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On the Transition State of the Thermal Propene Elimination from Allylphosphines

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ABSTRACT

*Diallyltetramethylpiperidinophosphine* **1***, diallyldiiso­propylaminophosphine* **2***, and diallylmesitylphos­phine* **3** *were pyrolyzed in a stirred flow reactor over the temperature range 400-450°C, using toluene as carrier gas, producing, in all cases, mixtures of phos­phorus-containing products. The pyrolysis of* **1** *pro­duced 1-tetramethylpiperidino-1-phosphabutadiene, in addition to a mixture of phosphines and polyphos­phines. Compound* **2** *produced the azadiphosphole* ***4****, the phosphinine* **5***, allylphosphine, and diisopropyl­aminophosphine as major phosphorated products. The pyrolysis of* **3** *produced a mixture of phosphines and polyphosphines. The complex mixture generated by the three diallylphosphines indicates the formation of free radicals during their pyrolyses. AM1 calcula­tions on the transition state of an expected retroene- type propene elimination reaction showed that, due to the phosphaalkene character of the transition state, the structure of the latter is very rigid and sensitive to steric effects. Steric hindrance of the substituents on the phosphorus atom compels the molecule to distort the half-chair transition structure, causing a rise on the activation energy to values in the range of a homo­lytic P-C bond dissociation energy. q 1997 John Wiley & Sons, Inc.*

*INTRODUCTION*

In previous work [1], we reported the generation of some transient 1-phospha-1,3-butadienes unsubsti­tuted on the carbon chain, by pyrolysis of the cor­responding diallyl phosphines (Figure 1).

The generated phosphabutadienes have shown a certain stability at low temperature, enough to char­acterize them by 31P-NMR spectroscopy. A subse­quent kinetic study [2] permitted the postulation of a unimolecular reaction mechanism through a six- center cyclic transition state (Figure 2), also valid for other allyl phosphines having a hydrogen atom in the ***a*** position with respect to the phosphorus atom [2].

The potential utilization of the phosphabutadi­enes generated by this novel reaction as synthetic intermediates in preparative heterocyclic chemistry (see, for example, Ref. [3]) makes it interesting to try to prepare a family of stable phosphabutadienes, starting from the easily available diallylphosphines with diverse substituents on the phosphorus atom.

Having in mind that one of the common meth­ods for stabilizing phosphaalkenes is to protect the phosphorus-carbon double bond by bulky substitu­ents on the phosphorus atom [4], we report here our results on the thermal decomposition of diallylphos­phines having sterically hindered substituents, such as tetramethylpiperidino (TMP), diisopropylamino and mesityl (2, 4, 6-(CH3)3C6H2), on the phosphorus

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rλwp=ch\*\*ch=ch2

ch3-ch=ch2

atom. Additionally, we discuss a theoretical study, using the semiempirical AM1 method [5], of the transition state of the retroene elimination of pro­pene from allylphosphines in order to explain the unexpected observed reactivity.

*RESULTS AND DISCUSSION*

The pyrolysis of diallyltetramethylpiperidinophos- phine **1** over the temperature range 400-4508C, using toluene as carrier gas, produces a complex mixture that, collected in a liquid-nitrogen trap, presents an intense yellow color that disappears at room tem­perature. A gas chromatography analysis of the gases produced showed a composition of about 2% C2, 78% propene, 19% C4, and traces of other heavier hydrocarbon products. The 31P-NMR analysis of the mixture (Table 1) at 1508C showed the formation of the expected 1-phosphabutadiene (*d 4* 195) in 10­15% yield; nevertheless, the spectra showed predom­inantly signals whose chemical shift can be attrib­uted to phosphines and polyphosphines as the main products. No remarkable changes are observed when the spectra are recorded at room temperature.

Under the same conditions, diallyl(diiso- propylamino)phosphine **2** showed the formation of about 88% of propene, 7% of propane, and other heavier products, such as gases. From the analysis of the 31P-NMR spectra, one can observe the forma­tion, in 15-20% yield, of a product that seems to be the 1-isopropyl-5-methyl-1,2,3-azadiphosphole **4** on the basis of the spectroscopic data (Table 1). This compound has been reported [6,7] as showing a 31P chemical shift of *d 4* 323 and *d 4* 244 with a *1J*pp 4 480 Hz; we think that the observed small differences in the chemical shift may be due to mixture effects, since the pure product has not been isolated. How­ever, the value of the coupling constant and the frag­mentation pattern in the mass spectra are both very similar to the reported ones [7]. Besides the azadi­phosphole, we observed formation of small amounts of the diphosphinine **5** (10%) (Table 1), arising from a [4'2] cycloaddition reaction of the expected 1- phosphabutadiene [1,2,8], together with allylphos­phine (10-15%), diisopropylaminophosphine (10%), and other products, probably polyphosphines, all products being assigned on the basis of their 31P chemical shift values and their gas chromatography­mass spectroscopy (GC-MS) analysis.

