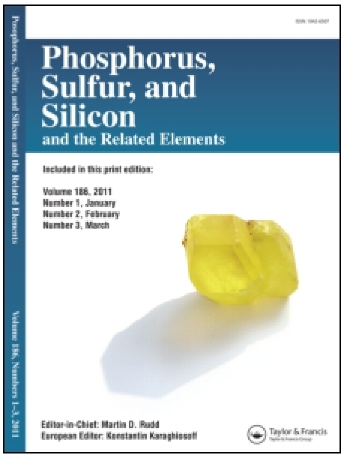

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SPECULATIVE NOVEL PHOSPHORUS (V) COMPOUNDS AND MODES OF REARRANGEMENT IN RPF$_5$-IONS

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SPECULATIVE NOVEL PHOSPHORUS (V) COMPOUNDS AND MODES OF REARRANGEMENT IN RPF_5^- IONS †

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A series of novel and somewhat speculative compounds of hypervalent phosphorus and other main group elements is presented. These include cyclic systems, oxides, ylides, acetylacetonates and π-cyclo-pentadienyl compounds. Modes of rearrangement in the ionic compounds RPF_5^- are developed along with the observable processes. It is hoped that suitable temperature dependent nmr studies of some appropriate such system will eventually be undertaken.

INTRODUCTION

In the past several years[1] I have discussed at length both the theory and the structure of a variety of hypervalent molecules. This has led to the preparation of some novel compounds including *bis*-xenon trifluoroacetate.[1] I will discuss briefly the following: (a) a variety of phosphorus (V) compounds and related systems of other main group elements, recognizing the fact that a theoretician is permitted to publish speculative predictions that an experimentalist may only write on his blackboard; and (b) the modes of rearrangement in RPF_5^- ions when studied by nmr.

SPECULATIVE NOVEL COMPOUNDS

The theory of bonding in all phosphorus (V) compounds involves "hybridized" *s-p* orbitals or hypervalent-II bonds. This applies to *all* such systems, whether pentacoordinate systems such as PF_5 or tetracoordinate systems such as phosphonium ylides and oxides. There are three important points to note. First, the popular way of writing oxides and ylides with P^+ ions is misleading since PF_5 is never written as $PF_4^+F^-$; secondly, there is no necessity whatsoever to consider *d*-orbitals as has been shown in recent *ab initio* calculations;[1] and thirdly, there is therefore no reason whatsoever to exclude the likely existence of analogous cyclic nitrogen (V) compounds.

The following are illustrations of three classes or types of compounds:

a) cyclic systems;
b) acetylacetonates;
c) π-cyclopentadienyls.

The synthesis of these compounds is not considered here.

a) The phosphoranes 1 and 2 as well as the N, As and Sb derivatives are all rather ordinary trigonal bipyramidal structures. The oxide 3 and the ylide 4 differ from the usual oxides and ylides since they are formed from two equatorial *s-p* orbitals rather than two axial pure-*p* orbitals. For this reason it is expected that the bond angle would be ~ 120°. Hypervalent-I sulfur (IV), selenium (IV) and tellurium (IV) analogs 5[2] differ considerably since they only utilize *p*-orbitals and assure the bond angles to be near 90° while 6 will be simply octahedral. The oxide 7 and the ylide 8 differ completely from 3 and 4 since they involve mixing the *s*-orbitals into purely *p*-orbital systems. The only effect of this is to open the C–X–C bond angle[3] to ~ 120° and probably increase the stability.

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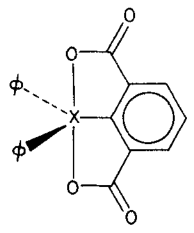
† Plenary Lecture. Vth International Conference of Organic Phosphorus Chemistry, Gdansk, Poland, September 1974.

‡ Deceased. Presented by A. H. Cowley.



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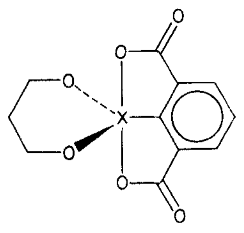

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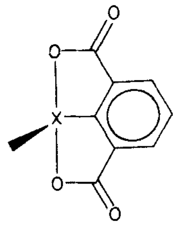

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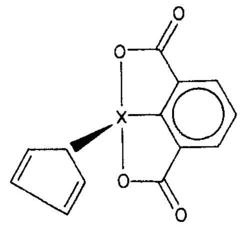

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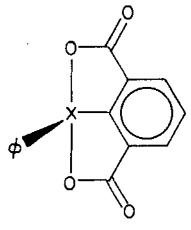
X = N, P, As, Sb



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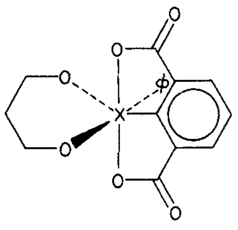

