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Stereospecific cyclodimerization of 1-methylphosphole 1-oxide: a theoretical study

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Abstract

PM3 semiempirical calculations on the transition states for the cyclodimerization of 1-methylphosphole oxide (**1**, Y = Me) suggest the selective formation of product **A** (**2**, Y = Me) that is one of the eight possible isomers. Ab initio calculations at the 3-21G* level of theory go even further by justifying the specific formation of isomer **A** (**2**, Y = Me) that is the exclusive product of the syntheses. The dimerization seems to be directed by kinetic factors. Calculations on the HOMO–LUMO orbital interactions also confirm the preference for the formation of isomer **A** (**2**, Y = Me) where the phosphole rings are joined with the *endo* fusion and where at both phosphorus atoms the oxygen of the phosphoryl group is projected to the center of the system.

Keywords: Phosphole oxide; Cyclodimerization; Stereospecificity; Semiempirical and ab initio calculations

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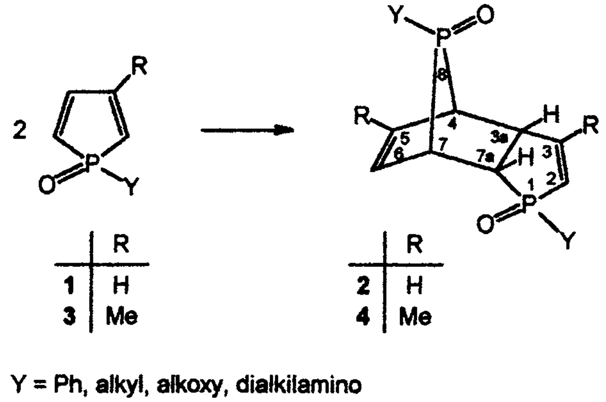
1. Introduction

It is well known that the P(IV) derivatives of phospholes undergo dimerization to the [4 + 2] cycloadduct. The product containing the 7-phosphanorbornene ring system attracted considerable attention due to the unique properties of its P-center [1–3]. On the basis of the pioneering observations of Westheimer [4,5], Mathey and Quin explored the possibilities for the synthesis of the dimers of phosphole derivatives including oxides, sulfides and quaternary salts. The dimerization is regio- and stereospecific, and in no reported case has an isomeric mixture been formed, even when a number of isomers are possible. The Diels–Alder cycloaddition of 1-substituted phosphole oxides (**1**) could, for instance, result in the formation of eight isomers, while the cyclodimerization of the 3-methyl-phospholes (**3**) may, theoretically, give as many isomers as 64. Conversion of the 3-methylphosphole oxides (**3**) to dimer **4** is not only stereospecific, but also regiospecific. The only isomers (**2** or **4**) isolated from the dimerization had the *endo*-fusion of the rings with the P(7)=*O* function located *anti* to the newly formed double-bond and with the P(1)=*O* function directed under the bicyclic framework (Scheme 1). Stereostructure of the dimers (**2** and **3**) was confirmed by a series of single-crystal X-ray analyses. The same geometry was suggested for dimers with the *tert*-phosphine oxide [6,7], the phosphinic ester [8], or the phosphinic amide function [9].



Scheme 1.

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Table 1
Energy and geometry for the transition sites leading to isomers **A**–**H** and heats of formation, calculated by the PM3 method [14]

Isomer	H_f (kcal mol^{-1})^a	H_f ($\Delta H^{\#}$) (kcal mol^{-1})^b	C(3a)–C(4) (Å)^b	C(7a)–C(7) (Å)^b	P(1)–C(4)–C(3a) (°)^b	P(1)–C(7)–C(7a) (°)^b
A (**2**, Y = Me)	−61.421	0.481	2.18	2.12	87.3	88.4
B	−61.221	1.258	2.18	2.13	87.2	88.4
C	−60.517	2.776	2.18	2.14	93.7	94.2
D	−61.544	2.589	2.18	2.14	94.0	93.6
E	−55.310	7.236	2.20	2.13	95.3	98.8
F	−54.734	8.203	2.21	2.12	94.4	100.0
G	−55.483	8.695	2.21	2.14	100.0	104.5
H	−55.582	8.717	2.20	2.15	100.7	103.5

[a] The results of the PM3 semiempirical calculations on isomers **A**–**H**.