Pyrolysis of diallylmesitylphosphine **3** under similar conditions yielded a more complex mixture of products. The analysis of the gases showed a com­position of about 3% C2, 87% propene, 4.5% C4, and other nonidentified heavier products. The 31P-NMR analysis of the nonvolatiles showed the formation of a mixture of phosphines and polyphosphines, among which one can distinguish mesitylphosphine (Ta­ble 1).

No further analysis of the reaction products was performed, since, in these three cases, the reaction did not follow the expected retroene fragmentation, producing instead complex mixtures of phosphorus derivatives. It seemed evident that the observed frag­mentation pattern can best be explained by the for­mation of free radicals during the reaction.

Nevertheless, with the aim to understand better this unexpected reactivity, and to verify that the pres­ence of bulky substituents prevents the molecule from achieving the appropriate transition-state ge­ometry of a retroene reaction, we have performed theoretical studies of the transition states of retroene reactions using the semiempirical AM1 method [5]. Calculations were performed on four allylphosphi­nes (Figure 3).

Phosphines **6**, **7**, and **8**, which are known decom­pose thermally by the retroene pathway [2], were chosen in order to verify that this method can be used for this qualitative analysis. We then computed the transition state on diallylmesitylphosphine **3**, which apparently prefers a homolytic dissociation pathway, in order to see what is different. The com­puted transition structures were confirmed by the presence of only one negative eigenvalue in the hes­sian matrix.

In Table 2 are reported the computed activation energies for the chosen allylphosphines and the ex­perimentally observed *Ea* values for propene elimi­nation. The calculations overestimate the activation

**TABLE 1** Spectroscopic Data of Products Detected in the Pyrolyses of Diallylphosphines 1-3

Reactant Product , Products spectroscopic data

( 31P NMR (CPC13) and GC-MS )

ΓMP^P,χ^ δ = 195; m/e (%) = 211 (100%) M+

Phosphinesand -75<δ>-107

Polyphosphines 180 Hz < Jph > 210 Hz

δ=318.4 ; δ=261.4 ; 1Jpp=477Hz

2Jph=41.8Hz

m/e (%)= 159 (40%) M+, 117 (100%) M+-

C3H6, 84 (80%) iPrNCCH3+, 75 (15%) PPCH+,

δ= 48.3; δ =-50.5 ; 1Jpp= 250.6 Hz

m/e (%) = 342 (20%) M+, 315 (15%) M+- C2H3, 262 (35%) (iPr2NP)2+

CH2=CH-CH2PH2 δ = -134,1⅛ = 191 Hz iPr2NPH2 δ= -82, 1Jph=194 Hz Mes-PH2 δ = 156.6, 1Jph = 205 Hz

Phosphinesand -70<δ>-108

Polyphosphines 19θ Hz < Jph > 218 Hz

TMP 4 2,2,6,6-tetramethylpiperidino. Mes 4 2,4,6-(CH3)3C6H2.

3 : R= Mesityl, R,= CH=CH2

**FIGURE 3**

energies by a factor of about 2.51. Using this as scal­ing factor, one can consider that the corrected acti­vation energies obtained by these calculations repro­duce the experimental values showing an overestimation of about 10% in the case of allylben­zylphenylphosphine **8**, acceptable for the method and for our qualitative analysis. On consideration of the activation energy for the putative propene elim­ination from diallylmesitylphosphine **3**, it can be seen that the computed value is too large (240 kJ mol**1**1), compared with values for molecules that are known to follow a retroene mechanism for propene elimination. The figure 240 kJ mol**1**1, however, is in the range of values for homolytic dissociation of some alkyl phosphines [9], explaining why radical splitting in this case competes favorably with the retroene mechanism.

Selected bond lengths and bond angles of the computed transition structures, for the atoms di­rectly involved in the transition state, as represented in Figure 4a, are listed in Tables 3 and 4. No re­markable geometrical differences are observed among the different phosphines. The results show analogies with reported values for bond lengths and bond angles obtained by ab initio calculations for the

**TABLE 2** Activation Energies for Propene Elimination in kJ/ mol

|  |  |  |  |
| --- | --- | --- | --- |
| *Phosphine* | *Ea* | *Ea(corr)a* | *Ea(exp)* |
| **6** | 354 | 141 | 144 5 9 |
| **7** | 365.2 | 146 | 143 5 4 |
| **8** | 388.6 | 155 | 135 5 6 |
| **3** | 602 | 240 | — |

*’*Corrected activation energy: *Ea*(corr) 4 *Ea*/2.51. *“*Experimental activation energy.

