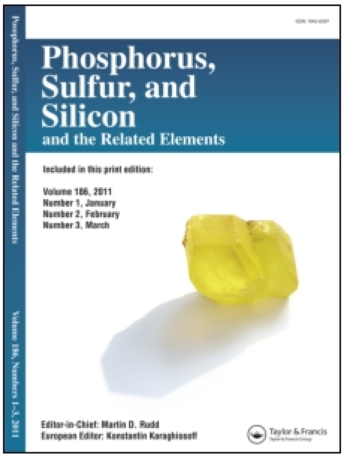

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EFFECTS OF A STERICALLY DEMANDING P–ARYL SUBSTITUENT IN PHOSPHOLE AND 7–PHOSPHANORBORNENE CHEMISTRY

LOUIS D. QUIN,* ALEXEY S. IONKIN,* RAJDEEP KALGUTKAR,* AND GYÖRGY KEGLEVICH†
*Department of Chemistry, Box 34510, University of Massachusetts, Amherst, MA 01003-4510 USA

†Department of Organic Chemical Technology, Technical University of Budapest, 1520 Budapest, Hungary

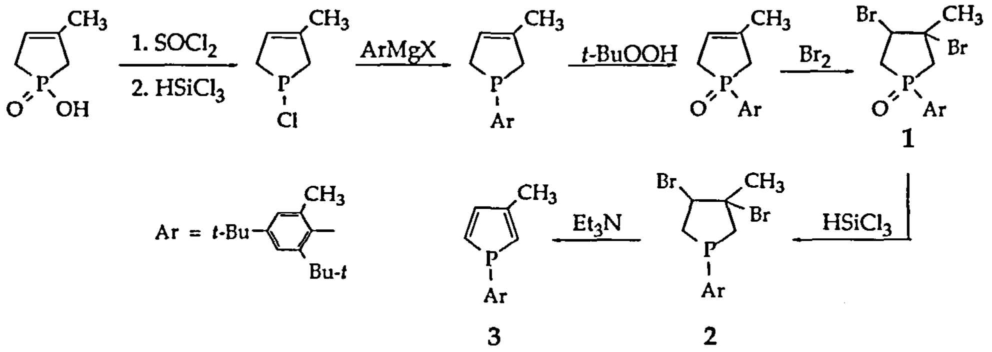
Abstract The 2,4–di–*tert*–butyl–6–methylphenyl substituent was placed on phosphorus of a phosphole, causing restricted rotation about the P–C bond and flattening of the phosphorus pyramid. Electron delocalization was greater in this phosphole as a result of the flattening. The 7–phosphanorbornene with this substituent had the most deshielded ^{31}P nucleus ever recorded in this series, and thermally decomposed with formation of a diphosphene, suggesting a phosphinidene intermediate.

Recognizing the profound stabilization influence of sterically demanding substituents in the field of low-coordination phosphorus (and other) species, we are led to inquire about the effect of such substituents on properties of certain phosphorus heterocyclic systems where crowding can cause measurable changes in geometry and properties.

THE PHOSPHOLE SYSTEM

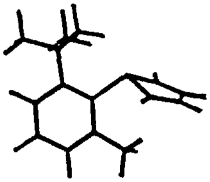
It is generally accepted that the phosphole ring lacks the extensive electron delocalization well-known in the S, N, O heterocyclic counterparts, largely because the P atom retains its pyramidal structure and the lone pair is prevented from efficient overlap with the π–system. From X-ray diffraction analysis,[1] it has been shown that for a simple phosphole (1–benzyl) the P–substituent is out of the phosphole ring plane by 66.9°. Theoretical studies suggest[2] that delocalization should increase as the pyramid is flattened and phosphorus shifts to sp^2 hybridization. We report here on attempts to perform the flattening experimentally, and to explore consequences of flattening on the delocalization and other properties. Molecular modeling studies have confirmed that placing a large substituent on phosphorus can indeed bring about the desired flattening effect. Thus, the angle formed between the ring plane and the P–substituent for phenyl (68.5°) decreased to 65.2° for mesityl, 63.2° and 58.0° (two conformations) for 2–*tert*–butyl–6–methylphenyl, and 55° for 2,4,6–tri–*tert*–butylphenyl. We attempted to synthesize a phosphole with the latter substituent, but the crowding prevented the necessary reactions. Better results were obtained with the 2,4–di–*tert*–butyl–6–methylphenyl substituent (Scheme 1).

