Poster Session: Model Complexes of Biochemical Interest

R1

Do 5B-Element Homologues of Sulfonamides exist?

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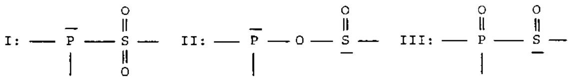
Sulfonamides are well-known and important substances. However the sulfonyl derivatives of the homologous 5B-elements are hitherto unknown because of the fast redox process for instance between phosphorus(III) and sulfur(VI). Now we have succeeded in their synthesis by metal coordination, where the complex fragment is acting as a protective group.

Results and Discussion

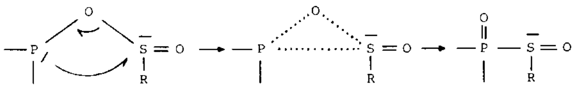
The ligand function of the ambidentate RSO_2-group to 5B-elements was initially investigated with respect to their graduated group properties. We have been successful in the synthesis and investigation of sulfinic derivatives of the type $R'_4E(O_2SR)$, $R'_3E(O_2SR)_2$ and $R'_2(O)P(O_2SR)$ with pentavalent 5B-elements or $E(O_2SR)_3$ and $R'_2E(O_2SR)$ with trivalent ones, by reacting the chlorides of the 5B-elements with silver sulfinates. They differ significantly in their physical and chemical properties (responsible for the reactivity pattern) as well as in their structures (ionic and covalent with linkage via one or two oxygen atoms and coordination numbers 3–5).

The 5B-element homologues of the sulfonamides with the formula $R'_2E(O_2SR)$ show the linkage via oxygen for E = As, Sb. In the case for E = P however we obtain – instead of the desired sulfonyl – phosphanes (I) or the sulfinylphosphinites (II) –only their tautomeric sulfinylphosphaneoxides (III) and only by the 'silyl method' (from trimethylsilyldiphenylphosphane and sulfonylchlorides):



$$\text{I: } -\overset{-}{\underset{|}{P}}-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}- \quad \text{II: } -\overset{-}{\underset{|}{P}}-O-\overset{O}{\overset{\|}{\underset{-}{S}}}- \quad \text{III: } -\overset{O}{\overset{\|}{\underset{|}{P}}}-\overset{O}{\overset{\|}{\underset{-}{S}}}-$$

Thus we were successful in getting the desired phosphorus–sulfur bond, but at the cost of a synchronous tautomerization similar to the ' Arbusov–Michaelis reaction'. We also assume an intramolecular mechanism, where the oxygen linkage initially formed is rapidly tautomerized through a three-center transition state into the oxide:



'Analogous reactions were carried out with metal-coordinated functional phosphanes to avoid this 'Arbusov-like rearrangement' by blocking both the free coordination site and electron pair on phosphorus. Thus we obtain the metal-stabilized sulfinylphosphinites (O-isomer, II) with the so-called 'silver-salt method' or with the 'sulfinylation of metal-coordinated phosphinite anions'. But with the mild 'silyl method' a highly reactive sulfonylphosphane (S-isomer, I) can be finally synthesized for the first time, but only in the protecting coordination sphere of a metal:

$$[H(CO)_4Re-P(C_6H_5)_2O]^- + RSOCl \rightarrow$$

$$H(CO)_4Re-P(C_6H_5)_2(O_2SR) + Cl^-$$

$$L_nM-P(C_6H_5)_2X + YO_2SR \rightarrow$$

$$L_nM-P(C_6H_5)_2(O_2SR) + XY$$

$L_nM = BrMn(CO)_4, Cr(CO)_5, C_5H_5Mn(CO)_2$

$X = Cl, Si(CH_3)_3, Y = Ag, Cl$

R2

The Template Synthesis and Characterization of Ni(II) and Co(II) Perchlorate Complexes of Quadridentate Macrocyclic Ligand 2,5,11,14-Tetramethyl-3,4,12,13,19,20-hexaazatricyclo[13.3.1.1.^{6,10}]eicosa-1(19),2,4,6,8,10(20),11,13,15,17-Decaene

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The intense interest in synthetic macrocycles and their metal complexes depends on the fact that they may mimic naturally occurring macrocyclic molecules in their structural and functional features, and on their rich chemical behavior. Macrocyclic complexes with four nitrogen donor atoms have attracted considerable attention. Most macrocyclic ligand complexes are best prepared with the aid of metal ions as 'templates' to direct the steric course