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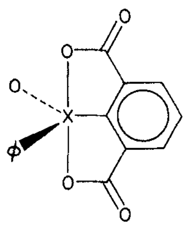

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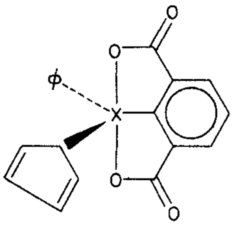


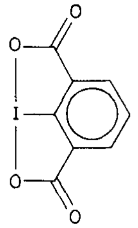
8

X = S, Se, Te

From the hypervalent-I iodine compound 9[2,4] a purely *p*-orbital oxide and ylide with near 90° bond angle can be formed. Only the dioxide **12**, the diylide **13** and the oxyylide **14** involve the *s-p* hybridized orbitals of hypervalent-II molecules. Xenon analogs are not considered.

Phosphoranes **15** and **16** are rather ordinary systems when the cycle should stabilize the P–P bond and **17** is a simple diylide. The compound **18** however is quite unusual as is most easily seen from the charged structure on the right-hand side which has three neighboring negatively charged carbon atoms. A given ylide's β-carbon is part of the other phosphorus hypervalent double bond. This bond thus differs from an ordinary double bond as it involves only two electrons rather than four.

The cyclic sulfuranes and per- or oxy-sulfuranes, **19-24**, bond the sulfur to a phosphorus (III) system whose three nearby perpendicular bonds should be noted. Again the P–S–P bond angle will be near 100° when Y is nothing and near 120° when Y is an oxide, a sulfide or an ylide.



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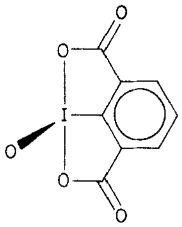

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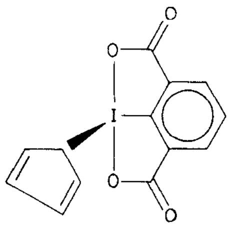

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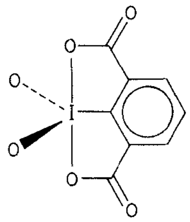

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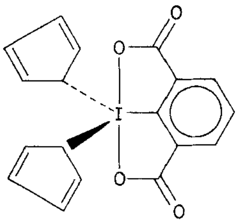

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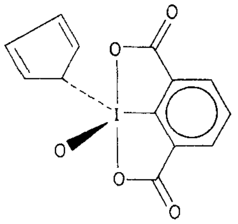

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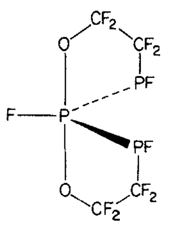
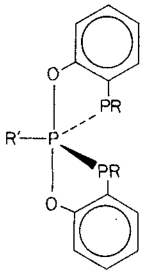


15

R = F, H, CF_3, NH_2 ....
R′ = R or PR_2



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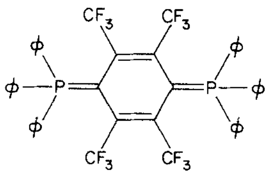

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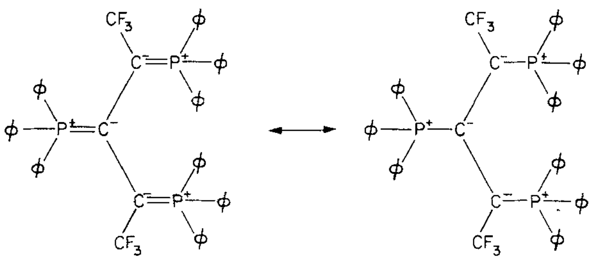

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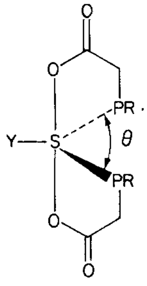

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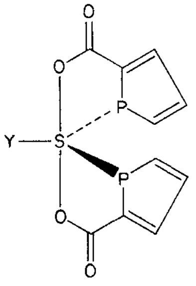

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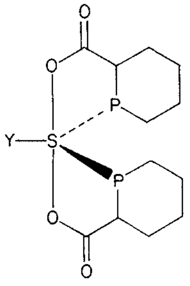

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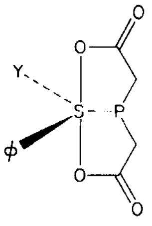
Y = nothing: θ ≈ 100°   Y = O, S, ylide: θ ≈ 120°



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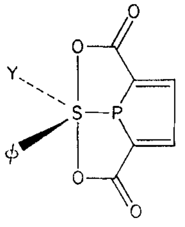