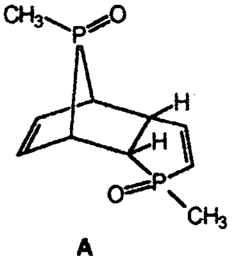
[b] Transition states leading to the results of the PM3 semiempirical calculations.

Cyclodimerization of the phosphole oxides generated from phospholes by oxidation, or from dibromophospholane oxides by elimination, is usually a fast process. In several cases, the intermediates could, however, be detected by ^{31}P-NMR [7,10–12]. Presence of a sterically demanding substituent on the P-atom increases the stability of the phosphole oxide [7,11,12]. Pentasubstituted phospholes were observed to be stable as monomers [13].

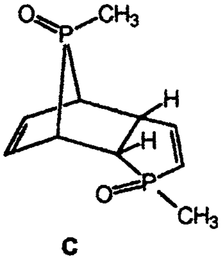
In the light of the above background it was a challenge for us to carry out a computational work on the cyclodimerization of phosphole oxides. We wished to explore if the specific cyclodimerization is controlled by thermodynamic or kinetic reasons.

2. Results and discussion

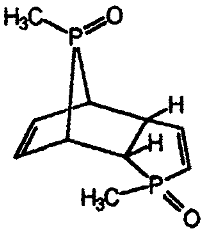
To ensure simple treatment of the problem, cyclodimerization of the 1-methylphosphole 1-oxide (**1**, Y = Me) was chosen as the model reaction of the semiempirical calculations. The energy and geometry of the transition states (TSs) leading to the eight possible isomers (**A**–**H**), together with the values of heat of formation for **A**–**H** were calculated by the PM3 method [14] and are listed in Table 1. The PM3 method is particularly well suited to computation of phosphorus-containing systems [14]. For the isomers with the *endo* fusion (**A**–**D**), the H_f is in the range of −(60.5–61.5) kcal mol^{-1}, while the similar range for the *exo* fused species (**E**–**H**) is −(54.7–55.6) kcal mol^{-1}, indicating that formation of the *endo* isomers (**A**–**D**) is favored by ca 5.8 kcal mol^{-1}.



A
(2, Y = Me)



C



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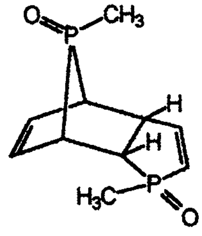
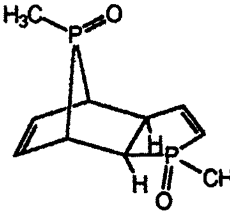
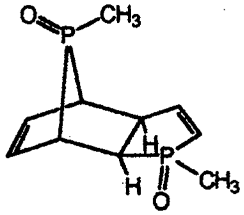


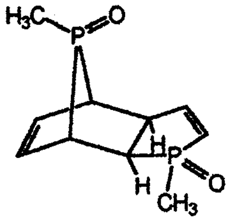
D



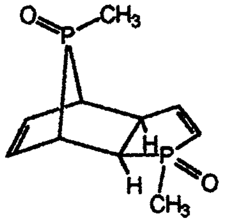
E



G



F



H

Calculated free enthalpies of activation ($\Delta H^{\#}$) for the formation of the isomers (**A**–**H**) also confirm the preference for the *endo* ring fusion: construction of the *endo* geometry requires only a $\Delta H^{\#}$ of 0.48–2.78 kcal mol^{-1}, while that of the *exo* fusion demands as much, as a $\Delta H^{\#}$ of 7.24–8.72 kcal mol^{-1}. The difference of 6–7 kcal mol^{-1} makes the formation of isomers **E**–**H** with the *exo* ring fusion less probable. Obviously, the steric hindrance prevents the formation of the unfavorable *exo* ring fusion with the *cis* disposition of the P(8)–C–C–P(1) moiety. In contrast to the close H_f

