

The role of electronic and steric factors in the fluorination of P(III) compounds by Ph_3BiF_2

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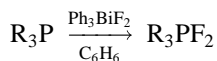
Abstract

The reactivity of P(III) compounds towards fluorination by Ph_3BiF_2 was studied from the viewpoint of frontier molecular orbitals theory. The highest occupied molecular orbital (HOMO) energies of phosphites and amidophosphites were calculated. A qualitative relationship between HOMO energy levels and reactivity was found. The difference in chemical behaviour of $(\text{Me}_2\text{N})_3\text{P}$ and $(\text{Et}_2\text{N})_3\text{P}$ was attributed to steric hindrance. © 1997 Elsevier Science B.V.

Keywords: Phosphite; Amidophosphite; fluorination; Chemical reactivity; HOMO; AM1

1. Introduction

Recently we have investigated the reaction of P(III) compounds with Ph_3BiF_2 [1] and the following P(III) reagents have been studied: $(\text{EtO})_2\text{POH}$, $(\text{EtO})_3\text{P}$, $(\text{EtO})_2\text{POSiMe}_3$, $(\text{CF}_3\text{CH}_2\text{O})_3\text{P}$, $(\text{Me}_2\text{N})_3\text{P}$ and $(\text{Et}_2\text{N})_3\text{P}$. The reaction proceeds according to the following general scheme:



It has been shown that the reactivity of these compounds depends on the nature of the substituents at the phosphorus atom.

The purpose of the present paper is to explain the behaviour of the above-mentioned phosphites and amidophosphites in the fluorination reaction, on the basis of the frontier molecular orbital theory.

2. Computational details

All calculations were carried out semiempirically with the PC Spartan version 1.0 program package [2] with the AM1 effective Hamiltonian [3] on an IBM-compatible personal computer with a Pentium-100 processor under Windows NT operating system. All the geometry parameters of the studied molecules were totally optimized. The geometries are shown graphically in Figs. 1–6.

Unfortunately, there is no semiempirical parametrization for the Bi atom either in the Spartan or in the MOPAC 93 program. But according to the qualitative nature of frontier molecular orbitals theory, we can omit the calculation of Ph_3BiF_2 from our consideration without loss of accuracy. In fact, we need to know only the relative energies of the highest occupied molecular orbitals (HOMOs) of the considered phosphorus compounds for estimation of their relative activity. Therefore, we have

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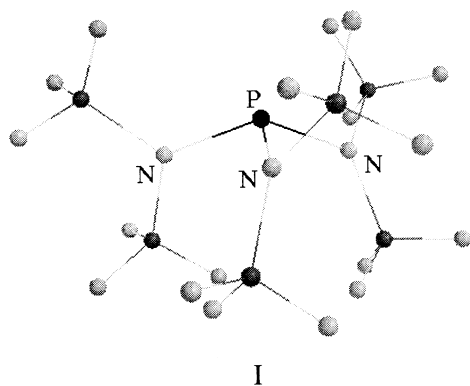


Fig. 1. Optimized structure of $(\text{Me}_2\text{N})_3\text{P}$.

to calculate the HOMO energy of P(III) compounds only.

3. Results and discussion

The frontier molecular orbitals theory is widely used for analysis of the reactivity of organic compounds. The applicability criteria of the frontier orbitals concept can be derived from Pearson's theory of hard and soft acids and bases [4].

According to this theory, hard acids and bases have small radius and tight electronic distribution. Therefore, the mechanism of interaction between hard acids and bases is determined by electrostatic forces. On the other hand, soft acids and bases have large atomic

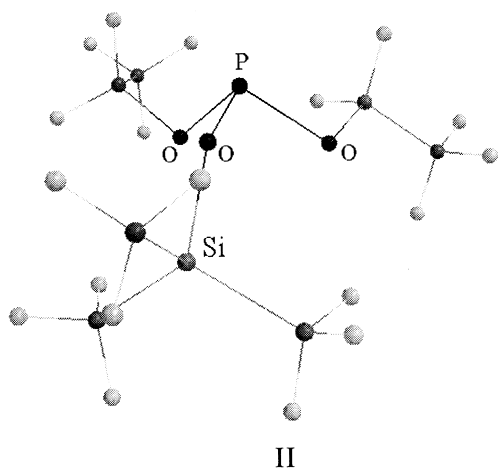


Fig. 2. Optimized structure of $(\text{EtO})_2\text{POSiMe}_3$.