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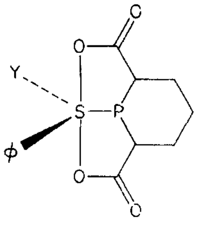
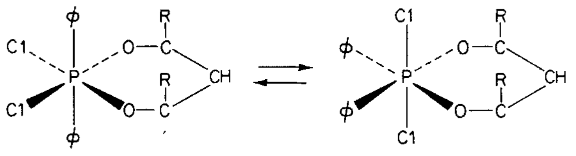


24

b) Acetylacetonates of antimony have been known for several years,[6] so that the phosphorus analog **25** should be preparable. Related compounds of iodine (III), **26**, have been recently prepared[7] and I have speculated[1] on an analogous compound of selenium (IV), **27**. It might even be possible to prepare the diacetylacetonate, **28**, depending on the synthetic mechanism involved, if either the trialkyl or triaryl group is so equatorially favored as to prevent the condensation into an ylide.



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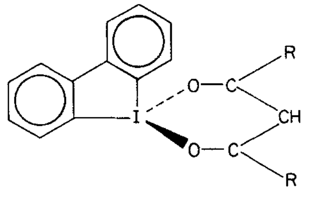
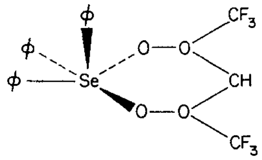
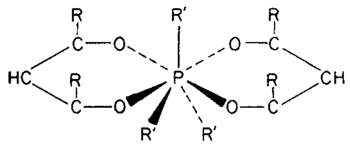


R=C_6H_5, t—Bu

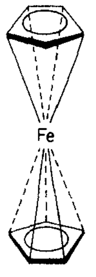




26   27   28

This ends the discussion of known hypervalent bonds but I think it worth pointing out explicitly that there are three types. These are the hypervalent "double bonds" as in the oxides, sulfides and ylides, the hypervalent "single" bonds as in most of the cyclic compounds discussed, and the hypervalent *half*-bonds as in the acetylacetonates.

c) π-Cyclopentadienyls. I have recently speculated[1] on the possible existence of cyclopentadienyl compounds of the main group elements. When the bonding in ferrocene, **29**, is described in the unorthodox but most realistic manner in which both the rings and the iron atom are essentially neutral, then the cyclopentadienyl phosphorus compound, **30**, should also be possible. It is significant that the p-orbital utilized in ferrocene[7] is *unoccupied* in the isolated iron atom, and therefore involves an excitation in energy, whereas the p-orbital utilized in the phosphorane is *occupied* in the phosphorus atom and doubly occupied when the three equatorial ligands are introduced.



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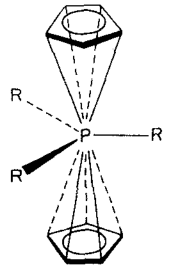

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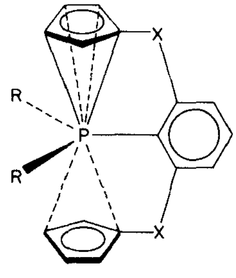
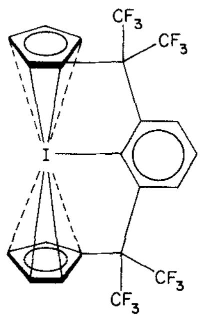


X=O, CH_2, $C(CF_3)_2$

31

Compound **31** is an analog to the iodine compounds such as **32** which I have discussed previously,[1] while the trivalent phosphorus system, **33**, utilizes nonparallel cyclopentadienyl rings (as in some metals) and should be more stable. It is bonded purely by p-orbitals. Compounds **34-36** possess only a single cyclopentadienyl group which prevents its condensation to an ylide just as in the acetylacetonate derivatives, **25-27**. These are somewhat analogous to **37** whose supposed preparation has been recently reported.



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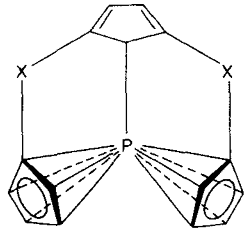

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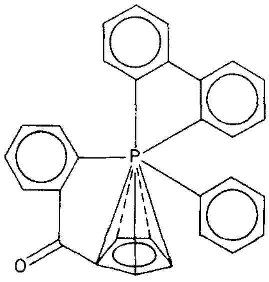
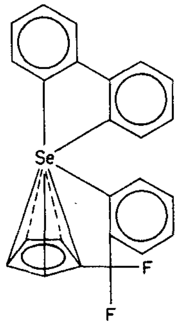


34

The set of analogs of phosphorene, **38**, should be stabilized by the additional π-bonding indicated in the orbital picture while the set of group VI compounds, **39**, do not involve the same π-structure but can be further stabilized by letting Y = O or S, thus allowing for the s-p hybridization.