SCHEME 1



Phosphole 3 is a crystalline solid, stable in the atmosphere. Unfortunately, at this writing, the crystals have not proved entirely satisfactory for the all-important determination of molecular parameters by X-ray diffraction analysis, and this work is not complete. The ^{31}P NMR shift, recently confirmed by theoretical studies to be rather unreflective of delocalization,[2] was δ +1.8 (*cf.* to δ +7.5 for the 1–phenyl derivative).[3] The proton NMR and mass spectra were typical of phospholes and lacked any special features. More informative of increased orbital interactions was the photoelectron spectrum of the phosphole. The ionization energy of the non-bonding electrons was 0.35 eV higher than that for the corresponding tetrahydrophosphole, indicative of interaction with the π^* orbital. This ionization in other phospholes is virtually the same as that of the tetrahydro counterparts.[4]

The ^{13}C NMR spectra of phospholes also reveal little about delocalization effects, but the spectrum of 3 proved to be of great interest for another reason: a marked preference for a conformation (4) where the two rings are orthogonal was detected, with the 2–*tert*–butyl substituent above the phosphorus pyramid and thus close to the lone pair. This places the 6–methyl on the opposite side of the lone pair. This conformation was suggested by the lack of 3-bond coupling between P and the 6-methyl carbon, as well as ring carbon 5; this coupling is controlled by the orientation of the lone pair to carbon, and can be zero if the lone pair is *anti* to the carbon. Another feature was the surprisingly large 4-bond coupling of P to the methyls of the 2–*tert*–butyl group (11.6 Hz). Molecular modeling studies have confirmed that conformation 4 is 0.8 kcal/mol lower in energy than conformation 5, and that the ratio of the conformers 4 to 5 is about 3:1 at 25°C.



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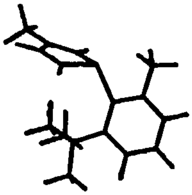

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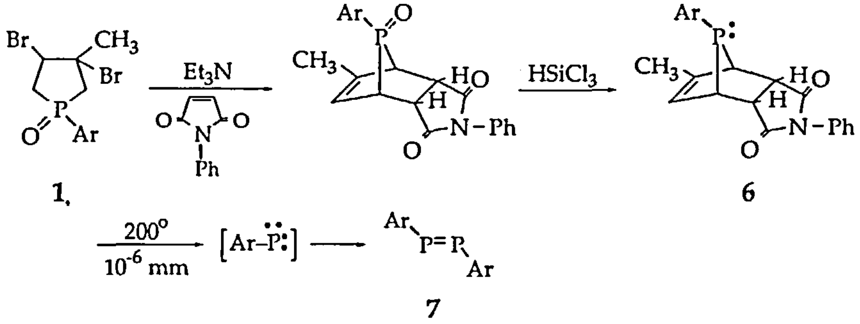
Another rotational effect arising from the large P-aryl substituent was noticed for the dibromophospholane oxide 1. This oxide, when synthesized in the usual way by adding bromine to the 3-phospholene oxide, had a ^{31}P NMR shift that was almost unreproducible over the range δ 54 to 76, and was controlled by concentration as well as by age of the solution. The same dibromophospholane oxide when prepared by peroxide oxidation of the phosphine 2 then gave a shift of δ 49.4. Mixing the two forms having separate shifts of δ 65.6 and 49.2 gave a solution with a *single* peak, at δ 54.2. Dreiding models suggest that there are preferences for the two conformations with the rings orthogonal to minimize steric interactions. Apparently the barrier for rotation about the P–C bond is sufficient to allow observation of the two conformers, which can undergo equilibration.

THE 7-PHOSPHANORBORNENE RING SYSTEM

This ring system is well known to abound in unusual reactivity and spectral features[5] as a result of the forced proximity of the bridging phosphorus functional group to the carbon–carbon double bond. For trivalent phosphorus, this results in extraordinary downfield shifting of the ^{31}P NMR signal. Values below δ +100 are common. A recent theoretical study[6] has shown that the deshielding is derived from a reduction in the HOMO-LUMO energy gap in the bridged system associated with the small "flap" angle relating the P group to the ring double bond. No experimental study has been made of the effect of P-substituent size on the ^{31}P shift. The availability of the dibromophospholane oxide 1 allows a synthesis of the very crowded *syn*-substituted 7-phosphanorbornene system 6 as seen in Scheme 2. This compound has the most downfield signal ever recorded for a phosphine in the 7-phosphanorbornene system, δ +153.3. Apparently, the orbital interactions controlling the size of the HOMO-LUMO gap are increased by the steric crowding of atoms in this molecule. The *anti* isomer from inversion of the configuration by treatment with methanol[7] had the most *upfield* signal (δ 0.6) ever recorded for this structural type.

Attempts in the past to produce phosphinidenes by thermolysis of 7-phosphanorbornenes have not been successful; fragmentation of the ring with loss of the P-bridge does occur, but through bimolecular reactions of the phosphines.[8] We have obtained an indication that the sterically crowded phosphine 6 may fragment by extrusion of the phosphorus bridge as the phosphinidene. Thus, at 200°C and 10^{-6} mm, about 55% of a sample was fragmented to give as the main product the diphosphene 7, as indicated by its ^{31}P NMR shift of δ +517.6 and its characteristic red color. The bimolecular interaction seems unlikely in this crowded molecule, and the diphosphene may be derived from the phosphinidene. Some formation of the C–H insertion product might have been expected, but none was detected.

SCHEME 2



CONCLUSIONS

It is very clear that placing very large substituents on phosphorus in both the phosphole ring and in the 7-phosphanorbornene ring system can produce important structural effects that modify the properties of these molecules. In the future, we plan to study other types of large P-substituents, with the continued goal of flattening phosphorus in the phosphole ring to an even greater extent, hopefully to the point where convincing evidence can be obtained that indeed the system can become "aromatic."

ACKNOWLEDGEMENTS

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