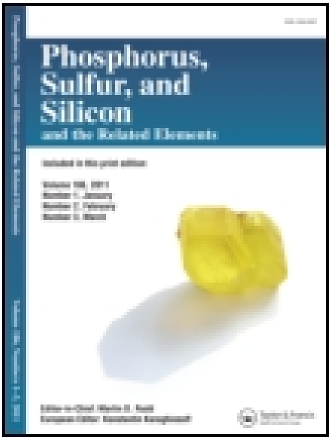

Phosphorus, Sulfur, and Silicon and the Related Elements

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Experimental and Quantum Chemical Studies of 2-Phosphinylphenol Derivatives

Jack B. Levy , Steven B. Sutton & Ronald E. Olsen

[a] Department of Chemistry , University of North Carolina at Wilmington
Wilmington , NC 28403, USA

[b] Department of Chemistry , University of North Carolina at Wilmington
Wilmington , NC 28403, USA

[c] Department of Chemistry , University of North Carolina at Wilmington
Wilmington , NC 28403, USA

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Experimental and Quantum Chemical Studies of 2-Phosphinylphenol Derivatives

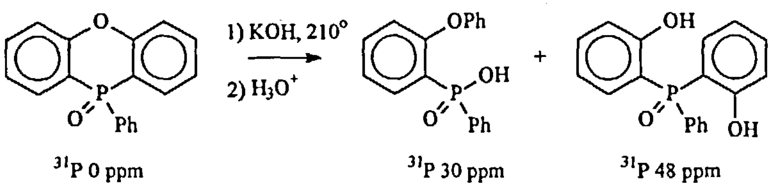
JACK B. LEVY, STEVEN B. SUTTON and RONALD E. OLSEN

Department of Chemistry, University of North Carolina at Wilmington Wilmington, NC 28403, USA

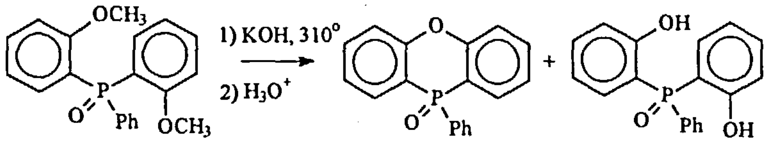
Carbon-oxygen bonds *ortho* to a phosphoryl group in triarylphosphine oxides undergo cleavage when the oxides are either fused with potassium hydroxide or treated with potassium *tert*-butoxide in refluxing toluene, presumably through a nucleophilic addition-elimination mechanism. Thus, bis(2-hydroxyphenyl)phenylphosphine oxide is produced along with the expected 2-phenoxyphenyl(phenyl)phosphinic acid from 10-phenyl-10H-phenoxaphosphine 10-oxide. The latter starting material is also *produced*, together with bis(2-hydroxyphenyl)phenylphosphine oxide, when bis(2-methoxyphenyl)phenylphosphine oxide is fused with potassium hydroxide. Fusion of bis(2-methoxyphenyl)phenylphosphine oxide with sodium hydroxide, however, yields 2-hydroxyphenyl(phenyl)phosphinic acid. Ab initio quantum chemical studies confirm that the downfield ^{31}P chemical shift that is observed in 2-phosphinylphenols is due to hydrogen bonding to the phosphoryl group.

Keywords: Nucleophilic addition-elimination; 10-phenyl-10H-phenoxaphosphine 10-oxide; 2-phosphinylphenols; KOH fusion; phosphorus NMR

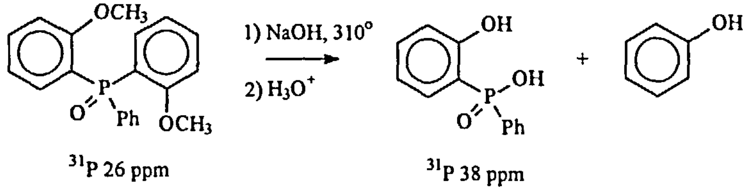
Fusion of bis(2-phenoxyphenyl)phenylphosphine oxide with KOH causes displacement of a 2-phenoxyphenyl anion and after acidification production of 2-phenoxyphenyl(phenyl)phosphinic acid. A similar ring C-P bond cleavage forms the same product from 10-phenyl-10H-phenoxaphosphine 10-oxide and KOH, as reported by others,[1] but we find that an alternative C-O bond cleavage also occurs to produce bis(2-hydroxyphenyl)phenylphosphine oxide. The two products are found in a 2:1 ratio. Similar results are obtained under milder conditions, treatment of 10-phenyl-10H-phenoxaphosphine 10-oxide with potassium *tert*-butoxide in refluxing toluene, except that under these conditions a small amount of 2-hydroxyphenyl(phenyl)phosphinic acid is also produced. These reactions presumably involve nucleophilic addition/elimination steps that are activated by the ortho phosphoryl group.