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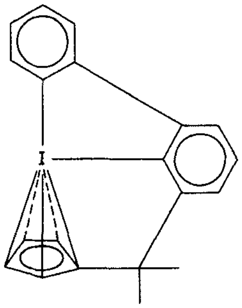

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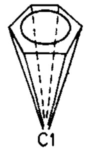

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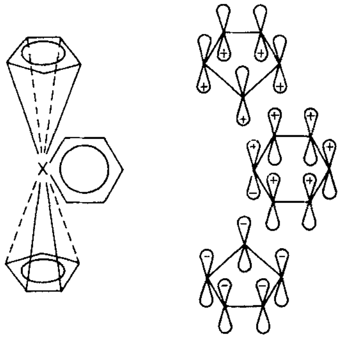
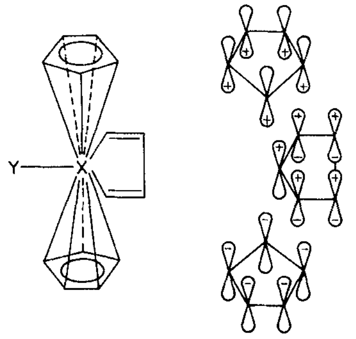


X= P, As, Sb, Bi

38

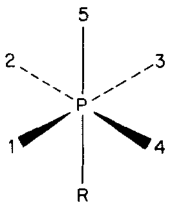


X= S, Se, Te
Y= O, S or nothing

39

MODES OF REARRANGEMENT IN RPF$_5^-$ IONS

Intramolecular rearrangements in phosphorus (VI) ions have not been observed. It seems reasonable to expect that with certain choices of R such rearrangements will take place. The temperature dependent nuclear magnetic resonance spectra will then be performed in order to determine the observable processes and the modes of rearrangement involved. There are thirty different pseudo-isomers in RPF$_5^-$, **40**, when all fluorine atoms are labeled.



40

The modes of rearrangement are exactly the same for the square pyramids discussed by Agosta and myself. These are:

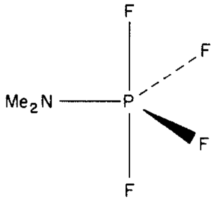
$M_0(1) = I$
$M_1(1) =$ *trans-ee*
$M_2(4) =$ *ea*
$M_3(4) =$ *cis-ee*
$M_4(4) =$ *trans-eea*
$M_5(8) =$ *cis-eea*
$M_6(8) =$ *cis-eexaa*

The observable processes are:

OP_0: I = *trans-ee* = *cis-ee* (4) (M_0, M_1, M_3)
OP_1: *ea* (4) = *trans-eea* (4) (M_2, M_4)
OP_2: *cis-eea* (8) = *cis-eexea* (8) (M_3, M_6)

and this indicates that there is no way to distinguish between the M_2 and M_4 rearrangements or between the M_5 and M_6 rearrangements. It also shows that both the *ee* rearrangements are unobservable due to the molecular symmetry. The ambiguity involved is exceedingly unsatisfactory.

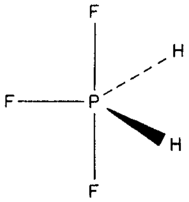
I have recently discussed the classic case of the phosphorane, **41**, whose modes of rearrangement cannot be distinguished uniquely. It is either an *aeae* rearrangement, which the popular Berry mechanism would provide, or an *aexae* rearrangement for which entirely different but equally likely mechanisms would operate. It is worth noting again[11] that the rearrangement energies for XPF_4 compounds vary from < 5 kcal for X = F to > 15 kcal for $X = NH_2$. I have suggested that this might indicate that the rearrangement takes place *via* an asymmetric dimeric intermediate. The other simple phosphorane studied, **42**,[10] possesses an analogous ambiguity. Since the two hydrogens remain equatorial, the observed equilibration of the two different types of fluorine peaks takes place either *via* an *ae* rearrangement or an indistinguishable *aae* rearrangement so that there is no information available from the intermediate temperature spectra.



OP_2 : aeae = aexae (M_1, M_5)

H_2N > 15 kcal
Me_2N = 9 kcal
Me ≃ 5 kcal
F < 5 kcal

41



OP_2 : ae(2) = aae(2) (M_2, M_4)

42

It is worth mentioning again that this entire discussion relates only to the stereochemistry of the rearrangements and has no bearing whatsoever on the mechanisms involved. Therefore, since we are usually unable even to determine the stereochemistry of the rearrangement due to the ambiguities in the OPs, it seems somewhat presumptuous to discuss at length the proposed mechanisms.

ACKNOWLEDGEMENT

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