values of isomers **A**–**D**, there were significant differences between the $\Delta H^{\#}$ values of the *endo* fused isomers (**A**–**D**), thus making possible further judgements on the stereostructure of the energetically favorable isomers. With a $\Delta H^{\#}$ of 0.48 kcal mol^{-1}, formation of compound **A** (**2**, Y = Me) seems to be the most favorable. This is where the P(8)=*O* is in *anti* position to the double-bond and where the P(1)=*O* is directed under the 7-phosphanorbornyl ring. The next isomer is **B**, with $\Delta H^{\#} = 1.26$ kcal mol^{-1}, where the configuration of the P(8) atom is the same, as in **A** (**2**, Y = Me), but the P(1) center is inverted. The formation of isomers **D** and **C** with comparable $\Delta H^{\#}$ values at the PM3 level of theory (2.59 and 2.78 kcal mol^{-1}, respectively) is less favored. From the above facts it is clear that the *endo* ring fusion and the *anti* position of the P(8)=*O* to the double-bond are required to minimise the energy of the TS and hence that of the product. The difference of 0.78 kcal mol^{-1} between $\Delta H^{\#}_{\mathbf{A}}$ and $\Delta H^{\#}_{\mathbf{B}}$ suggests a selectivity of ca. 75% in favour of isomer **A** (**2**, Y = Me). In the light of the experimental data according to which dimer **A** or the dimers of type **A** (e.g. **2** or **4**) are formed in a selectivity of 100% [2,3], we decided to refine the $\Delta H^{\#}$ values for the formation of the *endo* fused isomers (**A**–**D**). In fact, energies of the corresponding TSs were calculated at the HF/3-21G* level of theory (Table 2). As can be seen, the most favorable isomers are again **A** (**2**, Y = Me) and **B** with a total energy of − 1211.7519 and − 1211.7405 a.u., respectively. The difference of 0.0115 a.u. corresponding to 7.21 kcal mol^{-1} between the energies of **A** (**2**, Y = Me) and **B** justifies the selectivity of 100% experienced in the syntheses [2,3,15]. Hence, the theory and the practice seem to be in agreement as regards the exclusive formation of the dimer of type **A** (e.g. **2** or **4**). It is also seen from the data that from among the four *endo* fused isomers (**A**–**D**), the formation of species **D**, with opposite P-configurations relative to **A** (**2**, Y = Me), is the most unfavorable. Energetics for the TSs leading to the *exo* isomers (**E**–**H**) was also refined (Table 2). It is worthy of mention that the energies for the TSs leading to isomers **E** and **F** (− 1211.7307 and − 1211.7303 a.u.) precede the corresponding value of *endo* isomer **C** (− 1211.7276 a.u.). According to the ab initio calculations, the relative order for the energy content of the TSs leading to the eight isomers is

$$E(\mathbf{A}) > E(\mathbf{B}) > E(\mathbf{E}) > E(\mathbf{F}) > E(\mathbf{C}) > E(\mathbf{D}) > E(\mathbf{H}) > E(\mathbf{G}).$$

In the light of the refined data, the formation of *exo* isomer **G** is the most unfavourable.

Table 2
Energy for the transition states calculated by the HF/3-21G* method

Isomer	*E* (a.u.)
A (**2**, Y = Me)	−1211.75190
B	−1211.74045
C	−1211.72760
D	−1211.71833
E	−1211.73073
F	−1211.73031
G	−1211.69889
H	−1211.71459

Table 3
HOMO and LUMO coefficients of interacting orbitals calculated for the transition states leading to isomers **A**–**H**

TS	C(7a)–C(7) interaction		C(3a)–C(4) interaction	
	C(7a)$^{\mathrm{HOMO}}$	C(7)$^{\mathrm{LUMO}}$	C(3a)$^{\mathrm{HOMO}}$	C(4)$^{\mathrm{LUMO}}$
A (**2**, Y = Me)	0.20513	0.17825	−0.24541	−0.38779
B	−0.16638	−0.11265	0.23742	0.38442
C	−0.24283	0.24814	0.24957	−0.38688
D	−0.20223	0.18823	0.24111	−0.39586
E	−0.15027	−0.05526	0.27590	0.42843
F	0.19101	0.16337	−0.30298	−0.45207
G	−0.20029	0.21089	0.28685	−0.43526
H	−0.20223	0.18823	0.24111	−0.39586

The calculated lengths for the newly formed C(3a)–C(4) and C(7a)–C(7) bonds in the TSs correspond to the expectation (Table 1). The close values of the C(3a)–C(4) and the C(7)–C(7a) bond length within the single isomers (**A**–**H**) are in accord with a concerted cycloaddition. On the other hand, the increase in the C(3a)–C(4) bond lengths of the TSs leading to the *exo* fused isomers (**E**–**H**), as compared with those leading to the *endo* forms (**A**–**D**) (ca. 2.20 vs. 2.17 Å) may be the consequence of unfavorable steric interactions. The P(1)–C(7a)–C(7) and the P(8)–C(4)–C(2a) bond angles (Table 1) also bear relevant information. Values of the bond angles calculated for the TSs leading to the *exo* isomers (**E**–**H**), as compared with those leading to the *endo* forms (**A**–**D**) (94.4–104.5 vs. 87.2–94.2°) reflect again to more considerable steric interactions in the *exo* isomers.

