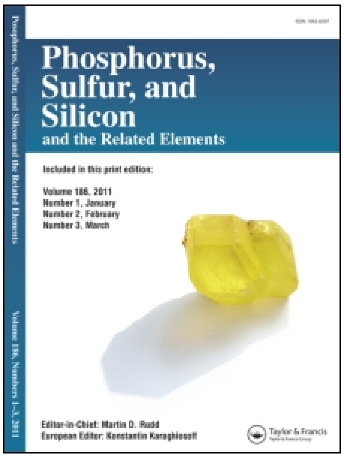

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Zoller, Uri(1991) 'Tricoordinate Hypervalent Three-Membered Thiahetero-Cycles', Phosphorus, Sulfur, and Silicon and the Related Elements, 58: 1, 275 — 279

To link to this Article: DOI: 10.1080/10426509108040635

URL: http://dx.doi.org/10.1080/10426509108040635

Phosphorus, Sulfur, and Silicon, 1991, Vol. 58, pp. 275–279
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TRICOORDINATE HYPERVALENT THREE-MEMBERED THIAHETEROCYCLES

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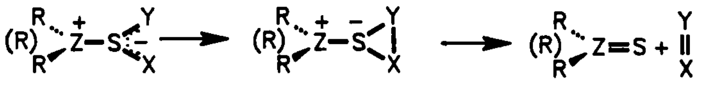
Abstract Tricoordinate hypervalent three-membered thiaheterocyclic intermediates of type **1** connect the starting zwitterionic imidazolium sulfinates **2**, thiourea dioxides **3** and phosphine sulfide-S-dioxides **4** with the corresponding products of their thermal fragmentation, imidazolium thione **5**, thioureas **6** and phosphine sulfides **7**, on the reaction surface.

The relative thermodynamic stability of these hypervalent, significantly ionic σ-bonding systems, explain their observed characteristic mode of thermally-allowed non-linear cheletropic fragmentation.

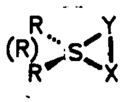
INTRODUCTION

Hypervalent molecules are those in which the central atom exceeds the number of valences allowed by the traditional Lewis-Langmuir theory[1]. Numerous examples of these compounds are found among the second- and third- raw main group elements and there is an enourmous amount of theoretical interest in them.[2,3] Thus, many hypervalent organosulfur systems are known and their chemistry and synthetic utility are well established[4]. Noteworthy in this regard are the tricoordinate, tricovalent sulfur molecules[5] (including charge transfer complexes such as **2h**[6]; i.e. Z=N, R=(R)=alkyl, X=Y=O) which were shown to have unique stability compared to their tetracovalent counterparts, and their structure/geometry has been unequivocally determined. Also their potential as organic reagents has been demonstrated[7].

Although three-membered thiaheterocycles are a well-known class of compounds[8-9], the hypervalent members of type 1 have not been isolated to date. However, recent studies suggest the intermediacy of both the tricovalent and tetracovalent (hypervalent) thiadioxiranes **1**[10] and **8**[11] respectively.



2-4 **1** **5-7**



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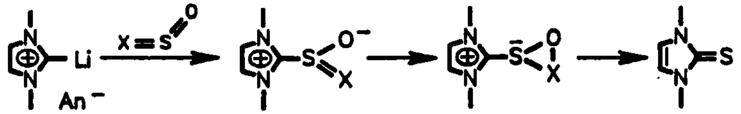
a-c. Z=C; $R=R^{1}_{2}N$; X=Y=O; X=CRR or NR, Y=O
d-e. Z=C; $R=R^{1}R^{2}N$; X=Y=O
f-g. Z=P; $R=R^{1}_{2}N$ or Ar; X=Y=O; $(R)=R^{1}_{2}N$

Our studies provide convincing experimental evidence for the intermediacy of hypervalent three-membered thiaheterocycles **1** and their mode of thermal fragmentation in the transformations **2-4→5-7**, and suggest their possible isolation and characterization under appropriate reaction conditions.

RESULTS AND DISCUSSION

Lithio-imidazolium salts **9**, generated _in situ_ from N,N-dimethylimidazolium salts[12] by the treatment of the latter in aprotic solvents with n-butyllithium at -78°C, readily undergo sulfonylation to give **2a-c** with sulfur dioxide, sulfines and N-sulfinylamines. On allowing the reaction mixture to gradually reach room temperature, the zwitterionic species **2** fragmented to yield the imidazolium thione **5** (yields: 21-61%) apparently via the tricoordinate, hypervalent three-membered thiaheterocycles **1**.



An=Br, I, BF_4, ClO_4, CF_3SO_3

9 **2a-c** **1a-c** **5**

Significantly, in each of these transformations, the combined yield of the thione **5** and the recovered starting imidazolium salt was almost quantitative. The other isolated products were in accord with the above scheme. Treatment of **9** with thiirane, under the same reaction conditions, gave the same results, except that the yield of thione **5** was rather low (7%).