**TABLE 3** Selected Bond Lengths in the Computed Transi- o

tion State (A)*’*

*Phosphine C1-C2 C2-C3 C3-P4 P4-C5 C5-H6 H6-C1*

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **6** | 1.41 | 1.40 | 2.30 | 1.66 | 1.67 | 1.74 |
| **7** | 1.41 | 1.42 | 2.30 | 1.64 | 1.78 | 1.67 |
| **8** | 1.40 | 1.40 | 2.29 | 1.65 | 1.73 | 1.68 |
| **3** | 1.41 | 1.41 | 2.34 | 1.69 | 1.89 | 1.69 |

*’*Atom numbers as in Figure 4.

ene reactions of ethylene with formaldehyde and propene [10,11], and with values obtained by semi- empirical calculations for different retroene-type re­actions [12-15].

The C-C bond lengths for the propene moiety about to be eliminated during the reaction show al­most the same value, 1.41 A, intermediate between a single and a double bond, pointing out the dis­placement of the double bond in the propene moiety during the reaction. The C3-P4 and C5-H6 bonds to be broken are remarkably stretched, 2.30 and about 1.70 A, respectively, instead of the characteristic cor­responding values of 1.85 A [9] and 1.10 A. At the same time, the P4-C5 bond, a bond to become dou­ble, presents an average value of 1.65 A, in the nor­mal range for a P-C double bond [4], showing that the transition state is considerably productlike. The hydrogen atom to be transferred from C5 to C1 is located slightly closer to the C1 atom and almost equidistant to the two other hydrogen atoms on the C1 carbon atom, improving the orbital overlap be­tween H6 and C1. The P4 and C3 atoms are situated so as to maintain optimum orbital overlap in the transition state. Both P4 and C3 atoms, which change hybridization from *sp*3 to *sp*2, show a ge­ometry between these two states. A remarkable dif­ference, however, is observed between the C1H6C5 angle of the migrating hydrogen, around 1338 in our calculations, and the reported 1568 for the ene re­action [10-14].

For compounds **6**, **7**, and **8**, the transition struc­ture resembles somewhat a half chair (Figures 4a- 4c), where C1, C2, and C3 are located in a plane, and the H atoms on the C1 and C3 carbon atoms are slightly out of the plane, showing a geometry inter­mediate between the characteristic *sp*2 and *sp*3 hy­bridization geometries for these two carbon atoms. C3, P4, C5, H6, and C1 are located in nearly the same plane (Figures 4a-4c).

The computed transition structure for molecule **3** (Figure 4d) is more boat-shaped than the others (Figures 4a-4c). One can think that the large phos­phaalkene character of the P4-C5 bond in the tran­sition state makes the structure of the transition state very rigid and sensitive to steric effects. In **3**,

**TABLE 4** Selected Bond Angles in the Transition State (deg)*a*

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| *Phosphine* | *C1C2C3* | *C2C3P4* | *C3P4C5* | *P4C5H6* | *C5H6C1* | *H6C1C2* |
| ***6*** | 125.0 | 102.5 | 99.1 | 118.8 | 134.5 | 90.8 |
| **7** | 124.0 | 102.9 | 99.1 | 118.0 | 133.3 | 92.8 |
| **8** | 124.7 | 102.4 | 99.0 | 118.7 | 132.9 | 92.8 |
| **3** | 124.6 | 101.0 | 99.9 | 107.6 | 127.7 | 93.0 |

*a*Atom numbers as in Figure 4.

for example, the steric hindrance of the substituent on the phosphorus atom compels the molecule to distort the half-chair transition structure, raising the activation energy. The rigidity of the transition struc­ture could also explain the experimental values of the activation entropy for propene elimination from allylphosphines [2], corresponding to frequency fac­tors in the lower limit of accepted values for six­membered cyclic transition states.

In conclusion, the thermal decomposition of sterically hindered diallylphosphines produced com­plex mixtures of products, indicating the generation of free radicals during their pyrolyses. The AM1 cal­culations of the transition state of the propene elim­ination from allylphosphines, made in order to eval­uate these results, showed that the transition structure is considerably productlike and very rigid. Bulky substituents on the phosphorus atom compel the molecule to distort the half-chair transition structure, causing the activation energy to rise to val­ues in the range of homolytic P-C bond dissociation energies.

*EXPERIMENTAL*

1H, 13G, and 31P-NMR spectra were recorded on a Bruker AM-300 instrument. Mass spectra were ob­tained on a Kratos GLCMS RFA25 instrument. Pub­lished methods where used for the synthesis of di- chloro(tetramethylpiperidino)phosphine [16] and dichloromesitylphosphine [17].