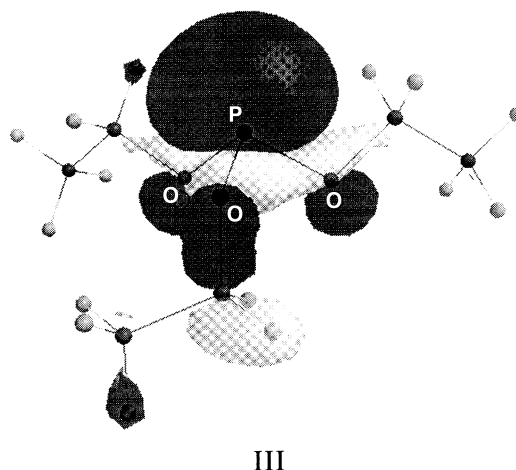


Fig. 3. Highest occupied molecular orbital of $(\text{EtO})_3\text{P}$ as a sample HOMO of phosphites.

sizes and are characterized by diffuse electronic distribution. The main interaction between soft acids and bases have, therefore, a pure quantum nature. The general tool for studying such interactions in organic chemistry is the theory of frontier molecular orbitals.

A three-coordinated phosphorus atom is a well-known soft base. It has a sufficiently large atomic radius and bears a lone electron pair. Ph_3BiF_2 is a soft species too because of the large atomic radius of bismuth and three directly connected phenyl substituents, making the Bi atom easy polarizable.

Thus, it is reasonable to consider the reactivity of P(III) compounds in a fluorination reaction by Ph_3BiF_2 on the basis of the frontier molecular orbital theory.

It follows from our calculations that the shapes of the HOMOs of the molecules studied are visually the same, and therefore we demonstrate only the HOMO of $(\text{EtO})_3\text{P}$ as a sample illustration in Fig. 3. It is easy

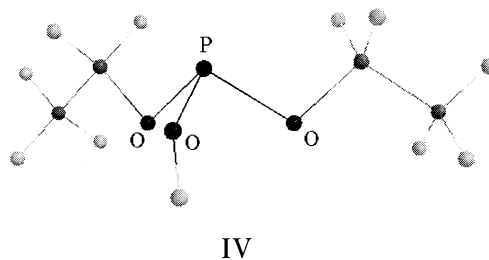


Fig. 4. Optimized structure of $(\text{EtO})_2\text{POH}$.

Table 1
Calculated HOMO energies and relative reactivity of P(III) compounds

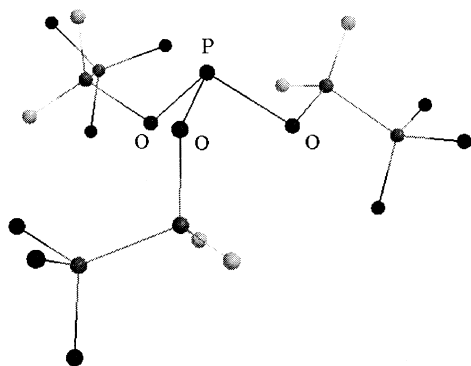
P(III) compound	Relative reactivity	HOMO (eV)
I: (Me ₂ N) ₃ P	Reaction proceeds at room temperature	-7.951
II: (EtO) ₂ POSiMe ₃	Reaction proceeds at room temperature	-8.961
III: (EtO) ₃ P	Reaction proceeds at room temperature	-9.805
IV: (EtO) ₂ POH	Reaction proceeds at heating	-10.065
V: (CF ₃ CH ₂ O) ₃ P	Reaction does not proceed even at heating	-11.074
VI: (Et ₂ N) ₃ P	Reaction does not proceed even at heating	-7.490

to see that the phosphorus lone electron pair makes the main contribution to the HOMO.