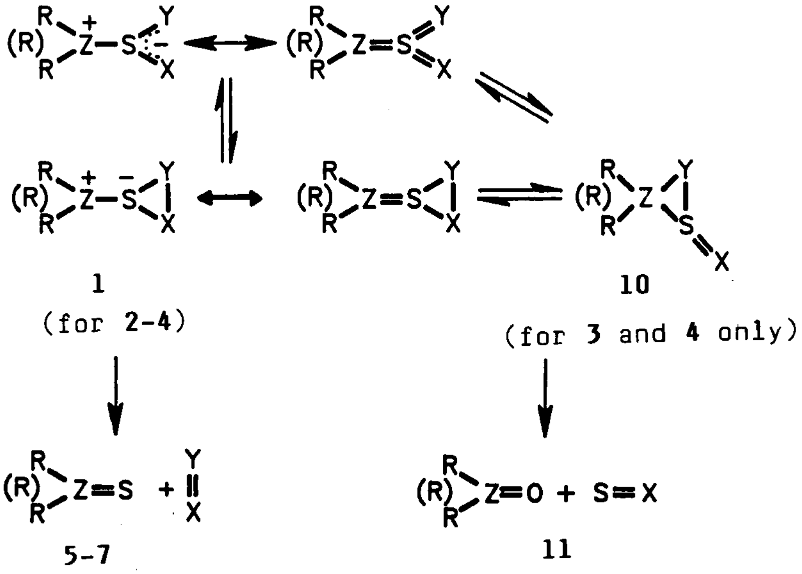
These results can be explained in terms of the thiaheterocycle intermediate **1**. The stabilizing effect of the LUMO of the imidazolium π-system on the adjacent incipient tricoordinate hypervalent sulfur atom is considerable enough to facilitate the rearrangement of **2** to **1**. Once formed, the three-membered ring sulfurane 1 has a life-time sufficient (before collapsing back to the highly resonance-stabilized acyclic zwitterionic isomer **2**) for undergoing a non-linear--type cheletropic fragmentation leading to **5**[12]. Thus, the hypervalent three-membered thiaheterocycles **1** enjoy considerable thermodynamic stability which can be accounted for (in addition to the stabilizing effect by the adjacent imidazolium π-system), in terms of both the high ionic nature of their σ-bonding resulting in considerable hyperconjugation[3], and the σ aromaticity[13] largely confined to three-membered rings (heterocycles included). Apparently, the thermally - allowed cheletropic fragmentation of **1** to give 5 is energetically the most favored one available to this intermediate in its ground state.

Similarly, thiourea dioxides[14] **3d,e** (**3d**: R=NH$_2$; **3e**: R==n-Bu; Z=C; X=Y=O) and phosphine sulfide-S-dioxides **4f,g** (**4f**: R=Ph, (R)=(CH$_3$)$_2$N; **4g**: R=(R)=(CH$_3$)$_2$N; Z=P; X=Y=O, - generated in-situ via the treatment of the phosphine with an axcess of sulfur dioxide at -78^{o}C), yielded on thermolysis the corresponding thioureas (i.e. **6d,e**) and ureas (**11d,e**) and the phosphine sulfides (i.e. **7f,g**) and phosphine oxides (**11f,g**) respectively.

The thermolysis, in warmed (45^{o}C) and in refluxing anhydrous acetonitrile for the thiourea dioxides (a 98% conversion after 0.7 hr for **3d** on reflux) was shown to be a first order reaction the ratio between the thiourea and urea is temperature dependent (1:2.8 and 2:3 respectively)^{10}.

The thermolysis of the phosphine sulfide-S-dioxide **4f** (-78^{o}-r.t) afforded 72% yield of the phosphine sulphide (**7f**) and oxide (**11f**) in a ratio of 4:3. However, under the same conditions in the presence of an equimolar amount of o-dibromobenzene, the yield was unchanged but the ratio of **7f** to **11f** was 7:3^{10}.

The formation of the thioureas and the phosphine sulfides is convincingly explained in terms of the tricoordinate, hypervalent three-membered thiaheterocycles **1d-g** analogous to the more stabilized intermediates **1a-c**, whereas the formation of the corresponding ureas **6d-e** and phosphine oxides **7f-g** can be accounted for in terms of a similar kind of three-membered ring intermediate (i.e.**10**) which looses sulfur monoxide on thermolysis. Since a singlet-triplet crossing was shown to occur along the fragmentation reaction coordinate of the hypervalent thiadioxiranes to dioxygen^{10}, an external heavy atom catalyst was responsible for an increased intersystem crossing efficiency in the case of **4f** in the presence of o-dibromobenzene, leading to the increased ratio of sulfide:oxide.



In summary, the above explanatory general scheme is proposed in order to account for all the experimental results[12]. Thus, the intermediacy of hypervalent three-membered thiaheterocycles and their mode of thermal fragmentation have been established. The experimental results are in accord with theoretical considerations and predictions.

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