*Synthesis of Diallylphosphines* **1**, **2**, *and* ***3***

In a typical procedure, a filtered solution of 0.242 mol of allylmagnesium bromide [18] was added dropwise to a stirred solution of 0.11 mol of the cor­responding dichlorophosphine in 100 mL of freshly distilled ether cooled at ι788C. When the addition had been finished, the mixture was stirred at room temperature for 2 hours, filtered, and the solvent evaporated. The diallylphosphine was distilled under reduced pressure through a 15 cm vigreux column (70-85% yield).

*Diallyltetramethylpiperidinophosphine* **1** : Liq­uid bp: 92-958C/0.1 torr. 31P NMR (CDCl3, H3PO4 ext): *d 4* 34.7; 13C NMR (CDCl3, Tms ext): *d 4* 17.7 (s, CH2), *d 4* 31.6 (s, CH2), *d 4* 33.7 (d,3*J*pc 4 22.1 Hz, CH3), *d 4* 38.9 (d, *1J*pc 4 25.1 Hz, CH2 allyl), *d 4* 56.6 (d,2*J*pc 4 30.9 Hz, C(CH3)2), *d 4* 115.8 (d,2*J*pc 4 11.6 Hz, CH = CH2), *d 4* 136.2 (d, *3J*pc 4 17.7 Hz, CH4CH2); 1H NMR (CDCl3, Tms ext): *d 4* 1.37 (m, 18H, TMP), *d 4* 2.69 (m, 4H, CH2), *d 4* 5.10 (m, 4H, CH = CH2), *d 4* 6.02 (m, 2H, CH = CH2).

*Diallyldiisopropylaminophosphine* ***2****:* Liquid bp: 83-878C/0.1 torr. 31P NMR (CDCl3, H3PO4 ext): *d 4* 26.9; 13C NMR (CDCl3, Tms ext): *d 4* 23.8 (d, *3J*pc 4 5.7 Hz, CH3), *d 4* 34.8 (d, 1*J*pc 4 17 Hz, CH2), *d 4* 45 (d, *2J*pc 4 7.4 Hz, CH(CH3)2), *d 4* 115.7 (d,*3J*pc 4 10 Hz, CH = CH2), *d 4* 134.6 (d, *2J*pc 4 11.8 Hz, CH4CH2); 1H NMR (CDCl3, Tms ext): *d 4* 1.03 (d, 3*J*pc 4 6.7 Hz, 12H, CH3), *d 4* 2.27 (m, 4H, CH2), *d 4* 3.25 (m, 2H, CH), *d 4* 4.95 (m, 4H, CH = CH2), *d 4* 5.77 (m, 2H, CH = CH2).

*Diallylmesitylphosphine* **3**: Liquid bp: 112- 1148C/0.1 torr. 31P NMR (CDCl3, H3PO4 ext): *d 4*

33.2; 13C NMR (CDCl3, Tms ext): *d 4* 20.8 (s, *p*- CH3), *d 4* 23.4 (d, *3J*pc 4 18.3 Hz, *o*-CH3), *d 4* 31.3 (d, 1*J*pc 4 16.4 Hz, CH2), *d 4* 116 (d,3*J*pc 4 10.9 Hz, CH = CH2), ), *d 4* 128.9 (d,2*J*pc 4 16.5 Hz, *m*-C); *d 4* 129.6 (d, 3*J*pc 4 3.5 Hz, *o*-C), *d 4* 134.5 (d, *2J*pc 4 12.1 Hz, CH4CH2), *d 4* 138.9 (s, *p*-C), *d 4* 144.4 (d, *1J*pc 4 14.6 Hz, *i*-C); 1H NMR (CDCl3, Tms ext): *d 4* 2.27 (s, 3H,*p*-CH3), *d 4* 2.56 (s, 6H, *o*-CH3), *d 4* 2.78 (d, *1J*ph 4 7.6 Hz, 4H, CH2), ), *d 4* 5.04 (m, 4H, CH = CH2), *d 4* 5.80 (m, 2H, CH = CH2), 6.86 (s, 2H, *m*-H).

The phosphines were pyrolyzed in a 265 mL stirred flow reactor [19] over the temperature range of 400-4508C and total pressures between 7 and 21 torr, using toluene as carrier gas. The outflow from the reactor was trapped at 1 1908C. It was then frac­tionated. The gases were collected at 1 1908C and analyzed by gas chromatography in a 4 m 2 3.2 mm O.D., 80/100 mesh activated Al2O3 column at 1708C using a flame ionization detector.

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