To compare the calculated HOMO energies with the reactivity of phosphorus compounds towards the fluorination reaction, we introduced the following qualitative scale of reactivity:

1. A reaction proceeds at room temperature. After mixing of the reagents the reaction mixture was allowed to react for 20 h and then completion of the reaction was checked by ³¹P nuclear magnetic resonance spectroscopy.
2. A reaction does not proceed at room temperature and needs heating for 1 h.
3. A reaction does not proceed even after prolonged heating.

The calculated HOMO energies and the relative reactivity of the P(III) compounds are presented in Table 1. We can make some conclusions from analysis of the data in Table 1. Four groups of compounds are observed on the basis of their reactivity.

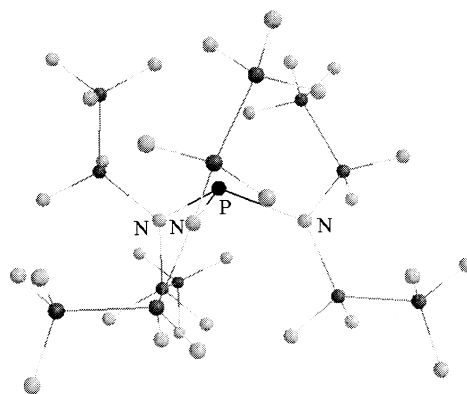


V

Fig. 5. Optimized structure of (CF₃CH₂O)₃P.

The first group includes relatively active P(III) compounds (**I**, **II** and **III**) with HOMO energies higher than -9.8 eV. The second and the third groups are represented by compounds **IV** and **V**, respectively. We could include **VI** in the third group, but there are reasons to consider it separately according to its HOMO energy level.

A remarkable difference in a chemical behaviour is observed for these three groups, where we see lowering of the reactivities and a decrease of HOMO energy levels simultaneously. The decrease in HOMO energies is also observed in the first group without a change in their relative chemical reactivity. There are two reasons for such a phenomenon. First, a very crude determination of reactivity scale hides the relative reactivity of **I**, **II** and **III**. More accurate kinetic investigations could bring light on the relative reactivity of **I**, **II** and **III**, and probably confirm our qualitative supposition. Second, the frontier molecular



VI

Fig. 6. Optimized structure of (Et₂N)₃P, where the phosphorus atom is hindered by bulky constituents.

orbitals theory is only a qualitative tool for the investigation of reactivity, therefore we cannot expect a quantitative difference in HOMO energies as compared with reaction rates.

It is interesting to compare the reactivity of **VI** and its HOMO energy level with the behaviour of other P(III) compounds. The nearest chemical analogue of **VI** is **I**. Their HOMO energies are very close as we expect, but we see that they exhibit opposite chemical reactivity. The reason for such a difference is clear from a comparison of the geometry of **VI** (Fig. 6) with that of other P(III) compounds (see Figs. 1–5). It is easy to see that even in the case of the bulky Me₃SiO substituent, hindrance of the phosphorus atom by substituent groups is much less than it is in **VI**. That is why we attribute the low reactivity of **VI** in the fluorination reaction to the steric hindrance by the bulky Et₂N groups.

4. Conclusions

The results obtained show the applicability and general usefulness of frontier molecular orbitals theory for description of the reactivity of P(III) compounds in the fluorination reaction by Ph₃BiF₂.

A qualitative relationship between the reactivity of the P(III) compounds and their HOMO energies is found. The lower HOMO energy level corresponds to a reduced reactivity.

The high reactivity caused by higher HOMO energy level can be altered by steric hindrance of bulky substituents at the phosphorus atom as occurs in the case of **VI**.

Acknowledgements

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