Preference for the formation of isomer **A** (**2**, Y = Me) may be the result of orbital interactions in the TS beside the obvious steric effects mentioned above. Orbital interactions are known to have an effect on the energy content of the TS leading to Diels–Alder cycloadducts [16]. Analysis of the HOMO and LUMO orbital coefficients as interacting orbitals revealed that these interactions are favoured for the TSs leading to isomers **A** (**2**, Y = Me), **B**, **E** and **F** (Table 3). The signs of the HOMO and LUMO coefficients in these cases are appropriate for a positive overlap. In the further judgements, only the more favorable TSs formed by the *endo* fusion were considered. As the Σc^2 value was found to be 0.0173 and 0.0121 for the TSs of isomers **A** (**2**, Y = Me) and **B**, respectively, it can be concluded

Table 4
The HOMO and LUMO energies calculated for the transition states leading to isomers **A**–**H**

TS	E^{HOMO} [eV]	E^{LUMO} [eV]
A (**2**, Y = Me)	−8.6593	−0.4261
B	−8.8865	−0.4667
C	−8.8689	−0.3833
D	−8.9636	−0.4529
E	−8.7555	−0.4491
F	−8.7831	−0.3739
G	−8.6671	−0.5528
H	−8.8269	−0.4872

that the formation of isomer **A** (**2**, Y = Me) is preferred by the orbital interactions.

The HOMO and LUMO energies were also calculated for the TSs leading to isomers **A**–**H** (Table 4). Although the HOMO–LUMO energy gap was found to be lower for most of the TSs formed with the *exo* fusion than for those with the *endo* geometry, the disfavored steric interactions make these products to be unpreferred. Regarding the *endo* series, the HOMO–LUMO energy difference is the least for the TS leading to isomer **A** (**2**, Y = Me). Moreover, the same TS has the highest HOMO energy. These data are also consistent with the selective formation of the TS leading to product **A** (**2**, Y = Me).

The preferred stereostructure of the dimers (**2** and **4**) is more obvious when the starting phosphole oxide (**1** or **3**) bears a more space demanding substituent. If, for instance, Y = Ph, structure **3** or **4**, where the relatively large phenyl groups are directed outside of the molecule, is the most favorable. The dimers always are seen to result from the approach of the two phosphole oxide molecules in the orientation that minimises interactions from the large P-substituents (Fig. 1).

It can be concluded that the semiempirical and the ab initio calculations on the cyclodimerization of 1-methylphosphole justify the specific formation of the isomer, where the phosphole rings are joined with the *endo* fusion and where at both phosphorus atoms, the oxygen of the P=O group is projected to the center of the system. As the specificity is based on the differences in the free enthalpies of activation, the dimerization is directed by kinetic factors.

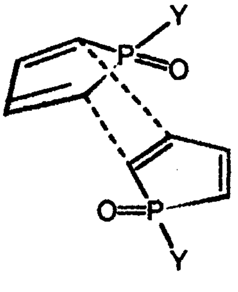


Fig. 1.

3. Experimental

All calculations were performed using SPARTAN 3.1 [17] on a HP9000 Apollo workstation. PM3 semiempirical parametrisation [14] was used for geometry optimisations and for the location of TSs. PM3 Hamiltonian was found to be useful for the calculation of Diels–Alder cycloadditions [18]. Structures corresponding to minimum energy conformations and saddle points were used as starting points in 3-21G* ab initio calculations. Full geometry optimizations with no symmetry constraints have been carried out at the RHF level, using the Davidon–Fletcher–Powell conjugate gradient technique [19]. TSs were located by the linear synchronous transit method as implemented in the SPARTAN package. All TSs were characterised through the correct number of negative eigenvalues of the energy second derivative matrix. TSs having only one negative eigenvalue were finally subjected to frequency calculation and vibrational analysis to verify that the imaginary frequency exhibits the expected motion.

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