Curiously, 10-phenyl-10H-phenoxaphosphine 10-oxide can also be *produced* through fusion of KOH with bis(2-methoxyphenyl)phenylphosphine oxide,



while under identical conditions NaOH yields 2-hydroxyphenyl(phenyl)phosphinic acid and phenol.



As previously observed by Dhawan and Redmore,[2] the ^{31}P chemical shift of bis(2-hydroxyphenyl)phenylphosphine oxide is downfield by about 23 ppm relative to triphenylphosphine oxide. The hypothesis that this deshielding may be due to hydrogen bonding to the phosphoryl oxygen led to our ab initio quantum chemical studies of the model compounds, 2-phosphinylphenol[3] and 2-dimethylphosphinylphenol,[4] each of which had three monomeric conformations that were minima on their potential energy surfaces. The global minimum in each case was the intramolecularly hydrogen-bonded conformer.

We have now computed, through Gaussian 94,[5] the Weinhold-Reed natural atomic charges[6] and the Wiberg bond orders[7] of the three conformers of 2-dimethylphosphinylphenol using the MP2 electron densities, and the results are shown below along with those of the parent compounds, phenol and dimethylphosphinylbenzene. The charges (italics) are not shown for the hydrogens (generally about 0.25), except for the OH hydrogen. The observed changes in bond orders for **A** are in line with the previously reported bond distance changes.[4] Calculation of the overall classical Coulombic potentials of **A**, **B**, and **C**, treating the computed atomic charges as point charges, suggests that electrostatic interaction of the polar groups is the primary determinant of the relative energies of the three conformers, in agreement with results obtained from the HF/6-31G*//MP2/6-31G* charges.[4] We have now also computed the nmr tensors of the 2-dimethylphosphinylphenol conformers at the HF/6-31G* level and have found that the computed phosphorus chemical shift of the intramolecularly hydrogen-bonded conformer **A** is downfield of the other two conformers, **B** and **C**, and of dimethylphosphinylbenzene by 14-16 ppm. This deshielding appears to be related to a weakening (and lengthening[4]) of the P-O bond in **A** rather than to an increase in the charge on the phosphorus. The computed downfield shift is comparable to the experimental difference of 15 ppm between the ^{31}P chemical shifts of triphenylphosphine oxide and 2-diphenylphosphinylphenol.[2]

ACKNOWLEDGEMENTS

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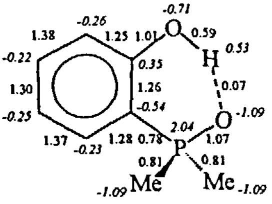
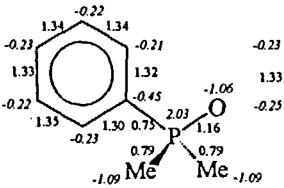
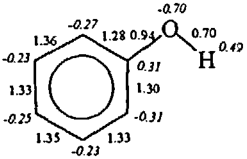
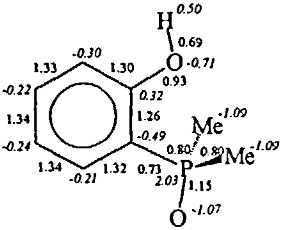
Natural Charges and Wiberg Bond Orders Computed at the MP2/6-31G* Level



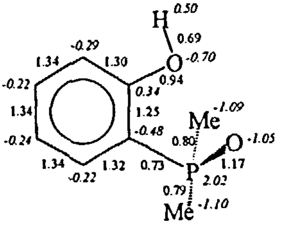
A







B



C

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